NREL Photovoltaic Program FY 1996 Annual Report

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PREFACE

This report summarizes the in-house and subcontracted research and development (R&D) activities under the NREL PV Program from October 1, 1995, through September 30, 1996 (fiscal year [FY] 1996). The NREL PV Program is part of the U.S. Department of Energy's (DOE's) National Photovoltaics Program, as described in the DOE *National Photovoltaics Program Plan for 1996-2000*. The mission of the DOE National Photovoltaics Program is to make PV a significant part of the domestic economy—as an industry and an energy resource. The two primary goals of the national program are to (1) maintain the U.S. industry's world leadership in research and technology development, and (2) help the U.S. industry remain a major, profitable force in the world market. The NREL PV Program provides leadership and support to the national program toward achieving its mission and goals.

The FY 1996 budget authority for carrying out the NREL PV Program was \$40.1 million in operating funds and \$0.3 million in capital equipment funds. Subcontract activities represent a major part of the NREL PV Program with \$22.5 million (over 55% of PV funds) going to almost 90 subcontractors. Cost sharing by industry added over \$5.8 million to the subcontract R&D activities with industry.

The activities of NREL's PV Program are to: conduct basic, applied, and engineering research, manage subcontracted R&D projects, perform research complementary to subcontracted work, develop and maintain state-of-the-art measurement and device capabilities, develop PV manufacturing technology and modules, transfer results to industry, and evolve viable partnerships for PV systems and market development. The research activities under the program are summarized under the five project areas: Crystalline Silicon and Advanced Devices Project, Thin-Film PV Technologies Project, PVMaT Project, PV Module and System Performance and Engineering Project, and PV Applications and Market Development Project.

Approved for the NATIONAL RENEWABLE ENERGY LABORATORY

A handwritten signature in black ink, appearing to read 'Thomas Surek', is written over a horizontal line.

Thomas Surek
Technology Manager, Photovoltaics

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1.0 INTRODUCTION

This report summarizes the in-house and subcontracted research and development (R&D) activities under the NREL PV Program from October 1, 1995, through September 30, 1996 (FY 1996). The NREL PV Program is part of the U.S. Department of Energy's (DOE's) National Photovoltaics Program, as described in the DOE *National Photovoltaics Program Plan for 1996-2000*. The FY 1996 budget authority for carrying out the NREL PV Program was \$40.1 million in operating funds and \$0.3 million in capital equipment funds. Subcontract activities represent a major part of the NREL PV Program with \$22.5 million (over 55% of PV funds) going to almost 90 subcontractors. Cost sharing by industry added over \$5.8 million to the subcontract R&D activities with industry.

1.1 Background

The NREL PV Program is part of the DOE National Photovoltaics Program managed by the Office of Photovoltaic and Wind Technology. This office is under the Office of Utility Technologies in DOE's Office of Energy Efficiency and Renewable Energy. Major program thrusts in FY 1996 continued to be implemented based on DOE's *National Photovoltaics Program Plan for 1996-2000*. The program mission is to:

Work in partnership with U.S. industry to develop and deploy photovoltaic technology for generating economically competitive electric power, making photovoltaics an important contributor to the nation's and the world's energy use and environmental improvement.

The two primary goals of the national program are to (1) maintain the U.S. industry's world leadership in research and technology development, and (2) help the U.S. industry remain a major, profitable force in the world market. The NREL PV Program provides leadership and support to the national program toward achieving its mission and goals.

The DOE strategy over the next few years will be to lay the groundwork for a growing U.S. PV technology and industrial base, with increased emphasis on market and project development activities with industry. To accomplish this, the national program embraces three relatively equal priority activities: (1) technology development and validation, (2) market conditioning, and (3) project venturing. The new strategy continues a strong technology development program, but emphasizes R&D for the technologies and companies that are positioned to substantially penetrate the market, reduce prices, and scale up manufacturing. Program activities include continuing efforts to form partnerships with manufacturers and utilities (the ultimate benefactors and users), with universities, and with federal and state agencies.

Under the DOE National Photovoltaics Program, the NREL PV Program supports long-term fundamental and mid-term applied R&D, near-term manufacturing development, and near-term systems and market development in PV energy technology. The project also provides services to industry, electric utilities, and other users, and provides overall programmatic support for the National Photovoltaics Program. The NREL subcontract program is responsible for most of the R&D, manufacturing technology development, and some of the systems and market development task areas

under the National Photovoltaics Program. It is implemented via competitive public solicitations. One of the most important subcontracting mechanisms is government/industry partnership, with industry sharing the cost of research with DOE/NREL.

Closer work with industry, utilities, and other end users on PV manufacturing technology, systems, and market needs is being increasingly emphasized. Approaches for this emphasis include mitigating barriers to PV adoption in the utility and international marketplaces, and project venturing with decision makers and organizations representing domestic and international market sectors for PV. As appropriate for the system and market development areas, NREL is supporting activities such as education; technical assistance and training; market, economic, and financial analysis; technology characterizations; regulatory, rate, and value analysis; codes and standards assessment and development; working with customers in project development activities; and co-financing demonstration projects. Under project venturing, DOE is placing particular emphasis on supporting and strengthening programs already in place, such as PV:BONUS (Building Opportunities for the U.S. for Photovoltaics) and the Utility Photo Voltaics Group (UPVG).

NREL's PV activities include laboratory research and subcontract project management. We also provide technical support to efforts contracted from the DOE Golden Field Office (GO), such as PV:BONUS and UPVG. The primary research activities are conducted in advanced PV material technologies, including amorphous silicon (a-Si) thin-film materials; polycrystalline thin films, such as copper indium diselenide (CIS), cadmium telluride (CdTe), and their alloys; and high-efficiency crystalline cells, including silicon (Si) and gallium arsenide and their alloys. These activities are conducted in-house and through subcontracts with industry (mostly cost shared) and universities. The research activities are closely coordinated through several NREL/industry/university "team" efforts. Improving PV device manufacturing is vital. We are pursuing two complementary approaches:

- Government/industry partnerships, such as the PVMaT project (which focuses on improving manufacturing processes and products, accelerating manufacturing cost reduction, and laying the foundation for increased production capacity).
- Module development research to evaluate modules (and module performance) and suggest solutions to manufacturers' module problems.

System and market development rounds out the balanced approach pursued. The objective is to create an environment in which system technology, user acceptance, and the PV industry can accommodate the continued expansion of PV into large applications and markets. NREL subcontracts also support research on future generation PV technologies for highly qualified research teams to expand the current limits of PV technology. Transferring research results into commercial products and applications in a timely and effective manner is another major activity of NREL's PV Program.

Subcontracted R&D is a significant part of the NREL PV Program; typically, over 50% of the program's budget is allocated yearly to subcontracts. Table 1.1-1 shows the history of distribution of both subcontract and in-house budgets. From FY 1978 through FY 1996, we awarded almost 1200 subcontracts totaling nearly \$356 million out of the total operating budget of \$561 million. In

FY 1996, we awarded almost 90 subcontracts with a total funding of \$22.5 million. Cost sharing by industry subcontractors added over \$5.8 million to the \$14.4 million in NREL funding to 39 industry subcontractors. NREL also subcontracted with 33 universities (not counting Sunrayce schools), with a total funding of \$5.9 million. Figure 1.1-1 shows the industry-university-government distribution of subcontract funds by categories in DOE's *National Photovoltaics Program Plan for 1996-2000*. Table 1.1-2 shows the contacts for the various NREL PV Program areas.

Figure 1.1-1. FY 1997 budget distribution.

Table 1.1-1 Budget History of NREL Photovoltaics Program.

Fiscal Year	1978-1992 \$M	1993 \$M	1994 \$M	1995 \$M	1996 \$M
Task Area					
In-House R&D	110.5	14.3	16.4	18.8	17.6
Capital Equipment	17.2	5.7	3.3	0.8	0.3
Subtotal (in-house)	127.7	20.0	19.7	19.6	17.9
Subcontracted R&D					
Amorphous Silicon Thin Films	80.1	3.4	4.3	4.2	3.4
Polycrystalline Thin Films	54.7	5.8	6.7	8.2	6.6
High-Efficiency Concepts	36.7	1.0	0.6	0.3	0.4
Crystalline Silicon	25.0	0.9	1.2	1.0	0.9
New Ideas ²	18.9	0.3	0.2	0.0	0.0
University Participation	7.6	0.8	0.8	0.8	0.5
Subtotal (R&D subcontracts)	223.0	12.2	13.8	14.5	11.8
Manufacturing Technology Development and Systems and Market Development Subcontracts					
PVMaT Project	18.6	10.6	16.6	10.7	8.4
Module and System Performance and Engineering Project ³	2.1	0.5	0.6	0.6	0.3
PV Analysis and Applications Development Project ⁴	0.7	2.5	2.9	3.3	2.0
Subtotal (other subcontracts)	21.4	13.6	20.1	14.6	10.7
Subtotal (subcontracts)¹	244.4	25.8	33.9	29.1	22.5
TOTAL NREL PV PROGRAM	372.1	45.8	53.6	48.7	40.4

¹ Includes 15% to 20% for technical program management, fees, etc.

² Includes \$9 million for photoelectrochemical cell research

³ Significant subcontract effort initiated in FY 1991

⁴ Significant subcontract effort initiated in FY 1992

Table 1.1-2. Program Contacts by Project Area

Project Area	Manager	Telephone
PV Program	Thomas Surek	(303) 384-6471
Crystalline Silicon and Advanced Devices	Bhushan Sopori Robert McConnell	(303) 384-6483 (303) 384-6619
Thin Film Technologies	Ken Zweibel	(303) 384-6441
PVMaT	C. Ed Witt	(303) 384-6402
PV Module and System Performance and Engineering	Richard DeBlasio	(303) 384-6452
PV Applications and Market Development	John Thornton	(303) 384-6469

1.2 Key FY 1996 Accomplishments

Table 1.2-1 describes some key achievements in the NREL PV Program during FY 1996. The accomplishments are grouped by the six project areas of the program. Sections 2.0 through 6.0 of this report provide further details of the in-house and subcontracted research performed under these projects.

Crystalline Silicon and Advanced Devices Project

NREL	Completed multiple subcontract awards to initiate collaborative projects among universities and national laboratories jointly funded by DOE's EE and ER programs.
NREL	In addition to measuring and characterizing thousands of modules, devices, and material samples for over 100 organizations, an NREL-developed technique (patent pending) for evaluating, in-line, device quality of a proprietary silicon material is being transferred to an industrial partner.
NREL	Completed installation of low-pressure chemical vapor deposition (CVD) system and added a metalorganic CVD system to the III-V cluster tool facility for depositing and characterizing III-V materials and devices.
Research Triangle Institute	Produced a high-efficiency (18.2% verified by NREL) polycrystalline GaAs solar cell on a Ge substrate with 0.5cm grains.
Texas Southern University	Established a working relationship with Port Elizabeth Technikon in Port Elizabeth, South Africa, in support of training installers of PV equipment.

Thin-Film PV Technologies Project

NREL	Added substantially to world-record cell efficiency by reaching 17.7% on a copper indium gallium diselenide cell.
Solar Cells Inc.	Fabricated a 9.1%-efficient very-large-area CdTe module, the most efficient thin-film module of its size.
Solar Cells Inc.	Demonstrated 1-3 year outdoor stability for CdTe systems at various locations.
Golden Photon	Fabricated the highest efficiency (14.8%) CdTe cells made on low-cost soda lime glass.
Golden Photon	Identified stability as a critical issue for their approach to manufacturing CdTe modules.
United Solar	Made a significant advance in world-record efficiency for a-Si cells, reaching a NREL-measured stabilized efficiency (total area basis) of 11.8%.

Photovoltaic Manufacturing Technology (PVMaT) Project

NREL	Showed that both private-sector and government investments in PVMaT are recaptured ten-fold and twenty-fold, respectively, within 10 years from the program start.
Utility Power Group	Developed the largest UL-listed PV modular panel rated at approximately 600 watts.
Solar Electric Specialties	Developed two readily manufacturable, fully-integrated PV power systems.
AstroPower	Introduced into the market the first of its Silicon-Film TM products, the AP-8225 module, developed under PVMaT.

Siemens Solar Industries, Amoco Corporation/Enron (Solarex Corporation), Energy Conversion Devices/United Solar, Photovoltaics International, and Solar Cells, Inc.	Each of these companies made significant increases in their module manufacturing capacities during the year.
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Photovoltaic Module and System Performance and Engineering Project

NREL	Completed the fit-up and installation of project equipment at the Outdoor Test Facility (OTF) laboratory building.
Arizona State University	Completed their work on module certification and laboratory accreditation, providing a framework (PowerMark Corporation) for a U.S. module certification program.
NREL	The Institute of Electrical and Electronics Engineers (IEEE) Standards Coordinating Committee 21 (chaired by NREL) completed the first consensus standard (IEEE Standard 1262) on flat-plate module qualification testing.

PV Applications and Market Development Project

NREL	Signed a memorandum of understanding with 16 State Energy Offices to assess state facilities for high-value PV applications.
NREL	Installed a temporary 4-kW system on the Mall in Washington, D.C. for a dedication by the Secretary of Energy on Earth Day.
NREL	Participated, along with 11 companies and nearly 100 individuals, to help finance and install 200-W and 1000-W PV arrays at a non-profit orangutan research station in central Borneo.
NREL	Provided support for the broader coordination of the DOE/China Protocol Agreements leading to reduced trade barriers for U.S. industry.
NREL	Launched a project in cooperation with the Ramakrishna Mission for installation of stand-alone and battery-recharge systems in India.

1.3 Technology Transfer

Consistent with DOE policy, technology transfer within NREL's PV Program is defined as collaborative R&D with industry to help industry commercialize products or services. An underlying theme of NREL technology transfer activities is the joint work accomplished by industry and NREL researchers focused on a common R&D objective. Among government laboratories, seven principal tools affect technology transfer: subcontracted R&D, cooperative R&D, industry-sponsored R&D, NREL user facilities, technology licensees, researcher exchanges, and information dissemination. NREL's PV Program conducts its technology transfer primarily through subcontracts, cooperative R&D, and information dissemination.

Subcontracts with Industry

About 44% of almost 90 subcontracts placed in FY 1996 were with the U.S. PV industry. The NREL funding of \$14.4 million to industry was supplemented by an additional \$5.8 million (estimated) of cost sharing by the industry partners. Technically knowledgeable NREL research managers participate in defining, evaluating, awarding, and negotiating statements of work submitted by industry researchers in competitive solicitations. Following subcontract awards, NREL subcontract managers direct and evaluate research progress by visiting subcontractor sites and evaluating subcontractor deliverables in the NREL laboratories.

Cooperative R&D

NREL in-house researchers frequently perform informal cooperative R&D with their industrial counterparts working under NREL subcontracts. These interactions have been ongoing since PV research started in 1977 at the Solar Energy Research Institute (now NREL). Most involve performance measurements and materials analyses performed with NREL's large and unique set of capabilities for PV efficiency and materials analysis. Informal cooperative R&D, as distinguished from formal cooperative research and development agreements (CRADAs), is a natural complement to NREL's subcontracted PV program. Informal cooperative R&D during FY 1996 included more than 15,000 measurements on PV materials, devices, and modules on properties ranging from composition and microstructure to cell and module performance. More than 150 organizations from the worldwide PV community worked with NREL researchers in this fashion.

CRADAs, as authorized by the National Competitiveness Technology Transfer Act of 1989, are formal agreements signed by the NREL Director and his industrial counterparts for conducting joint research projects that involve NREL and industrial researchers. We performed research under 11 CRADAs during FY 1996: DayStar Technologies, Inc. (CIS module design), Golden Photon, Inc. (CdTe nanoparticle precursors), Ebara Solar, Inc. (Si ribbon growth), International Radiation Det. (Si gettering), Energy Photovoltaics, Inc. (CIS development), Energy Conversion Devices, Inc. (module characterization), Lockheed Missiles & Space Co. (III-V cells), Crystal Systems, Inc. (Si processing), UniSil Corp. (Si characterization), Spectrolab, Inc. (III-V cells), and a company wanting confidentiality for their CRADA on III-V solar cells.

Information Dissemination

Effective traditional ways of transferring technology are to report R&D results to the technical community by publishing in scientific journals and by presenting at technical conferences and meetings. Section 8.0 contains a bibliography of FY 1996 publications, including subcontractor reports. During FY 1996, PV program staff helped organize several conferences and workshops, including the Sixth Annual NREL Silicon Workshop, the NREL Photovoltaic Performance and Reliability Workshop, the NREL Photovoltaics Standards and Codes Forum, and the Twenty-Fifth IEEE Photovoltaic Specialists Conference. These gatherings provide important opportunities for industry researchers to exchange technical information with NREL and university researchers.

NREL's program also distributes its quarterly newsletter, *NREL PV Working With Industry*, to approximately 1000 addresses. Adding to traditional information dissemination was the creation of NREL's PV Program Web site in FY 1996. This site (<http://www.nrel.gov/pv/>) quickly became a major instrument for exchanging information between NREL and individuals from around the world with a variety of interests in photovoltaics. The interest in the site is evident in that all major search engines tend to include the NREL PV Program Web site in their first 10 to 20 suggested sites for photovoltaics.

1.4 Conclusions

This report reviews the in-house and subcontracted R&D activities under the NREL PV Program in FY 1996. Major PV program thrusts during FY 1996 continued to be implemented based on DOE's recent *Photovoltaics Program Plan, FY 1996-2000*.

In summary, the activities of the PV Program are to: conduct basic, applied, and engineering research; manage subcontracted R&D projects; perform research complementary to subcontracted work; develop and maintain state-of-the-art measurement and device capabilities; develop PV manufacturing technology and modules; transfer results to industry; and evolve viable partnerships for PV systems and market development.

This report describes the in-house and subcontracted R&D activities, many of which encompass close collaborations between NREL and outside researchers.

The research activities under the program are summarized under the five project areas in the following sections: Crystalline Silicon and Advanced Devices Project, Thin-Film PV Technologies Project, PVMaT Project, PV Module and System Performance and Engineering Project, and PV Applications and Market Development Project. The sections include a brief overview that includes the objectives, approaches, and some key developments. Following that are technical summaries of the in-house and subcontract activities. The subcontract sections were provided by the subcontractors themselves. Section 7.0 provides a list of FY 1996 subcontracts and Section 8.0 lists major research publications and subcontractor reports.

2.0 CRYSTALLINE SILICON AND ADVANCED DEVICES PROJECT—Introduction

Contributors: John Benner, Robert McConnell, Bhushan Sopori

The Crystalline Silicon and Advanced Devices project supports basic and applied research to ensure that the U.S. photovoltaics (PV) industry has access to leading-edge technologies needed for continuing improvement of silicon cells used in current modules, for definition of next-generation PV technologies, and for the achievement of the long-term goals of the DOE Photovoltaics Program. This project develops and maintains capabilities in crystalline silicon, high-efficiency solar cells, advanced measurement techniques, and exploratory materials and devices. It also supports the Historically Black Colleges and Universities program. With these capabilities, the project supports a directed program in research on crystalline semiconductors in key topics selected to maximize the PV program's benefit from the existing national infrastructure in silicon electronics and photonic technologies. These activities are intended to provide manufacturers with future options to silicon wafers based on lower-cost, potentially higher-efficiency, crystalline films.

Crystalline Silicon

The efficiency of silicon solar cells fabricated on commercial low-cost substrates remains limited primarily by the material quality. The material-related factors that influence the cell behavior are impurities, defect density, defect distributions, grain size, and residual stresses. It is known that the deleterious effects of impurities and defects can be partially offset by a proper selection of the material parameters like resistivity, oxygen and carbon concentrations, and suitable device design. It is, however, imperative that efficiencies exceeding 12% can only be attained by further improvement in the material quality as a result of processes such as impurity gettering and defect passivation. Fortunately, such processes occur naturally in various steps of solar cell fabrication—such as in the formation of N/P junctions and metal contacts—and during the deposition of antireflective coatings. However, to take full advantage of such quality-enhancement processes, it is necessary that the process conditions for optimizing the material quality also yield optimum device parameters. This optimization can only be done with a thorough understanding of the mechanisms involved in such processes. The research under the NREL Silicon Materials Research Program is aimed at developing the basic understanding of the mechanisms involved in the quality-enhancement process. This research has a two-fold objective. It strives to establish the mechanisms that limit the cell performance and to arrive at processes that can ameliorate the influence of defects and impurities present in the as-grown material.

The research under this program has been very successful in identifying performance-limiting mechanisms as well as process conditions that can yield >18% cells on multicrystalline substrates. Although it has been known for a long time that impurities and defects lower the performance of solar cells, the mechanisms associated with such degradation have only recently been identified. For example, researchers have determined that the concentrations of Fe and Cr present in commercial photovoltaic silicon materials can exceed $10^{12}/\text{cm}^3$, and that many metallic impurities are getterred during certain solar cell fabrication processes such as phosphorus diffusion for junction formation and Al alloying used for contact formation. These results show that in spite of the fact that high

that high concentrations of impurities may be present in the starting material, it is possible to getter many of these impurities by post-growth processing. Other important gettering results obtained through this program are:

- TCA gettering can be as effective as phosphorus gettering.
- Certain synergistic effects of impurity diffusion and segregation result in the enhanced gettering efficiencies of some impurities; this feature can be exploited for improved gettering by simultaneous phosphorus and Al treatments.
- Researchers have found that heavily dislocated regions could not be gettered well because such regions "trap" impurities as precipitates, making them immobile.
- Some defects (unidentified thus far) are present in the zero-dislocation regions that have been found to act as precipitation centers for certain interstitial impurities.

Likewise, new insight into the interactions of hydrogen with impurities and defects in silicon was gained through theoretical calculations. Experimentally, it was determined that hydrogen can diffuse via formation of a vacancy-hydrogen complex, and that the presence of vacancies can enhance hydrogen diffusion at low temperatures. This mechanism has explained the dependence of the degree of passivation in solar cells fabricated on substrates containing different concentrations of oxygen and carbon. Researchers also developed some understanding of the passivation caused by plasma-enhanced chemical vapor deposition nitridation. Additionally, under this program, a variety of new characterization and processing techniques have been developed. However, some of these processes have not yet been fully exploited by the PV industry to improve the commercial solar cell efficiencies.

High Efficiency

In FY 1996, we continued the sequential development of low-cost, high-efficiency solar cells. Subcontractors completed their second year of effort on new projects exploring the high-efficiency potential of imperfect materials on low-cost substrates. The Research Triangle Institute (RTI) produced a GaAs solar cell on a Ge substrate with 0.5 cm grain size with 18.2% efficiency, as verified at NREL. An even higher efficiency (not confirmed by NREL) of 21% was measured by RTI on a GE substrate with grain sizes ranging from 0.05 cm to 0.1 cm. The key to these high-efficiency results has been the development of a thin, undoped GaAs spacer between the emitter and solar cell base that significantly reduces the cell's dark current and increases its open-circuit voltage. The RTI work dovetails nicely with a project at the California Institute of Technology to fabricate large-grain GE films on glass substrates. By selectively nucleating grain growth in a previously deposited amorphous Ge film, Cal Tech researchers are growing grains with dimensions as large as 20 microns. Another approach under exploration at the University of California, Los Angeles, is an innovative epitaxial liftoff process whereby a GaAs solar cell grown on top of a sacrificial layer of AlAs is subsequently etched to release the device from its substrate. These efforts complement NREL's in-house research directed toward GaAs solar cells having the highest recorded solar cell efficiencies and on potentially low-cost GaAs concepts with efficiencies above 20%.

A 27%-efficient $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}/\text{GaAs}$ cell measured at the Solar Research Corporation in Victoria, Australia, led NREL researchers to study the two-junction cell as a function of cell temperature. Spectrolab, which is converting its III-V cell production of 500,000 wafers per year to the two-junction design, is pushing ahead with work (in collaboration with NREL) on a three-junction cell with an AM0 efficiency of 25.7%. The latter design, which uses the Ge substrate for formation of the third junction, should have manufacturing costs only slightly higher than those of single-junction GaAs devices grown on Ge.

Advanced Characterization Techniques

The mission of the NREL materials characterization task is to provide measurement support and develop new measurement techniques for in-house and industry-driven PV research and development. This task uses a wide variety of state-of-the-art materials and surface characterization techniques. Electron microscopy techniques such as transmission electron microscopy, high resolution electron microscopy, scanning electron microscopy in its various modes, electron beam induced current, cathodoluminescence, secondary electron, and electron channeling are used to investigate the chemical, compositional, structural, electrical, and luminescent properties of PV and semiconducting materials and devices. In addition, surface analysis techniques such as secondary ion mass spectrometry, Auger electron spectroscopy, and x-ray photoelectron spectroscopy are used to investigate the impurities, compositional uniformity, and interface properties. The mission of the electrooptical characterization task is to provide routine electrical and optical measurement support and to develop new measurement techniques for in-house and subcontract PV device research that will accelerate commercialization of the respective technologies.

We continued our efforts to develop and provide electrical and optical measurement support for both NREL and subcontract researchers. We also work to provide technology transfer of new measurement techniques to industry to assist in quality control of manufacturing processes. Among the areas receiving measurement support were CdS/CdTe and CIGS thin-film solar cells, crystalline silicon solar cells, and high-efficiency polycrystalline devices. Collaborative research projects using such advanced techniques as time- and energy-resolved photoluminescence and photoexcited carrier relaxation and recombination were conducted with a variety of partners, including Golden Photon Inc., Solar Cells Inc., Institute for Energy Conversion, University of Toledo, and Colorado School of Mines. These new techniques will help improve our understanding of the significant parameters of PV materials.

Exploratory Materials and Devices

This project supports the more exploratory investigations of the PV program. Researchers at Johns Hopkins University are exploring an approach for overcoming a limiting factor in photoelectrochemical cells: the presence of a liquid electrolyte. They have shown that ionically conducting polymer gels can be used in the fabrication of a quasi-solid-state cell employing a dye-sensitized, nanocrystalline TiO_2 electrode. Researchers at the University of Washington are exploring alternative dyes ranging from rhodamines to platinum complexes. They also discovered two effects, one upon exposure to ultraviolet light and the second a process for making TiO_2 films, yielding increased incident photon-to-current efficiencies in their dye-sensitized heterojunctions.

These efforts complement NREL's in-house program supported through DOE's Office of Energy Research (OER), Basic Energy Sciences, Divisions of Chemical Sciences and Advanced Energy Projects.

A related NREL program funds university research integrated with NREL's Thin Film Partnership project. Researchers at the University of Illinois, University of Utah, and University of South Florida are performing fundamental studies of CIGS and a-Si in support of Thin Film Partnership Teams.

The integration of research activities across programs with the U.S. Department of Energy continues to build stronger support for solving fundamental issues in PV and exploring innovative approaches for future-generation PV technologies. Principal investigators in projects supported by the Materials Science Division in Basic Energy Sciences meet at NREL's PV Program Review Meeting to review existing research and consider materials science issues associated with PV technology. Funding from OER supports travel by principal investigators to important research conferences or to other research laboratories, thereby stimulating collaborations, new ideas, and new research efforts directed toward topics of relevance to PV.

At NREL, PV research efforts are focusing on increasing the efficiency of solar cells based on the prototype CuInSe_2 , which currently stands at 17%. However, further increase of the cell efficiency will require further investigation—which is now being conducted—of the defect physics of CuInSe_2 . NREL researchers are also investigating the basic theory of silicon-based nanostructures in order to predict the optical and materials properties of such structures as they relate to PV. In addition, experimentally testable predictions of the consequences of ordering on the optical (PV) properties of GaInP_2 continue to be formulated at NREL.

Historically Black Colleges and Universities (HBCUs)

This program, initiated by DOE and NREL in FY 1995, provides undergraduate support for PV research and education at HBCUs. Participants include Clark Atlanta University, Wilberforce University, Texas Southern University, Central State University, Southern University, Mississippi Valley State University, and Hampton University. Fourteen professors and sixteen undergraduate students are involved in projects ranging from materials characterization of PV materials, device characterization and modeling, design of buildings with integrated PV systems, and solar resource measurements, to support for applications projects in Africa for using PV for water pumping and house lighting. The program provides additional support for summer internships of the students working (at NREL or elsewhere) on PV projects.

Crystalline Silicon In-House Research

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1876-1877

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1884-1885

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1888-1889

1890-1891

Title: Crystalline Silicon Materials Research

Organization: National Renewable Energy Laboratory, Golden, CO
Basic Sciences Center, Crystal Growth and Devices Team

Contributors: T. F. Ciszek, Principal Investigator; Y. Tsuo, B. Sopori, T. Wang, M. Landry, C. Akers, M. Symko, R. Roze, K. Jantzen, M. Heben, J. Moore, R. Murphy

Introduction

Our focus in crystal growth has recently been on next-generation technologies, and particularly on thin-layer silicon growth (thickness less than 50 μm) on a supporting substrate. Use of a unique Cu/Al solvent has allowed fast (1 $\mu\text{m}/\text{min}$), isotropic, liquid-phase epitaxial (LPE) growth of Si on metallurgical-grade silicon substrates, with properties suitable for PV devices. A number of other growth approaches are also under investigation. The team's work on the materials science of impurities and defects in Si has provided new insight into the physics of hydrogen passivation and impurity gettering, introduced new gettering methods, and quantified the effects of impurities, such as iron, and various defects on minority charge carrier lifetime. Growth of controlled samples with selected impurities and defects is a feature of this research. Recent progress in growth, materials science and devices will be summarized in this report. Details can be found in the references.

Silicon Growth

Liquid Phase Epitaxy

Work in this task [1] examines growth of thin-layer c-Si films on low-cost metallurgical-grade c-Si substrates (MG-Si) by liquid phase epitaxy (LPE). LPE is an attractive technique because it has adequate growth rates (around 1 $\mu\text{m}/\text{min}$) at moderate temperatures (around 900°C), has high quality (near-equilibrium crystal growth), and uses relatively simple equipment. We developed a Cu-Al solvent [2] that is able to wet the surface well without a melt-back step, even when an open-tube, argon-purged, vertical dipping technique is used. The high solubility of Si in Cu-Al (20-35%) at a growth temperature of ~900°C also creates an atomically rough solid/liquid interface, facilitating isotropic growth and a macroscopically smooth crystal surface (Fig. 1), as compared to the rough-faceted surface characteristic of low-solubility solvents such as indium (Fig. 2). This solvent also allows control of Al dopant and Cu impurity incorporation into the grown layers [3], and resistivities up to 0.2 Ohm-cm can be achieved. Cu levels are below the threshold for solar cell degradation.

Figure 1. Surface morphology of a LPE-Si/MG-Si layer grown from a 23%Si-28%Al-49%Cu solution.

Figure 2. Surface morphology of a LPE-Si/MG-Si layer grown from a 3%Si-97%In solution.

Electrodeposition

Thin-layer Si electrodeposition is a small activity in this task. A student from the University of Colorado (Jon Moore) applied for and won an AWU/DOE Fellowship to support this exploratory work. We have completed design, construction, and testing of a Si electrodeposition system and plan to use it to form thin-films of Si on low-cost substrates. Our approach is to develop electrolyte baths which can be used at or below 500 °C. Currently available molten salts require temperatures in excess of 700 °C and preclude the use of many low-cost substrates such as float glasses.

Other Si Growth Methods

We continued to prepare apparatus to test a new method for electromagnetic Czochralski growth of large Si crystals. A review of our pioneering cold crucible work, including electromagnetic continuous casting was recently presented [4].

Silicon Materials Science

The silicon materials science portion of this project investigates the role of defects and impurities in c-Si materials, with the goal of ameliorating their deleterious effects in c-Si solar cells, particularly when lower cost Si feedstock and c-Si growth methods are used.

Float-zone Growth of Si with Controlled Fe Impurity Levels

Iron is a very common metallic impurity in silicon that is also a recombination center. Developing a fundamental understanding of Fe in silicon, including interactions with crystal defects and with other impurities (dopants, oxygen, etc.), is of increasing importance due to the wider usage of less pure Si feedstock and interest in new thin-layer c-Si growth techniques using metallurgical-grade c-Si substrates. The float-zone (FZ) method for silicon crystal growth allows a high degree of control over background impurity and defect levels and is an excellent vehicle for controlled studies of deliberately introduced impurities and/or defects. We grew Fe-doped multicrystalline ingots by the FZ method to study Fe effects on minority charge carrier lifetime, grain structure, and electron-beam-induced current characteristics of multicrystalline silicon [5]. Representative data for the effect of Fe on lifetime is presented in Fig. 3. The minority-carrier lifetime decreased monotonically with

Figure 3. Measured bulk minority-carrier lifetime vs. target Fe-doping level for float-zoned multicrystalline-Si ingots with various grain sizes.

increasing Fe content for similar grain sizes (from ~10 μs to 2 μs for < 10⁻³ cm² grains, from ~30 μs to 2 μs for ~5 x 10⁻³ cm² grains, and from ~300 μs to 2 μs for > 10⁻² cm² grains) as the Fe content increased to 1·10¹⁶ atoms/cm³. We had previously observed that grain size alone has a strong effect on lifetime. We also saw evidence of constitutional supercooling in the heavily doped samples, with a dramatic accompanying effect on grain structure. Such observations might aid in understanding the precipitation of Fe during ingot crystal growth and design of new thin-layer c-Si growth techniques.

We completed and published nitrogen doping effect studies [6] prior to starting the Fe impurity studies. We plan to next examine co-doping of Fe with various p-type dopants using the FZ method to produce controlled samples.

Passivation, Gettering, and Characterization Studies

Work on hydrogen diffusion modeling for solar cells continued. A model was developed to explain hydrogen diffusion and passivation characteristics of silicon solar cells. Our previous work has shown that a variation in the degree of passivation in solar cells fabricated on the substrates from different vendors is caused (in part) by a variation in the diffusivity of hydrogen. The variation could be explained on the basis of a model that involves hydrogen diffusion via a hydrogen-vacancy complex. This model also explains passivation of cells during a PECVD nitridation process. In the past, this model had assumed that surface damage, such as that arising from a phosphorous diffusion, is responsible for

Figure 4. SIMS profiles of EFG sample regions with and without surface damage, annealed in deuterium forming gas

dissociation of molecular hydrogen. This assumption was made to explain passivation of some solar cells during a forming gas anneal. We now have experimentally verified this mechanism. Figure 4 compares SIMS profiles of deuterium in a sample with two regions - with and without surface damage. The sample was annealed in a deuterium forming gas at 400°C for one hour. This figure illustrates that surface damage can dissociate D₂ with a concomitant deep diffusion. Ab initio calculations (performed by Stefan Estreicher of Texas Tech) show that a hydrogen molecule can spontaneously dissociate by a vacancy. Further work is being done to characterize the surface damage and identify the minimum damage needed for passivation from a forming gas anneal.

In other Silicon Materials Science activities, we explored porous silicon gettering [7]; we achieved part-per-trillion B and P detection limits via photoluminescence in high-purity Si [8]; and we hosted another workshop on crystalline-silicon PV technology, with a focus on defects and impurities.

Silicon Devices

Optical Modeling of Thin Solar Cells

We have completed the first version of a theoretical model for thin solar cells. This optical model also includes the effect of back reflection. Results show that thin cells of a-Si as well as c-Si can incur significant losses due to metal absorption. This theory was used to develop a new thin-layer Si solar cell design. Figure 5 shows expected maximum achievable current density (MACD) as a function of thickness of the silicon layer with and without an Al back reflector.

Figure 5: Calculated MACD, as a function of Si thickness, for a solar cell with textured front and planar back.

Diagnostic Cell Processing

In FY96, we completed the upgrade of our Tempress high-temperature furnace system, which is used for processing small diagnostic solar cells on experimental crystalline-silicon materials in a clean-room environment. The furnace has eight quartz tubes with three temperature zones per tube, for a total of 24 temperature control loops. Each tube has its own process gas control and delivery system. Customized programs and hardware interface were installed for automated control of the furnace and to provide extensive safety interlocks. Distributed process control and monitoring in a multitasking personal computer environment were used to improve the ease of use, reproducibility, and safe operation of the furnace system [9]. We also completed a study of high-flux solar furnace Si PV cell processing and demonstrated an optical enhancement of junction diffusion using that method [10].

Silicon Industry Interactions

CRADA activities were carried out with Crystal Systems, UniSil, and EBARA Solar, Inc.

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Crystalline Silicon Subcontracts

Title: Influence of Self-Interstitials Injected by Phosphorus Diffusion on Defect Structures and Electronic Properties in Crystalline Silicon

Organization: Department of Mechanical Engineering and Materials Science,
Duke University, Durham, North Carolina 27708

Contributors: T. Y. Tan and U. M. Gösele, principal investigators;
R. Gafiteanu, S. Joshi, and P. Plekhanov, graduate students

Objective

In this program we are identifying strategies for effective gettering of crystalline silicon in order to improve the carrier lifetime, and subsequently, the solar cell efficiency. Physical and numerical modeling of gettering metallic impurities away from Si device active regions has been carried out. The modeled gettering aspects include the dissolution of precipitated impurity (if any), diffusion of dissolved impurities from the gettered to the gettering region, and gettered impurity stabilization in the gettering region via segregation and/or precipitation processes. Extrinsic gettering by wafer backside Al layer deposition (EG) and intrinsic gettering (IG) are the modeled gettering techniques.

Approach

As opposed to the IC industry, where gettering is used only to guard against the processing introduced contaminants, in commercial solar cell production gettering is needed both for improving the starting Si substrate quality as well as for guarding against contamination during processing. We have recently implemented a program to model the impurity gettering process physically and numerically. Results of such studies have been reported previously [1]. These include the gettering of fast diffusing interstitial (*i*) and substitutional-interstitial (*s-i*) species as the model impurities. The modeled gettering techniques included wafer backside Al layer deposition, wafer frontside indiffusion of P, and both aforementioned techniques implemented simultaneously (P+Al).

Solar grade polycrystalline Si substrates contain bad regions wherein the minority carrier diffusion lengths are extremely low, and cannot be significantly improved by a normal gettering treatment such as the use of P indiffusion or Al. These regions contain dislocations and metal silicide precipitates up to high densities. The reason that the quality of these regions is difficult to improve by gettering is that now the gettering process involves also precipitate dissolution which requires more extensive treatment. To model the impurity gettering process involving both precipitated and dissolved metal atoms in Si, a basic set of equations has been written by assuming that the precipitate dissolution process is limited by diffusion of the dissolved impurity atoms. These are

$$\partial C / \partial t = \partial \{ D [\partial C / \partial x - (C/m) (\partial m / \partial x)] \} / \partial x + 4 \pi r \rho D (C^* - C), \quad (1)$$

$$C^* = C^{eq} \exp \left(2 \Omega \sigma / r k_B T \right), \quad (2)$$

$$dr/dt = - \Omega D (C^* - C) / r. \quad (3)$$

In Eqs. (1)-(3) C is the impurity concentration in Si, m is the impurity segregation coefficient, r is the precipitate radius, ρ is the precipitate density, C^* is the impurity dynamic equilibrium concentration existing at the precipitate-Si interface, C^{eq} is the impurity thermal equilibrium concentration in Si, Ω is the volume of one impurity atom in the precipitate, σ is the precipitate-matrix interfacial energy density, and k_B is Boltzmann's constant. It is noted that Eqs. (1)-(3) also apply to the precipitate growth process. The reason for regarding the precipitate dissolution process as diffusion limited is for the purpose of obtaining a best case estimate of the effectiveness of a get-

tering process, i.e., it is the fastest. This means that no kinetic barrier against the dissolution of the precipitate is assumed. Most silicide precipitation and precipitate dissolution processes are associated with a precipitate-matrix volume misfit, which leads to a kinetic barrier slowing down the process. However, the diffusion limited precipitate dissolution assumption should be fairly realistic for solar grade Si and for IG in CZ Si, because the high density of dislocations can serve to eliminate the kinetic barrier incurred by the misfit, via mediations by point defects.

Results

Previously, Eqs. (1)-(3) have been used to numerically model the gettering process of both dissolved and precipitated Fe, for this case a 200 μm thick Si wafer was assumed to have been saturated with Fe at 900°C and precipitated at 700°C to completion and then gettered at different temperatures by a 2 μm thick Al layer situated at the backside of the wafer [2]. We have found that it will be quite ineffective to getter precipitated impurities at a temperature much lower than an effective temperature at which the impurity solubility corresponds to the total amount of the impurity present in the Si wafer [2]. This suggests that a higher temperature may be more effective, since for a given precipitate density and size the needed gettering time is decreased. Now we have completed our previous study of dissolution and gettering of precipitated impurities, by checking the influence of the precipitate density and gettering temperature on the gettering completion time. Figure 1 shows the summary of data obtained using the criterion that 99% of Fe introduced at 900°C is gettered into the Al layer, with gettering temperature and precipitate density used as modeling parameters. We believe that the present simulation results have provided a plausible explanation to the experimental results that gettering by Al of multicrystalline Si substrates may be ineffective. If carried out at a temperature somewhat higher than the precipitation completion temperature, the gettering process may even have an inverse effect. This is because on one hand the gettering time is too short and hence the process is not complete, and on the other hand the substrate dissolved impurity concentration may actually also have increased due to precipitate dissolution at the higher gettering temperature used. In experiments, one should also be aware of the problem of further contamination in using an unclean furnace at a fairly high temperature, e.g., 1000°C.

We have also used Eqs. (1)-(3) to numerically model the intrinsic gettering (IG) data obtained by Gilles et al. [3] and by Hieslmair et al. [4]. The data were obtained by measuring the concentrations of dissolved Fe atoms. In the experiments of Gilles et al. [3], Fe was diffused into CZ Si wafers with different densities of IG sites at 1100°C to the solubility value (monitored using FZ Si wafers). The wafers were then quenched to room temperature and subsequently annealed at 235°C for various times for Fe to precipitate out on IG sites. The use of the present expressions allowed to obtain the precipitate density and radius independently, see Fig. 2 for the precipitated density data, indicated as fitting parameters used in the simulation. Dependent upon the precipitate density, the corresponding precipitate radii (not shown) are in the order of 10-20 Å. In obtaining the fits, $m=1$ holds everywhere in the wafer and we have used $\sigma=0$ for simplicity. Their data showed that precipitation had already begun during the quenching process, and this is accounted for by an effective previously existing precipitation time of ~ 35 min at 235°C. The data of Hieslmair et al. [4] were obtained using Fe introduced at 950 and at 800°C. After quenching, the wafers were annealed at different temperatures to different times for Fe precipitation to occur. Their data with Fe introduced at 950°C, together with fittings obtained using Eqs. (1)-(3) are shown in Figs. 3. Equally satisfactory fits have been also obtained for their data with Fe introduced at 800°C (not shown).

Conclusions

Our simulation results indicate that if initially impurities are precipitated, they can only be efficiently gettered in a reasonable time at temperatures much higher than the precipitation temperature.

We believe that most of the basic physics and expressions for modeling the gettering process of a given impurity species, from the dissolution of the impurity precipitates to the diffusion and segregation (stabilization) of the impurity atoms, now exist. Accurate modeling parameters, such as the impurity charge states, level positions, solubilities, diffusivities, and interfacial energy densities between the silicide precipitates and Si are needed. Furthermore, we need also a realistic treatment of the precipitate nucleation problem.

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Fig. 1 Calculated effective completion times of gettering dissolved and precipitated Fe by a Si wafer backside Al layer. Various precipitate density ρ and gettering temperature T values have been considered. Other conditions are the same as for the case shown in Fig. 5. The effective completion time is defined by the criterion that 99% of all Fe introduced at 900°C was gettered into the Al layer.

Fig. 2. The Gilles and Weber [3] IG data (symbols) of gettering Fe at 235°C and simulation results obtained using Eqs. (1)-(3). The vertical axis shows Fe still in solution after the IG process. IG site creation annealing was carried out at 700°C for various times: filled circle for 4 h, filled triangle for 47h, open circle for 64 h, and open square for 192 h. The assumed precipitate density for calculating the fits is indicated on each simulation profile. See text for details.

Fig. 3 The data of Hieslmair et al. [4] obtained by introducing Fe at 950°C and quenching to room temperature before precipitation anneals. Their data were fitted using Eqs. (1)-(3). The temperatures indicated in the insets were the Fe precipitation temperature used in the experiments, while precipitate density ρ are values used in obtaining fits.

Title: Fundamental Research on Post-Growth Quality Enhancement Techniques

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Objective

The objective of this program is to investigate and optimize quality enhancement techniques, such as PECVD SiN deposition for defect passivation, phosphorus and aluminum treatments for defect and impurity gettering, and integrate the best gettering and passivation techniques to achieve high-efficiency multicrystalline silicon (mc-Si) solar cell.

Gettering and Al-BSF Effects on HEM mc-Si Solar Cells

The as-grown lifetime of the HEM mc-Si used in this experiment was found to be 10-15 μs by photoconductance decay (PCD) measurements. This is well short of the τ_b required ($> 35 \mu\text{s}$) to achieve efficiencies in the range of 18-19%. Therefore, a controlled experiment was performed to determine the effects of four different gettering schemes on the τ_b in HEM mc-Si. The four gettering conditions were: 1) heat treatment alone in N_2 , 2) phosphorus gettering alone, 3) aluminum gettering alone (in which 1 μm of Al was evaporated onto the material prior to the heat treatment), and 4) phosphorus and aluminum co-gettering (involving Al evaporation followed by a drive-in during the phosphorus diffusion). In all four cases, the thermal cycle was kept constant: 870°C/20 minutes. The results of this experiment are shown in Figure 1. Four important conclusions can be drawn from this data. First, phosphorus gettering alone provided the most substantial improvement in minority carrier lifetime, raising τ_b to an average of 111 μs . Secondly, heat treatment alone did not provide any gettering action. Instead, the τ_b measured after this process fell below 10 μs , probably due to the dissolution of precipitates. Third, aluminum gettering alone raised the τ_b to 69 μs , which is less than the level achieved by phosphorus gettering alone. Finally, co-gettering raised the as-grown lifetime to only 56 μs , which is also considerably less than the lifetime level achieved by phosphorus gettering alone. This indicates that the presence of aluminum during co-gettering retards the gettering efficiency of phosphorus. A possible explanation for this finding is that silicon self-interstitials generated by phosphorus diffusion, which aid in the "kick-out" of substitutional impurities during gettering, are absorbed by vacancies generated by the aluminum layer during drive-in.

After determining the effectiveness of phosphorus gettering, its process parameters were optimized further. Figure 2 indicates an optimal gettering temperature of 900°C for the HEM mc-Si used here. (The results presented in Figure 2 are normalized; however, the maximum τ_b values reached 135 μs). The existence of an optimal gettering temperature is evidence of the competition between gettering efficiency and the formation of lifetime reducing defects (i.e. dissolution of metallic precipitates or decoration of existing structural defects) as the gettering temperature is raised. Such behavior is typical for most mc-Si materials.

After achieving the desired τ_b , HEM cells were fabricated using the following process sequence. First, the n^+ emitter was formed using the 900°C phosphorus diffusion cycle. The as-diffused emitter ($\approx 30 \Omega/\text{sq.}$) was subsequently etched back to a reasonable sheet resistance ($\approx 80 \Omega/\text{sq.}$). Next, 10 μm of aluminum (99.999%) was evaporated onto the backside of the device. The wafer was then annealed at

850°C for 30 minutes in order to form the Al-BSF. At the beginning of this cycle, a passivating thermal oxide was grown on the emitter by exposing the sample to oxygen for 10 minutes. The remaining 20 minutes of the anneal was done in nitrogen. Upon cooldown to 400°C, the wafer was annealed in forming gas in order to improve the oxide/silicon interface quality and provide atomic hydrogen for possible bulk defect passivation. Finally, contacts were formed by lift-off photolithography, and a ZnS:MgF₂ double-layer antireflection coating was applied.

Characterization and Analysis of Record High Efficiency HEM Solar Cells

Figure 3 shows the IQE and output parameters of the best cell fabricated in this experiment with the 10 μm evaporated Al-BSF (V_{oc} of 636.0 mV, J_{sc} of 36.48 mA/cm², FF of 804, and efficiency of 18.6%, confirmed at the NREL). On the same wafer, six adjacent 1 cm² devices had an efficiency range of 17.2% to 18.6% with an average efficiency of 18.0%. This suggested a nonuniform distribution of electrically active defects in the material. Light beam induced current (LBIC) scans were carried out on the high and low efficiency devices in order to understand the role of extended defects on cell performance. A comparison between the LBIC response of an 18.6% and a 17.2% cell is shown in Figure 4. The scan of the 18.6% device reveals that the active area is free from detectable electrically active defects. Furthermore, the high bulk lifetimes measured in the processed material indicate that phosphorus gettering was effective in removing impurities from the as-grown silicon. On the contrary, the LBIC response of the 17.2% cell shows the presence of a significant density of electrically active defects (primarily dislocation clusters decorated with impurities). The PDG, forming gas anneal, and aluminum treatments used in this study could not improve the current response in these defective regions.

Passivation of EFG mc-Si by PECVD SiN

PECVD SiN deposition process is quite complicated to fully understand from the first principles. Therefore, first neural network modeling was performed to establish the correlation between deposition parameters and film properties. Then, optimal parameters were used to maximize the influence on cell performance. In this study, six PECVD silicon nitride deposition parameters (substrate temperature, chamber pressure, RF power, and the flow rate of silane, ammonia, and nitrogen) were used as inputs to the neural network and positive charge, bonded hydrogen content, and effective lifetime were the desired outputs.

Neural network modeling showed that lower RF power and higher growth temperature increases positive charge density and improves surface passivation, while lower temperature increases bonded hydrogen content and improves bulk defect passivation.

Figure 5 shows a correlation between the refractive index and the bonded hydrogen content of the SiN films before and after a 650°C/1.5 minute photoanneal in a N₂ ambient. Even though in all cases the bonded hydrogen concentration decreases after the anneal, films with higher as-deposited refractive indices release more bonded hydrogen and show greater increase in the refractive index value. Thus, photoanneals result in an increase in refractive index, but decrease in hydrogen content of the silicon nitride film. In addition, the magnitude of this effect is proportional to the as-deposited refractive index value.

Figure 6 shows the change in average efficiency of eleven 1 cm² EFG cells (randomly selected from different wafers) as a function of annealing temperature. The average efficiency of the cells increased gradually with the increase in annealing temperature up to 650°C, and then the efficiency started to decrease at higher temperatures. It should be recognized that due to the inhomogeneous defect distribution in EFG material, the impact of the PECVD SiN deposition and RTP anneal could be different on different small area EFG cells. In another study, it was shown that the increase in the absolute cell efficiency after

the 650°C post PECVD anneal can vary from 0.2% to 2%, depending upon on the location of a cell on the wafer [1].

Figure 7 shows the effect of higher temperature anneals on the IQE response of EFG cells. The anneal time was reduced to 5 minutes and 1.5 minutes for 500°C and 650°C anneals, respectively, to reduce junction leakage and shunting effects caused by contact metal diffusion. The IQE analysis showed that the 500°C anneal increased the diffusion length from 63 μm to 77 μm , and after the 650°C anneal, the diffusion length increased to 97 μm . Thus, SiN coating with an index of 2.3 increased solar cell performance of EFG mc-Si solar cells by 45% (due to antireflection coating) and another 25-30% due to bulk defect passivation.

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FIGURE 1. The effects of gettering treatments on the τ_b in HEM mc-Si.

FIGURE 2. Effects of phosphorus diffusion temperature on the gettering efficiency of HEM mc-Si material.

FIGURE 3. IQE curve and IV data for the record high HEM mc-Si solar cell.

FIGURE 4. LBIC scans of the a) 18.6% HEM mc-Si solar cell and the b) 17.2% device.

FIGURE 5. Change in bonded hydrogen content of PECVD SiN films after a 650°C/1.5 minute photoanneal.

FIGURE 6. Change in efficiency of EFG solar cells with SiN films applied as a function of photoanneal temperature.

FIGURE 7. Effects of photoannealing SiN on the IQE response of EFG mc-Si solar cells.

Title: The Role of Point Defects and Impurities in the Processing Performance of Crystalline Silicon Solar Cells

Organization: Massachusetts Institute of Technology

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Introduction

Our purpose is to develop and demonstrate processes that will enhance the yield and performance of crystalline silicon solar cells by the discovery of critical factors in defect control. Studies of wafer handling and Al backside contact formation have yielded 1) a predictive model for contamination during etching to guide specification of chemical purity; 2) an in-situ monitor of process and materials quality; 3) a model for gettering efficiency of transition metal contaminants by Al contact formation; 4) determination of the highest diffusion length process window (time, temperature, lifetime, interface morphology) for backside Al contact formation; and 5) theory and experiment to explain lifetime instabilities in iron contaminated cells.

Experimental Results

We have completed a process design optimization for the alloyed aluminum backside contact. This metallization system is the PV industry standard. By heating an Al on Si metallization above the eutectic temperature of 565C, solid silicon is dissolved into a liquid eutectic. Upon cooling an aluminum-doped region is formed that acts as an ohmic contact and as a "backside field" that repels minority carriers away from the high recombination velocity region at the contact interface. The quality of the backside contact plays a determining role in the V_{oc} of the finished cell. Three primary factors for good contact performance were identified: morphological stability in the formation of the backside field; contact stress due to the difference in thermal expansion coefficients of Si and Al; and gettering of unwanted contaminants from the base.

Interface Morphological Stability

Planar Al/Si and p+/p interfaces are required for effective protection from surface recombination and for effective light trapping. However, a planar liquid / solid interface is morphologically unstable, because solute segregation is more efficient for a curved surface. Weak thermal fluctuations are amplified in a way that a smooth interface becomes rough. We have determined two paths to morphological stability: surface energy engineering and kinetic limiting. The lowest free energy silicon surface, the (111) surface is the most stable, because surface tension drives planarity. Wafers of a (111) surface orientation exhibit uniformly, planar alloy fronts and interfaces. For other orientations planarity is unstable.

This morphological instability can be suppressed by not allowing time for the driving fluctuations to develop. Figure 1 compares results obtained by a 30 minute furnace anneal and a 10 second Rapid Thermal Anneal (RTA). The fast temperature ramps produce a significantly more planar interface morphology.

Thin Film Stress

The thermal expansion coefficients of Al and Si differ considerably. Following solidification of the Al eutectic and cooling to room temperature, we measure stresses in the Si wafer of >125Mpa. These stress levels are relieved very gradually by fracture of the Al film. Figure 2 shows a Scanning Electron Micrograph of a crack in an alloyed Al film.

Besides loss of film continuity, strain transmitted to the underlying Si can modulate the band structure and introduce inhomogeneities in charge collection, reducing V_{oc} . Stresses can be reduced by decreasing the thickness of the Al film but at a cost of backside field depth and reduced gettering capacity. The thickness of the p+ field region increases with the alloy temperature and the thickness of the original Al film as shown in Figure 3. The design constraints may be summarized as follows. Thicker, more heavily doped p+ (BSF) regions enhance charge collection efficiency. These regions may be produced by long time, high temperature heat treatment of thick Al films on Si. These process parameters also optimize gettering as is discussed later. However, these beneficial effects are retarded by the high state of stress and morphological roughness of the resulting interfaces.

Gettering of Contaminants

Transition metal impurities introduce deep electronic states in the band gap that act as e^-h^+ recombination centers. These elements are the primary source of contaminant related limitations to charge collection efficiency. Effective gettering processes, when integrated into the cell process flow, provide a low cost way to use metallurgical grade source material. The backside contact getters during the alloy step and subsequent processes by solid phase segregation into the liquid eutectic and to the p+ layer. We have modeled the solubility enhancement of Fe in Si with p+ doping. This enhancement determines the segregation coefficient of the p/p+ interface that governs gettering during cell processing. Figure 4 shows the dependence of the segregation coefficient, K, on p+-doping and temperature.

We have conducted experiments on the removal of Fe from the center of a wafer during the Al alloying step. The Fe concentration rapidly decays to the solubility limit at the process temperature as shown in Figure 5. An outdiffusion dominated mechanism should have no such limit. Our data are consistent with a mechanism in which internal precipitation competes with outdiffusion (ref Weber, JEM). We have developed a macroscopic level model that describes the competing mechanisms as shown in Figure 6. The model predicts that the competition is independent of temperature, but strongly dependent on the density of sites for heterogeneous nucleation of metal precipitates. For a wafer thickness of 500 μ m, a nuclei density of greater than 10^9 cm⁻³ is required for competition with outdiffusion.

Process Optimization

Process optimization involves a compromise among the conflicting design parameters. Each process flow will have a unique optimization based on its particular constraints. The following concepts serve as a guide for process design. The alloy step should be performed at as high a temperature as possible, for a highly doped BSF and to dissolve contaminant precipitates, using RTA to maintain a flat interface. An extended anneal below the Si:Al eutectic temperature (350-550C) allows relaxation of mechanical stress by grain growth in the Al film and segregation of contaminants into the p+ BSF region. Thinner films reduce stress levels, but also reduce the BSF volume. These process design rules should lead to enhanced cell performance for both J_{sc} and V_{oc} metrics.

Conclusion

This program addresses the limiting factors in cell performance with low cost manufacturing. We have created tools to monitor cleanliness; processes to specify chemistries for handling; and fundamental formalisms to guide process development. The understanding and development of robust process technologies are key to PV energy sources.

Figure 1 a. Combined SEM and EBIC image (3 kV) of the BSF junction region. This sample has an n-type base and was annealed at 950°C for 30 minutes. The sample was beveled (4 degrees) and shows the following: (i.) the Si-Al interface, and (ii.) the p+-n junction.

Figure 1 b. Image showing the junction formed with a rapid thermal annealed sample (1000°C for 10 seconds.) The sample was beveled (4 degrees) and shows the following: (i.) the Si-Al interface, and (ii.) the p+-n junction.

Figure 2. SEM micrograph of Al film shows the visible signs of stress relief (fracture) 24 hours after processing.

Figure 3. p+ layer thickness as a function of alloying temperature (temperature in degrees C.)

Figure 4. The iron segregation coefficient, k , as a function of boron concentration has been calculated for various temperatures using fermi-dirac statistics.

Figure 5. Iron concentration as a function of annealing time for sample with Al contact. Samples were quenched after anneal and data was taken with DLTS.

Figure 6. Precipitation at heterogeneous nucleation sites competes with out-diffusion for interstitial Fe removal for samples contaminated above the solubility limit at the annealing temperature.

Title: Detailed Non-Contact Electrical and Structural Characterization of Photovoltaic Silicon Substrates

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Introduction

The objectives of this work are (i) the determination of recombination-trapping levels using a contactless laser microwave technique, and (ii) a study of extrinsic gettering using Ti thin films.

I. Measurement of Deep Recombination Levels Using Frequency Resolved (FR) Photo Microwave Spectroscopy

In the frequency domain, the microwave reflection coefficient $R(\omega)$, depends on the free carrier mobility and $N_{ac}(\omega)$, the total number of excess carriers generated by a sine modulated light source¹. We have calculated $N_{ac}(\omega)$ for both one and two trap-recombination levels using the Shockley-Read-Hall (SRH) model. In this analysis we have assumed that Δn and Δp , as well as the electron and hole lifetimes, are different. The above assumptions are important when we deal with recombination center concentrations above $1E14\text{cm}^{-3}$, and when the levels are in the upper part of the band gap, e.g., for the acceptor level Fe-B ($E_c-0.29\text{eV}$) in p-type Si.

To check the accuracy of the method two p-type Si wafers with doping concentration of $1E15\text{ cm}^{-3}$ have been measured. The wafers were Fe contaminated during crystal growth to $1E11$ and $1E13\text{ cm}^{-3}$. Figure 1 shows a Nyquist plot², $\text{Im}(R(\omega))$ versus $\text{Re}(R(\omega))$ of the wafer containing $1E13\text{ cm}^{-3}$ Fe measured at 80°C . The left dashed semi-circle in the figure is affected by e-h recombination, while the larger right semi-circle corresponds to an electron trapping process. To obtain the recombination parameters the error function:

$$\chi_r^2 = \sum_{\omega} \left(\frac{R(\omega)}{\text{Im } R(\omega)_{\max}} - \frac{N_{ac}(\omega)}{\text{Im } N_{ac}(\omega)_{\max}} \right)^2$$

was minimized at different measurement temperatures using the Nedler-Mead simplex method³. One difficulty in minimizing χ_T is the fact that there are many local minima and the final result depends on the starting point. To overcome these difficulties we added a random noise function (simulated annealing simplex³ technique).

The best parameter set that makes the fitting reliable is: the product of electron capture cross section by recombination center concentration $\sigma_n N_R$, and the surface recombination velocity v_s . These parameters have been used for the levels located at the lower band edge,

whereas one more parameter $\sigma_p N_R$ has been used for energies located at the upper band edge (σ_p : the hole capture cross section). The three well known recombination levels^{4,5}: $E_v+0.1$, $E_v+0.4$ and $E_v+0.8$ eV have been tested with this fitting procedure. Fig. 2 shows $\sigma_n N_R$ versus $1/T$ for the first wafer. The standard deviation χ in regard to temperature ($\chi = \sqrt{\sum \chi_i^2}$) have the same value for these three levels, indicating that recombination processes via these levels are operative. However, the level 0.1eV leads to unrealistic $\sigma_n N_R$ values, therefore it has to be excluded. From the curves shown in Fig.2 one can distinguish three regions. In the first region labeled I, $\sigma_n N_R$ decreases slowly, most likely due to Fe-B pair formation⁶. In the region II, the reappearance of Fe_i^+ , due to Fe-B dissociation, is evident and results in an enhancement of the $\sigma_n N_R$. At high temperatures, region III, $\sigma_n N_R$ again decreases as Fe_i^+ is neutralized due to Fermi level changes. In Fig.3 three lifetime characteristics versus $1/T$ are shown. The frequency resolved (FR) lifetime τ_{FR-H} correlated with $E_v + 0.4$ eV level has been measured with high (H) DC excitation level. The lifetime τ_{eff} has been measured using the time resolved LM-PCD technique. A discrepancy between both lifetimes appears at room temperature are due to trapping processes, and Fe-B pair dissociation by IR laser irradiation. In the FR method¹ an IR - LED excitation source is used at a much lower power density than the laser beam PCD procedure. The trapping process is better seen on the third characteristic τ_{FR-L} shown in Fig.3. This characteristic has also been measured by the FR technique but using a low (L) DC excitation level. Figure 4 presents $\sigma_n N_R$ for the second wafer ($N_{Fe} = 1E13 \text{ cm}^{-3}$), where the two levels 0.4 and 0.8eV also give the "best" fitting, indicating that both centers are involved in recombination. As above, three regions I, II and III, can be distinguished; however, the region III is flat, because the Fermi level is below 0.4eV. The TR and FR lifetime characteristics, which are not presented here, have shown that the traps are also involved in free carrier transitions.

In the above simulation the recombination levels 0.4 and 0.8 eV were investigated separately using a one trap-recombination model. A two trap-recombination model has also been tested, which shows that: (i) the function χ is essentially the same as that for the single trap-recombination simulation, and (ii) the 0.4eV level parameters are stable, while the 0.8eV level parameters are unstable and depend on the initial condition, indicating that the recombination process is dominated by the deep level at 0.4eV.

II. Ti Thin Film Extrinsic Gettering

It is known that metallic impurities introduce g-r centers within the bandgap and these centers can be reduced or eliminating using extrinsic gettering. The extrinsic gettering can be achieved using a thin film metal deposition, usually at the back side. A number of metals are mentioned in the literature⁷; however, for PV applications Al is the most popular. In our experiment we have used Ti film to getter the upper part of a silicon wafer, because the Ti oxide grown during the annealing time can be used as an antireflective coating on the cell. Ti films of 1000 Å have been deposited by sputtering. We have also sputtered Al film to compare gettering efficiency of both materials. P-type Si wafer ($1E15 \text{ cm}^{-3}$) contaminated with Fe of $1E12 \text{ cm}^{-3}$ and tri crystal p-Si ($\rho = 0.5-5 \text{ } \Omega\text{cm}$) of Helios Tech. have been coated with Al and Ti. Then, the samples were annealed in forming atmosphere at 400°C for 300 min and at 600° for 80 min. After annealing, the upper layers were stripped off by dipping the samples in CP-4 solution for 30 sec. To monitor the gettering process the effective lifetime has been measured using LM-PCD, and impurity levels have been determined by DLTS. For Al gettered samples, the carrier

lifetime of the tri crystal sample increases from 7 to 23 μs , while for the p-Si sample the lifetime changes from 1.5 to 8.5 μs (400°C) and to 7.5 μs (600°C). In the case of Ti gettering, the lifetime increases to 10 μs (400°C) and to 9 μs (600°C). Figure 5 shows the DLTS spectra for R reference, Al, and Ti extrinsic gettering samples. The reference sample reveals an Fe-B pair peak at 55K, and a broad peak at 230K. Note that the absence of peaks in the DLTS spectra demonstrates the Ti film extrinsic gettering ability.

III. Conclusions and Future Work

The results presented above show that the frequency resolved (FR) microwave technique provides useful information about recombination levels at low impurity concentration. Controlling the DC and AC levels allows one to investigate trapping and recombination processes. The Fe-B pair dissociation effect is less significant in FR than in the standard LM-PCD method, which uses a laser pulse as an excitation source. However, the FR microwave technique has the disadvantage of long light generation time which is comparable to the transient time. This requires both generation and recombination processes to be considered simultaneously, which results in a more complex analysis. The effective recombination centers revealed by fitting of FR experimental data correspond to 0.4 and 0.8eV levels.

Concerning the Ti gettering ability at low temperature, both lifetime and DLTS data show good results. The work with Ti gettering is continuing and we are looking for the enhanced concentration of positively charged impurities at the edge of the depletion layer⁸ created by Ti-Si Schottky barrier.

Fig.1. Nyquist plot $\text{Im}R(\omega)$ vs. $\text{Re}R(\omega)$ for the wafer containing $1\text{E}13\text{ cm}^{-3}$ Fe measured at 80°C.

Fig.2. $\sigma_n N_R$ vs. temperature for the wafer containing $1\text{E}11\text{ cm}^{-3}$ Fe, for the levels at 0.1, 0.4 and 0.8eV.

Fig.3. Lifetime characteristics vs. temperature for the wafer containing $1\text{E}13\text{ cm}^{-3}$ Fe; $\tau_{\text{FR-L}}$, $\tau_{\text{FR-R}}$ FR lifetimes at low/high DC excitation levels, τ_{eff} TR lifetime.

Fig.4. $\sigma_n N_R$ vs. temperature for the wafer containing $1\text{E}13\text{ cm}^{-3}$ Fe.

Fig.5. DLTS spectra of gettered samples.

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Title: **THEORETICAL ANALYSIS OF
HYDROGEN-VACANCY-IMPURITY
FORMATION AND DISSOCIATION**

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Objectives

Poly-Si solar cells often benefit substantially from the passivation [1,2] by H of dangling bonds at vacancies, dislocations, grain boundaries, and other defects. However, it is not clear which defects benefit the most from hydrogenation. In fact, the microscopic structure of the defects themselves is not known. Dislocations for example, are referred to as 'good' (those that can be passivated) and 'bad' (those that cannot). The latter are often the efficiency-limiting factor in solar cells. Further, hydrogenation is very efficient in O-poor material but does not lead to improved cells in O-rich material.

The long-term objectives of this research is to investigate this problem theoretically at or near the ab-initio level, and provide new insights into the issues of defect-defect, hydrogen-defect, and hydrogen-impurity interactions. The results obtained in previous years dealt with H diffusion, H-vacancy complex formation, and IR active vibrational modes for experimental identification.[3,4] Ongoing research focuses on vacancy-vacancy interactions and hydrogen-oxygen interactions. Two key results have been obtained this year. (i) The 'discovery' that vacancy-vacancy interactions lead to the formation of a very stable defect, the ring-hexavacancy, which is electrically and optically inactive. Yet, this defect is likely to be a gettering center and the building block of more extended defects. (ii) Molecular-dynamics simulations of H-O interactions and H-enhanced diffusion of oxygen.

Theoretical Approach

The equilibrium geometries, electronic configurations, diffusion paths, and potential energy surfaces are calculated at various levels of ab-initio Hartree-Fock (HF) theory in molecular clusters. The outputs provide precious chemical information on the details of the rebonding around a complex. The dynamics of complex formation and dissociation, vibrational frequencies, and diffusion properties are obtained with the ab-initio tight-binding molecular dynamics (MD) method developed by Sankey *et al.* [5,6] In the MD approach, the host crystal is represented by periodic supercells of 64 atoms. For details about the theoretical techniques and the cluster and supercells approximations, see Ref. [1].

Vacancy-Vacancy Interactions

We used MD simulations to find all the possible configurations of aggregates of N-vacancies (V_N), with $N = 1, \dots, 6$. We removed all the combinations of symmetrically inequivalent sets of N silicon atoms from a 64-atoms periodic supercell and quenched. This

procedure forces convergence toward a local minimum of the potential energy and allows a comparison of the (fully relaxed) structures and energies of inequivalent V_N complexes. The lowest-energy configuration of all the V_N 's occurs when Si atoms are removed successively from a hexagonal ring in the crystal. V_1 , V_2 and V_3 have only one possible configuration. V_4 and V_5 have several, but only one of the metastable configurations is close in energy ($\sim +0.1$ eV) to the one where the atoms come off of a ring.[7] The lowest-energy configuration of V_6 (missing hexagonal ring) is much more stable than any other of the fifteen or so configurations of V_6 (the next one is at $\sim +0.9$ eV).[8]

The lowest-energy structures of each V_N are being re-optimized at the HF level using gradient techniques with no symmetry assumption. This will provide a second set of energetics and the chemical details of the rebonding.

The formation energies $\Delta E_N = \{E_N + E_0\} - \{E_{N-1} + E_1\}$ are shown in Fig. 1. E_N is the energy of the most stable (fully reconstructed) V_N aggregate. Thus, ΔE_N is the energy gained by adding an isolated monovacancy to the most stable aggregate of $N-1$ vacancies. The energy of the heptavacancy was obtained by removing one Si atom adjacent to the ring-hexavacancy and allowing the crystal to reconstruct. The open circle shows the experimental binding energy of the divacancy (1.5 eV).[9]

FIGURE 1: Energy gained by forming the V_N aggregate starting with V_1 and V_{N-1} . The ring-hexavacancy is by far the most stable defect. The open circle is the experimental binding energy of the divacancy.

V_6 is remarkable not only for its stability but also because the crystal is able to reconstruct almost perfectly around it. This results in no 'dangling-bond-like' character for this defect. A comparison of the energy eigenvalues of the perfect cluster to those of V_N , $N = 1, \dots, 7$, shows that V_6 has no deep level in the gap, and that the top of the valence band does not shift. Only the bottom of the conduction band is affected by V_6 , with unoccupied levels shifting into the gap (this band-tailing is more pronounced in the MD than the HF calculations). In contrast, all the other vacancy aggregates have clearly visible deep levels in the gap. These (qualitative) features imply that V_6 is not an electron-hole recombination center and should be electrically inactive.

The charge distribution calculated at the ab-initio HF level indicates that V_6 has the smallest dipole moment of all the vacancy aggregates we considered. The net dipole moment points along the trigonal axis but has negligible magnitude (0.0007 atomic units), implying that V_6 should not be infra-red active.

The reconstructed hexavacancy is almost planar and has trigonal symmetry. It resembles a small prismatic dislocation and could be a precursor of platelets and/or other extended defects. It is a fairly large void in the crystal, and could be a gettering center for impurities such as H, O, or transition metals.

Hydrogen-Enhanced Diffusion of Oxygen

There is ample experimental evidence that hydrogen considerably enhances the formation rate of O-related thermal donors in Si (earliest observation: Ref. [10]; recent work: Refs. [11,12]; recent review: Ref. [13]).

There is no direct experimental information on the mechanism involved. However, there are strong indications that atomic hydrogen is the key species, and that concentrations of H as low as 10^{14} cm^{-3} are sufficient for the process to take place in samples containing some 10^{18} cm^{-3} interstitial O. It looks like H acts as a catalyst: H does not participate in the final state, but lowers the reaction energies. The estimate is that the activation energy for diffusion of interstitial O drops from 2.59 eV to may be half that value.

There FTIR[14] and muon spin rotation[15] evidence that H is attracted to interstitial O. Recent SIMS studies[16] are also consistent with a strong attraction between H and O in silicon. The results of our MD simulations[17] are as follows.

- (1) Bond-centered (BC) and tetrahedral interstitial (T) H are attracted to interstitial O. However, H self-traps in the vicinity of O. This suggests that in O-rich samples, H remains trapped near O (the most abundant defect) instead of diffusing toward and passivating deep centers.
- (2) We do not know at this time if several H interstitials must reach the same O before a catalytic reaction is initiated.
- (3) If H is placed near O, it attaches to O almost immediately. This makes sense since the formation of an H-O bond (bond strength $\sim 5.2 \text{ eV}$) should be favored over the formation of an H-Si bond (bond strength $\sim 3.7 \text{ eV}$). The formation of the H-O bond results in the replacement of the configuration where O is attached to two (fixed) Si atoms by one where O is attached to one (fixed) Si atom and to H. At this point, the {O,H} pair begins to oscillate around the only fixed point. If given a 'kick', the {O,H} pair can be made to jump through the crystal within a picosecond (Fig. 2).

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FIGURE 2: MD simulation in which interstitial O starts at an unrelaxed BC site (the relaxation gives a kick to O), and H at an adjacent T site. H attaches to O almost immediately, then the pair remains bound as O hops to other BC sites. For clarity, only a few of the 64 Si atoms in the supercell are shown.

Title: Aluminum Gettering and Transition Metal Precipitates in PV Silicon

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OBJECTIVES

Transition metals have been studied in silicon for many years. In the Integrated Circuit (I.C.) industry, transition metals have a detrimental effect on device performance and yield. Similarly, for good photovoltaic cell efficiencies, low transition metal impurity concentrations are required in order to have high minority carrier diffusion lengths and solar cell efficiencies. In photovoltaic (PV) grade silicon, commonly present metallic impurities are Fe, Cr, Ti, Mo and V in either dissolved or precipitated states (1). Our own studies indicate that the type and amount of impurity vary greatly from one PV silicon to the next, with up to 10^{14} Fe/cm³ in some PV grade CZ silicon samples. The object of our continuing studies is getting of transition metals and minimizing the deleterious effects of transition metals in PV grade silicon.

DISSOLVED IMPURITIES

Dissolved impurities can have an effect on minority carrier lifetimes if they create a deep trap level in the silicon bandgap. In p-type silicon, interstitial iron forms Fe-acceptor pairs, and is generally used as a model for other transition metals. Iron-boron pairs are easily detected with Deep Level Transient Spectroscopy (DLTS) with a deep level at $E_v + 0.1\text{eV}$ and $E_c - 0.29\text{eV}$. A simplified S-R-H expression relating minority carrier diffusion length, L , and the dissolved impurity concentration as follows (2):

$$L_n = \sqrt{D_n \tau_n} \quad \tau_n = \frac{1}{\sigma_n \langle v_{th} \rangle N_t} \cdot e^{(E_F - E_t)/kT} \quad \text{Eq. 1}$$

where σ is the minority carrier capture cross section, v_{th} is the thermal velocity of the carriers and N_t is the impurity concentration.

Figure 1a. As-quenched diffusion lengths of FZ silicon vs dissolved Fe concentration and Figure 1b. Diffusion length as iron precipitates, i.e. dissolved concentration drops as the iron forms clusters and precipitates.

Figure 1a shows data from samples of various experiments. These FZ silicon samples ('As-quenched' and 'Pre-gettered') were annealed in the presence of iron and then quenched to room temperature. After room temperature storage, iron forms FeB pairs as confirmed by DLTS.

Also shown are data from Zoth et al. (2) The two lines differ in the value of the effective carrier capture cross section.

PRECIPITATED IMPURITIES

Iron and other transition metals can also precipitate from solution. Usually precipitation occurs at nucleation sites which include structural defects such as dislocations (3,4) found in most PV silicon materials. Precipitation at structural defects can greatly exacerbate the recombination activity of the structural defects. However, the effects of impurity precipitation on overall diffusion lengths and cell efficiencies is uncertain. The types of defects present in the material as well as the cooling rates greatly affect the recombination activity of the defects. Studies with EBIC and metal impurities decorating various dislocations, performed by Shen et al.(5) and Sumino (6), hint at the complexity of the effects of impurity precipitation on recombination activity of defects and thus bulk minority carrier diffusion lengths. Our results, shown in Figure 1b, strongly suggest that Fe is as efficient as a recombination center in the dissolved state as in the precipitated state. Minority carrier diffusion lengths neither increased nor decreased by a significant amount as iron was precipitated, as indicated by the arrows in Figure 1b. Thus iron, as well as other transition metals, must be *removed* from the bulk in order to improve the minority carrier diffusion length.

ALUMINUM GETTERING

Demonstration of Aluminum Gettering in FZ Silicon

One of the most interesting approaches to removing iron or other transition metals from the bulk is aluminum backside gettering. A comprehensive study was begun to fully understand the nature of aluminum segregation gettering, both qualitatively and quantitatively (7). In this study, p-type float zoned silicon, with a boron concentration of approximately $1.15 \times 10^{15} \text{ cm}^{-3}$, was used to avoid possible complications arising from the interactions of the intentional iron contamination with dislocations, grain boundaries, oxygen precipitates, and other unintentional impurities. Additionally, the aluminum p^+ backsurface field, formed during the anneal at high temperatures, was removed with a strong etchant before any SPV measurements. Precipitation was also avoided as much as possible by performing the aluminum gettering at the same temperatures as the iron diffusion and by using a rapid thermal anneal and quench (RTAQ) to re-dissolve any remaining precipitates. The FZ had an initial minority carrier diffusion length $>400\mu\text{m}$. Iron was used for our model impurity because its kinetics and solubility are well known and it is a common impurity element in I.C. and PV materials. Iron was diffused into the samples at the times and temperatures shown in Table 1.

After the iron diffusion, the samples were quenched in ethylene glycol with a quenching rate of the order of 1000°C/s . This fast quench ensures that the iron

Table 1: Iron diffusion and aluminum gettering temperatures and times

Sample	1	2	3	4	5
Temp $^\circ\text{C}$	950	900	850	800	750
Time (min)	40	60	85	110	150

remains in the dissolved state and does not precipitate. The iron diffusion times were chosen such that $\sqrt{D_t} \geq 700\mu\text{m}$ while our sample thickness was only $500\mu\text{m}$. The samples were etched, removing any surface FeSi_2 , and cleaned. Then, minority carrier diffusion measurements were measured with surface photovoltage (SPV) technique and iron concentrations were measured with deep level transient spectroscopy (DLTS).

Aluminum was then evaporated or sputtered onto the samples. All annealings were performed in a TCA cleaned furnace used for I.C. fabrication. The samples are slow cooled at the end of the gettering anneal, thus precipitating the remaining dissolved iron. In order to detect all the iron with DLTS, it must be re-dissolved. After a strong etch (to remove the Al-Si gettering layer) and clean, a rapid thermal anneal and quench (RTAQ) at 1000°C for 10 seconds is used to

dissolve any residual precipitated iron in the bulk of the sample. After the RTAQ, the samples are etched again to avoid surface effects before DLTS and SPV measurements.

Figure 2a shows the minority carrier diffusion lengths for each process. Figure 2b shows the initial and after RTAQ iron concentrations. In both figures, the sample numbers denote the iron diffusion and gettering temperatures as shown in Table 1. Additionally, the first group of five samples (*) had iron diffused and a back side aluminum layer, the middle group (-) had iron diffused and no back side aluminum layer, and the last group (0) had no iron and no aluminum back side layer. From these results we see significant diffusion length improvements via iron concentration reductions in the aluminum gettered samples to below solubility and background levels. For example, at a gettering temperature of 950°C, the aluminum gettering process removes iron to a level which is three orders of magnitude *below* the solubility of iron at that temperature.

The minority carrier diffusion length of the samples is plotted vs the iron concentration in Figure 1a. The aluminum gettered samples reflect the improvement by gettering, but they lie to the left of the dashed 'as-quenched' line. This indicates the presence of other recombination centers such as still undissolved iron (despite the RTAQ), other contaminants, or lifetime degradation resulting from the RTAQ. The iron detected in the samples with no intentional iron contamination (0), may have been initially present in the float-zone silicon.

PV Silicon Materials Do not Respond Similarly

The experiment just discussed showed that Al gettering improved a 40 to 50 μm minority carrier diffusion length sample to 170 - 180 μm . Unfortunately, such improvements have not been observed in typical PV grade silicon materials such as low cost CZ or EFG. We have studied aluminum gettering of solar materials extensively, again using iron as a model impurity. A summary of gettering experiments is shown in Figure 4a and represents an average of numerous gettering results (8,9). These experiments were performed on various PV grade silicon materials without any intentional contamination and gettered at 850°C with various thicknesses of aluminum. The results for solar cell materials were not as positive as had been hoped for. Various gettering times and temperature treatments were explored and no significant minority carrier diffusion length

Figure 2a Minority carrier diffusion lengths and Figure 2b iron concentrations for various silicon samples, see Table 1.

Figure 4a. Comprehensive summary of numerous gettering experiments. Each point is an average of experimental data. Figure 4b. As-grown iron impurities measured by DLTS after an RTAQ

improvements were observed. Generally PV silicon does not respond well to Al gettering processes.

Reasons for Poor Gettering Response in PV Materials?

At first glance, one might conclude that the segregation coefficient of aluminum gettering is too small. However, segregation coefficients, obtained from the previous aluminum gettering experiments involving FZ silicon, indicate that segregation coefficients range from 10⁵ to 10⁶ or higher, sufficiently high to improve PV materials. Thus, aluminum gettering should remove transition metals from the wafer silicon.

Perhaps aluminum gettering requires more time? Modeling of aluminum gettering indicates that, at least for dissolved iron, gettering performance should be better than it is. Figure 5 shows iron concentration profiles calculated using a finite difference technique which will be discussed later. For an initial iron concentration of 10¹³ Fe/cm³, approximately three hours are necessary to reduce iron concentrations to well below DLTS detection limits. This is in the range of iron contamination in numerous as-grown PV silicon materials shown in Figure 4b. It is also possible that the PV grade silicon materials contain slow diffusing transition metals, although we have not observed other DLTS signals.

Precipitated impurities could slow the gettering process by simple kinetics or with barriers to precipitate dissolution. The situation shown in Figure 3 is extreme, but serves to illustrate how high concentrations of precipitated impurities can greatly prolong the gettering process. While this may seem to explain the lack of gettering response of solar cell materials, gettering at higher

Figure 5. Iron concentration profiles during aluminum gettering

Figure 3. Iron concentration (dissolved and precipitated) vs wafer depth for increasing times during aluminum gettering.

temperatures, would greatly accelerate the gettering process. At 950°C this same process would only take a few hours. Yet experiments at higher gettering temperatures such as 950°C show no significant improvements.

Thus, it seems likely that there exist barriers to precipitate dissolution. Such barriers could arise from strain fields around dislocations or precipitate/lattice mismatch strains which would slow the gettering process. It is entirely possible that some barriers are so high as to prohibit gettering. Unfortunately, there is a poor understanding of transition metal dissolution in silicon.

SUMMARY

Aluminum gettering has been shown to work for iron dissolved in FZ silicon material. The aluminum gettering experiment allowed us to estimate a lower limit for the segregation coefficient at 1×10^5 . An experiment more sensitive to higher segregation coefficients will be designed by modeling. The insensitivity of solar grade silicon materials to aluminum gettering is hypothesized to be due to barriers to dissolution of the impurity precipitates. Precipitate dissolution needs to be studied further. More comprehensive simulations have been developed and will be used to help design experiments to better understand precipitate dissolution in solar grade silicon materials in order to design effective gettering procedures for this material.

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Title: Optimization of Gettering Processes for Photovoltaic Silicon

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Objectives

Our efforts were focused on the hydrogenation improvement using ultrasound treatment (UST) in polycrystalline silicon (poly-Si) thin films - a perspective material for a new generation of solar cells. We also developed a new experimental approach to defect characterization in bulk solar-grade poly-Si wafers using room-temperature photoluminescence (PL) spectroscopy. PL intensity mapping is a complimentary technique to surface photovoltage monitoring of recombination properties of solar cells.

Approach : Fast Hydrogenation Using Ultrasound Treatment in poly-Si Thin Films

Low-amplitude ultrasonic vibrations can be generated into a bulk semiconductor or thin film on glass using piezoelectric UST transducers operating in a resonant acoustic mode. A sample has to be placed on UST chuck and tightly pressed against chemically-polished transducer surface with a vacuum to provide a good acoustical contact. Computer controlled UST station optimizes and adjusts "in-situ" UST parameters: amplitude, frequency, duration and temperature. UST station operates in a feedback loop with a non-contact UST probe and non-contact infrared temperature sensor and is capable to process up to 12" diagonal wafers by delivery a homogeneous distribution of UST amplitudes and temperature up to 300C. The station can be easily scaled up by adding ultrasound transducers at any custom designed configurations of UST chuck.

Results

UST was applied to semi-insulating LPCVD poly-Si films on glass or fused silica substrates with thickness from 0.35 to 0.55 μ m. It was previously reported, that UST in plasma-hydrogenated films at $T < 100^{\circ}\text{C}$ promotes an additional passivation of grain-boundary defects [1]. We observed that this process can be strongly facilitated at higher UST temperatures. A dramatic increase of infra-red PL intensity by a factor of two orders of magnitude is observed after *a few minutes* of UST applied at 280°C [2]. In poly-Si films obtained by recrystallization of amorphous Si during 550°C annealing, UST activates a broad PL band at about 0.9eV and also enhances the oxygen related PL maximum at 0.7eV as shown in Fig.1. After a few minutes of UST the 0.9eV band dominates the entire PL spectrum and clearly observed at room temperature. Using a set of films with controlled fraction of amorphous to crystalline phase we proved that the 0.9eV PL band is identical to "defect" luminescence observed in α -Si:H films. UST processing was performed at $T_{\text{ust}} = 150$ to 280°C . The data of isothermal kinetics at two temperatures and their single exponential fit are shown in Fig.2. For a comparison, this picture also comprises PL kinetics of a control sample annealed without UST at 280°C . The comparison proves that the effect of 0.9eV band activation is entirely UST related. UST kinetics is characterized by a time constant of 3min at 280°C and 25min at 150°C . From the Arrhenius plot of UST time constant we found UST activation energy of

0.33eV. This value is close to the activation energy of H^+ diffusion in crystalline Si.

We proposed a model of UST effect (Fig.3). In hydrogenated poly-Si films a total hydrogen concentration exceeds the concentration of grain boundary dangling bonds by a factor of two orders of magnitude. This implies, that a "reservoir" of trapped and non-active hydrogen is available to accomplish the passivation of dangling bonds. We suggest, that part of trapped H can be released by UST. This UST process will be followed by a fast H diffusivity and a capture at non-passivated dangling bonds. In this model, ultrasound enhances a trap-limited diffusivity and promotes a delivery of atomic hydrogen to dangling bonds. The decreasing concentration of non-radiative centers (dangling bonds) results in a dramatic increase of total PL intensity. FTIR study will be performed to justify this model. The results strongly suggest, that UST of poly-Si thin films solar cells can benefit their operational parameters.

Approach: Room Temperature Photoluminescence Mapping in EFG Poly-Si

We reported, that EFG and cast poly-Si wafers exhibit an intensive band-to-band emission at room temperature, which can be noticeably improved by using the UST [3]. It was suggested, that PL mapping of the whole wafer can assess a statistically valid database for local improvement of recombination properties in solar-grade poly-Si after consecutive steps of solar cell fabrication.

PL was excited with 514nm Ar^+ -laser line with power from 20 to 50mW and a beam diameter 100 μ m to 5mm. Band-to band PL spectra ($h\nu_{max}=1.09eV$) were recorded using SPEX 500M spectrometer coupled with cooled Ge photodetector and a lock-in amplifier. PL mapping (70x68 points with 2mm step) was performed at room temperature using a computer controlled X-Y stage. Diffusion length of minority carriers (L) was measured by SPV using the commercial system CMS-III by Semiconductor Diagnostics, Inc.

PL mapping was compared with SPV mapping of the diffusion length (L) at exactly the same wafer points. Illustrative result of PL-scan and L-scan is shown in Fig.4. A remarkable similarity of both data is straightforward: regions with a larger diffusion length correspond to a higher PL intensity. This proves, that the mapping of band-to-band PL is determined by a microscopic distribution of non-radiative recombination centers, which is reflected in L mapping. We noticed, however that PL data show significant variation which are totally missing in the L distribution. This is due to a higher spatial resolution of PL method compared to SPV, and PL sensitivity to properties of the p-n junction.

We used PL mapping to monitor microscopic changes in EFG poly-Si wafers (A.S.E.America) after each of three consecutive steps of solar-cell processing: (a) P-diffusion, (b) P-diffusion + H-passivation, and (c) P-diffusion + H-passivation + Al-firing. Controlled EFG sample was used to assure a stability of PL alignment between each processing step of a wafer. Changes in band-to-band PL intensity in a whole wafer were analyzed using a local upgrading factor $r=(PL_{n+1}-PL_n)/PL_n$, where PL_n and PL_{n+1} are PL intensities at exactly the same wafer point before and after a processing step. Five 4"x4" EFG wafers from the A.S.E. product line were subjected to this PL analysis.

The average value of PL intensity across the whole poly-Si wafer is monotonously increased after (a), (b) and (c) processing steps. PL intensity is enhanced after the final step (c) by a factor of *two orders* of magnitude for each of five wafers with illustrative example shown in Fig.5. In fig.6, the upgrading factor versus initial PL intensity after step (a) and step (b) for one of wafers is shown. It is evident, that after the step (a) PL

intensity is increased by factor of 2-3 almost homogeneously across the wafer, while a diffusion length is unchanged according to Ref.4. This can be accounted for by an improvement of material properties in p-n junction after P-diffusion and negligible effect on bulk properties. The regions with initially lowest PL benefit the most from H-passivation and Al-firing. This result is consistent with a previous SPV study, and was interpreted as hydrogenation of macro-defects and gettering of heavy metals in the bulk of poly-Si [4]. We intend in our future efforts to explore a feasibility of room temperature PL mapping for in-line express monitoring of solar-grade poly-Si wafers.

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Fig 1. PL spectra of 550°C annealed film before and after two UST processings at 250°C.

Fig 2. UST kinetics of 0.9eV PL band (points) and exponential fit (solid). Control sample was at 280°C without UST.

Fig.3 The model of UST enhanced hydrogenation of dangling bonds in poly-Si films

Fig.5. Increase of band-to-band PL intensity after three processing steps of EFG poly-Si

Fig 4. Comparison of PL and SPV line scans in the

Fig 6. Increase of PL intensity after the first (a) and the second (b) processing

High Efficiency Materials and Devices In-House Research

Title: III-V Materials and Devices Team

Organization: NREL High-Efficiency Concepts and Concentrators

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GaInP/GaAs Cell Development

On-sun measurements of Ga_{0.5}In_{0.5}P/GaAs cells at the Solar Research Corporation in Victoria, Australia, showed a 27% ($\pm 1\%$) efficiency in the concentration range of 80-400 suns [1]. The actual cell temperatures varied from 32°C to 50°C and prompted a study [2] of the behavior of the two-junction cell as a function of cell temperature. Increasing temperature is known to decrease the open-circuit voltage and increase the short-circuit current because of a decrease in the band gap with increasing temperature. The Ga_{0.5}In_{0.5}P cell follows this trend, but the temperature coefficient is quite low because of the high band gap and resulting relative insensitivity to the voltage loss. However, the GaAs bottom cell has a much lower increase in the current with temperature because it loses current to the Ga_{0.5}In_{0.5}P top cell at almost as fast a rate as it gains current from the decreased band gap. Because of the different temperature coefficients for the top- and bottom-cell short-circuit currents, a device with top-cell limited short-circuit current at room temperature may be limited by the bottom-cell short-circuit current at higher temperature. Therefore, the temperature coefficient of the tandem-cell efficiency sometimes changes with temperature and may differ from cell to cell depending on whether the sample is limited by the top or bottom cell.

Although high-quality Ga_{0.5}In_{0.5}P cells have been grown, there are some aspects of the cell growth that are poorly controlled or unknown. In FY96, one study [3] showed that dopant diffusion, dopant passivation, and oxygen contamination of the Al_{0.5}In_{0.5}P window layer often affect the device performance in ways that may be unknown or uncontrolled. The sensitivity of the window layer to oxygen can be reduced by using higher dopant levels in the window. However, if oxygen contamination is not a problem, lower dopant levels in the window can reduce the dopant diffusion that often occurs. Cooling a p-on-n device under arsine can lead to passivation of the zinc dopant in the emitter, causing poor fill factor. Information like this and our emphasis over the years on developing a complete knowledge of the fundamentals of the cell fabrication have resulted in a relatively smooth commercialization process.

Commercialization of the Ga_{0.5}In_{0.5}P/GaAs Tandem Solar Cell

As described in the FY95 Annual Report, TECSTAR (Applied Solar Energy Corporation) and Spectrolab have both developed a production capability for the Ga_{0.5}In_{0.5}P/GaAs cell. These cells are very valuable for space applications. Spectrolab is rapidly converting its III-V cell production of 500,000 wafers/year to the two-junction design. This represents a billion dollars/year industry and is comparable in dollar amount to the entire terrestrial photovoltaic industry. Spectrolab is pushing the technology one step further and has developed (in

collaboration with NREL) a three-junction cell with an AM0 efficiency of 25.7% [4], using the Ge substrate for formation of the third junction. The average efficiency of 164 2 cm X 2 cm three-junction cells was 22.6 % (AM0). The three-junction cell should have manufacturing costs almost identical to those of the two-junction technology and only somewhat greater than single-junction GaAs devices grown on Ge. Even now, the costs of the production cells are low enough that they are economically attractive for terrestrial concentrator systems working at 500 to 2500 suns. Some modifications will need to be made to the one-sun cells to make them work well as concentrator cells, but these changes are expected to be fairly minor.

Ga_{0.5}In_{0.5}P/GaAs Cells in Concentrator Systems; Mitigating Chromatic Aberration Losses

Previous studies have shown that tandem cells in concentrator systems may experience losses may tend to strike the center of the cell while the light absorbed by the bottom cell may strike the outsides of the cell. This sort of loss is anticipated for all refractive designs, but can be reduced by appropriate design of the lenses [5, 6]. We had suggested that appropriate cell design could also mitigate the chromatic aberration loss if the emitter of the bottom cell (and adjacent layers) could conduct current laterally. The incorporation of Ga_{0.5}In_{0.5}P/GaAs cells into a space concentrator system raised the question of how to quantify this effect. Our investigation [8] developed tools for modeling the chromatic aberration loss as a function of the midlayer sheet resistance (parallel combination of the bottom-cell emitter, the tunnel junction, and the top-cell base). This allowed us to determine that small chromatic-aberration losses appear as series resistances, while severe losses look more like unusually shaped shunts. We also developed a technique for measuring the midlayer sheet resistance on a finished cell, and showed how the modeled I-V curve matched the measured I-V curve within experimental uncertainty.

Laboratory Development

The hard work on laboratory development in FY95 led to completion of all systems in FY96. The MBE system was commissioned in early November, 1995 and the MOCVD system in June, 1996. This unique system is now fully functional and provides a very powerful tool that is useful to DOE through both the PV and the BES programs. The MBE system is charged with elemental Ga, In, As, P, and Si sources. The low-pressure MOCVD system is capable of growing complete devices and provides a tool for studying device fabrication under the low-pressure conditions usually used by Spectrolab and TECSTAR. The analytical chamber includes an ultra-high vacuum scanning tunneling/atomic force microscope and a low-energy electron diffraction system. All three are connected by a transfer line, allowing study of surfaces without exposure to air.

The MBE system provides a different growth method for Ga_{0.5}In_{0.5}P. The III-V Team has no previous experience with this growth technique, and only a handful of research groups around the world have used solid phosphorus for the growth of Ga_{0.5}In_{0.5}P. Under the direction of D. Friedman, the procedures for growing high-quality GaAs and Ga_{0.5}In_{0.5}P films were quickly developed and the growth rates were calibrated, etc. Intermittent problems with growing the Ga_{0.5}In_{0.5}P films were traced (in November, 1996) to a small leak in the phosphorus source.

The MBE system is being developed for use as a Mighty Big Evaporator. The first study toward this direction has already been completed and is described in the next section.

Polycrystalline GaAs

GaAs layers were grown on molybdenum-coated glass under a range of temperatures and arsenic pressures. Because this represented a new direction of research for the III-V team, methods for quickly characterizing the growing films were developed. The photocurrent generated by an aqueous/semiconductor junction was shown to correlate with the photoluminescence intensity. There were some differences between the two measurements, implying that they are measuring slightly different things. The largest grain material had better optoelectronic properties and was formed at higher temperatures and lower arsenic pressures (Figure 1). However, growth temperature above 500°C led to reduced photocurrent and very low arsenic fluxes, which caused Ga droplets to form on the sample surface. One of the first important things we learned was that hazy samples may be significantly better than mirror-like samples—exactly the opposite trend from what is observed for single-crystal growth. Figure 2 shows the very large crystals that were grown underneath a Ga droplet. This work was presented at the Program Review Meeting in November, 1996 [9]. Clearly, the conditions that lead to high-quality growth on a single crystal may be different from those that lead to large grain growth. We are now investigating many different approaches including growing the entire film from one big Ga drop.

FIGURE 1. SEM micrographs of GaAs layers showing the effect of arsenic flux on growth mode/grain size. The corresponding photocurrent (PC) at 1.6eV, in percent of the PC for an epitaxial GaAs layer, is also noted. The arrows denote the interface between the semiconductor layer and the molybdenum film coating the glass.

FIGURE 2. SEM micrograph of surface of GaAs film grown with V/III so low that Ga droplets formed on the surface. This picture shows the area under one such droplet, after the Ga itself was etched away.

We would like to thank members of the CIS Team and the Characterization Teams for their help with this project.

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High Efficiency Materials and Devices Subcontracts

Title: Novel Low-Temperature Substrate Technology for Compound Semiconductor Solar Cells on Low-Cost Substrates

Organization: Thomas J. Watson Laboratory of Applied Physics, California Institute of Technology, Pasadena, CA 91125

Contributors: Harry A. Atwater, Principal Investigator, Jimmy C.M. Yang, Claudine M. Chen

Objectives

The objectives of this program are to develop low-temperature solid phase growth approaches to obtaining large-grained (20-100 μm) crystalline Ge films on low-cost amorphous (e.g., glass) substrates, which can serve as templates for GaAs growth for thin film GaAs solar cells. Similar techniques are also being studied to enhance grain size in polycrystalline Si films for potential application to Si thin film cells.

Approach

The overall approach for fabrication of large-grained Ge films on glass consists of selective nucleation and solid phase epitaxy of crystalline Ge seeds in an amorphous Ge thin film. Selective nucleation results from reactions between a patterned array of deposited In islands and amorphous Ge to yield large grains (20-30 μm) in the fully crystallized film at temperatures below 450 $^{\circ}\text{C}$. These large-grained polycrystalline Ge thin films are being used as templates for epitaxial growth of GaAs, in collaboration with the Research Triangle Institute and the National Renewable Energy Laboratory.

Results

Selective Nucleation

Selective nucleation is accomplished by patterning an periodic array of 5 μm diameter In islands by mechanically masked evaporation on top of an amorphous Ge film. Array periods range from 20-100 μm . Post-deposition annealing leads to heterogeneous nucleation of Ge crystals under the In pattern but not elsewhere in the amorphous Ge film. Further annealing causes the nucleation Ge crystals to seed growth of large (20-30 μm) Ge. By contrast, random crystallization in an amorphous Ge film typically yields average grain sizes of 0.25-1 μm . A variety of materials other than In (e.g., Sn, Ni, Co, Pd, Cu and Al) have also been used for selective nucleation. To date, the island seed regions produced by selective nucleation are polycrystalline, rather than a single grain per island. Efforts to produce a single grain in each seed region are underway.

Dopant Enhanced Solid Phase Epitaxy of Ge

In the course of this work, it was determined that doping of the amorphous Ge starting material with electronic dopants significantly enhances the solid phase epitaxy rate.

Similar results have been observed in silicon but this work reported a similar phenomenon for Ge for the first time. Doping of a-Ge was performed by ion implantation of B and P to yield peak concentrations in the range of 0.3-0.6 at.%. In samples doping with P, an increase in the solid phase epitaxy rate by a factor of 5 relative to undoped films was found, enabling Ge grain sizes as large as 20-30 μm . In samples co-doped with both B and P, a compensation of the solid phase epitaxial growth rate enhancement is observed, i.e., equal amounts of B and P yield no enhancement in the growth rate.

Texture Development and Grain Size in Polycrystalline Ge

It was found in the experiments (characterized by transmission electron microscopy) that the lateral Ge solid phase epitaxy rate in films produced by selective nucleation was much higher (up to approximately 10x higher for 20 nm a-Ge films) than that for crystalline films produced by random nucleation of Ge grains.

The selective nucleation and solid phase epitaxy process leads to a restriction in crystallographic texture. Transmission electron microscopy and X-ray diffraction both indicate that the texture is restricted to mostly (100) and (110) orientations.

One possible explanation for this is that the In metal-induced selective nucleation process leads to a large distribution of starting crystallographic textures and orientations at the beginning of solid phase epitaxy, the fastest-growing orientation "wins" a competition among grain orientation as lateral solid phase epitaxy goes on. Thus this process yields large grains with a texture or textures yielding the highest possible growth rate. On the other hand, random nucleation yields a random crystallographic texture for each grain, yielding a lateral solid phase epitaxy rate which is slower than that characteristic of the fastest-growing orientation. It was found that while the lateral solid phase epitaxy rate had a weak dependence on film thickness (essentially independent of a-Ge film thickness from 20-80 nm) for films produced by selective nucleation, there was a strong dependence of the lateral solid phase epitaxy rate on film thickness (a factor of 10 for a-Ge film thickness from 20-80 nm) for films produced by random nucleation.

We have continued our research into producing the largest possible grain size in Ge thin films via metal-induced selective nucleation, followed by lateral solid phase epitaxy. The limitation of grain size at the present time is due to randomly nucleated grains impeding the growth of selectively nucleated grains. Therefore we investigated the dependence of the random nucleation rate on Ge film thickness. For Si thin films on SiO_2 it has been demonstrated that the number of nucleated Si crystals per unit area increases linearly with Si film thickness, as would be expected for homogeneous nucleation. If this is also true for Ge films on SiO_2 , then the Ge film thickness should be reduced as much as possible to minimize the number of randomly nucleated grains. For Ge films of 20, 50, and 80 nm thickness annealed in high vacuum at 475 °C for 10 min, all three film thicknesses showed about the same density of crystals, about 0.1 crystal per μm^2 , as observed by transmission electron microscopy. This result suggests that the random

nucleation is heterogeneous, and probably originates from either the Ge/ SiO₂ interface or the Ge film surface, rather than within the interior of the thin film.

30 μm

Figure 1. Plan-view optical micrograph of Ge grains (light circular regions) growing in a partially-crystallized 100 nm thick amorphous Ge film (dark background) annealed at 400 °C for 100 min. Grain growth occurs radially outward from selective nucleation sites (dark circular regions inside light circles).

Silicon Selective Nucleation and Solid Phase Epitaxy Effort

Under the additional funding from the BES Center for Synthesis and Processing of Advanced Materials, we have begun investigation of a selective nucleation and solid phase epitaxy process for Si thin films that is broadly in parallel to our efforts for Ge thin films. To date, we have demonstrated the basic viability of a selective nucleation process for Si,

and have made simple estimates of the maximum grain size anticipated in Si films for different processing conditions. A very important contributing factor in the maximum grain size is the effect of doping on the lateral solid phase epitaxy rate in Si, and the focus of our current effort is to maximize the lateral solid phase epitaxy rate by maximizing the concentration of electronic dopants such B,P and Al in a-Si films that can be introduced without precipitation, which would produce unwanted heterogeneous nucleation.

Summary

Selective nucleation and solid phase epitaxy leads to large grained Ge films on SiO₂. Ge grain sizes of 20-30 mm have been achieved. Current work is focused on achievement of a single grain per nucleation site, and to further enhancement of grain size, as well as studies of heteroepitaxial GaAs growth on Ge/SiO₂ and on Ge/glass, in conjunction with NREL and the Research Triangle Institute.

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Title: High Efficiency GaAs Solar Cells on mm and Sub-mm Grain-Size Polycrystalline Ge Substrates

Organization: Research Triangle Institute, RTP, NC 27709

Contributors: R. Venkatasubramanian, Principal Investigator
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Introduction

High-efficiency single-junction GaAs (25.7%) [1] and tandem GaInP₂/GaAs (29.5%) [2] solar cells have been demonstrated on single-crystal GaAs substrates under 1-sun conditions. However, the cost of GaAs solar cells on GaAs substrates are prohibitive for flat-plate terrestrial systems. Therefore, it is important to investigate and effect a transition of these high-efficiency cells on to low-cost, large-area substrates for flat-plate applications. Several low-cost substrate alternatives have been considered recently. One approach utilizes single-crystal Ge substrates. For example, the highest AM1.5 efficiency for a GaAs solar cell (4-cm²-area) on single-crystal Ge substrate is ~24% [3]. In addition, the use of Ge substrates lead to an enhanced yield in a manufacturing environment, when compared to using GaAs substrates. However, the cost associated with single-crystal Ge substrates are also likely to be high for flat-plate applications.

Large-area cast poly-Ge substrates, with an average grain size of sub-mm to several mm, are attractive as low-cost substrates for GaAs solar cells. Our first attempt at developing GaAs solar cells on such cast optical-grade poly-Ge substrates was successful [4]. In addition, the availability of large-area (as much as 24" diameter) cast poly-Ge substrates, in combination with well-established large-scale growth feasibility, would allow cell-processing costs to be drastically reduced; this is necessary to meet the long-term cost-goal for flat-plate applications. Also, the understanding developed in ameliorating the detrimental effects of grain-boundaries in GaAs cells with poly-Ge substrates, containing small grain structures, are relevant to the development of GaAs cells on glass. The objective of this program, therefore, is to understand the issues and improve the GaAs solar cells on mm and sub-mm grain-size poly-Ge substrates.

Key Issues with Polycrystalline Substrates and Templates

There are two basic issues related to the growth and device optimization for solar cells on polycrystalline substrates or similar polycrystalline templates on glass. We can consider two situations to the growth of materials on polycrystalline substrates - an *ideal*, two-dimensional, uniform, layered growth across the various orientations so that we essentially preserve the grain-structure of the starting substrate and do not create additional grain boundaries in the active regions of the solar cell. A second situation could be a *non-ideal*, three-dimensional, non-uniform growth across the various orientations leading to the formation of additional grain boundaries. Thus, the key to minimization of the grain-boundary effects in deposited polycrystalline materials appears to being able to develop uniform, two-dimensional, layered growth across the various crystalline orientations [5].

From a device point of view, the grain boundaries reduce photo-collection through minority-carrier recombination. However, if we develop (p⁺-n) GaAs solar cells with a thin emitter, a majority of the photo-current would be generated in the n-base region. If group-VI dopant like Se or S is used for the n- GaAs base, it has been suggested [6] that a favorable n/n⁺ minority-carrier mirror could be naturally formed at the grain-boundaries due to dopant segregation at these regions. These minority-carrier mirrors have been attributed to the relatively high short-circuit current density (J_{sc}) (> 20 mA/cm² under 1-sun) that can be readily obtained even in μ m-grain-

size poly-GaAs solar cells [6]. While high J_{sc} values can be readily obtained in poly-GaAs solar cells, V_{oc} values are typically low (~ 0.55 to 0.6 Volts) and the fill-factor has been low as well [6,7]. This is probably due to the generation of dark currents at grain boundaries. We have proposed the use of a "thin" undoped spacer at the depletion layer of the p^+ -n junction and experimentally demonstrated that a significant reduction in dark current can be obtained leading to an increase in V_{oc} and fill-factor of GaAs solar cells grown on large-grain poly-Ge substrates [4]. The work presented here, describes the mechanism of dark-current reduction in p^+ -n GaAs solar cells on poly-Ge with the use of the spacer using low-temperature dark I-V measurements.

GaAs Growth on Poly-Ge

High-quality growth of GaAs-AlGaAs layers across the various crystalline orientations of a polycrystalline Ge substrate is critical to obtaining high-performance GaAs solar cells. First of all, the polishing of the poly-Ge substrate prior to the MOCVD growth of the GaAs cell needed attention [8]. Polishing defects such as dents/ledges/steps have been found to be more detrimental, compared to grain-boundaries in the substrate, for GaAs solar cell performance. In addition, we have optimized the MOCVD growth process on large-grain and small-grain poly-Ge substrates, recognizing the need for maintaining a higher concentration of As-growth species on the growth-surface to promote a two-dimensional layered growth [8]. Optimization studies of minority-carrier lifetime in GaAs layers on poly-Ge substrates have revealed that lifetime-spread across various grains can be reduced through the use of lower doping for the $Al_{0.8}Ga_{0.2}As$ confinement layers [9].

GaAs Solar Cell Device Optimization on Poly-Ge Substrates

Shown in Fig. 1, is a schematic of a GaAs solar cell device structure that we have developed for use on polycrystalline Ge substrates. Note the undoped spacer between the base and the emitter, which has been shown to reduce the dark current and improve the cell V_{oc} and fill-factor [4]. We have shown in Figure 2, the effect of an undoped spacer on dark-current reduction in GaAs cells on poly-Ge. For comparison, the I-V data of GaAs p^+ -n junctions grown on single-crystal Ge, with and without the spacer, are also shown in this figure. We see no effect of the spacer on GaAs cells on single-crystal substrates, while there is a 40-fold reduction in the saturation dark current in GaAs cells with the spacer on poly-Ge substrates.

The reduction in dark current and the improvement in cell V_{oc} are believed to be associated with the reduction of tunneling currents near the depletion-layer of the p^+ -n junction in polycrystalline materials. We have conducted an experimental study of dark currents in p^+ -n GaAs junctions as a function of temperature (77K to 288K) to support this hypothesis. The temperature dependence of saturation dark currents in p^+ -n GaAs junctions, with and without the undoped spacer, are shown in Figure 3. We observe that the junction without the spacer shows a stronger reduction with temperature. The activation energy for the saturation dark current with temperature is ~ 0.07 eV. We also note the apparent convergence of the two curves near zero Kelvin. Based on band-diagram considerations near the vicinity of a grain boundary as well as dark-current activation energy related to the amount of degeneracy in the n^+ -region, due to n-type dopant accumulation at the grain-boundaries, we have shown that the key to reducing dark-currents in p^+ -n GaAs solar cells on polycrystalline-Ge substrates may be to avoid carrier tunneling into the heavily-doped regions near the grain boundaries [5].

GaAs Cell Structure Optimization

We have indicated in a recent publication [5] that the p^+ -n GaAs cells on poly-Ge typically have a J_{sc} of ~ 22 mA/cm² under AM1.5 illumination and that further improvement in the J_{sc} can be obtained mainly through an improved blue response. To improve the blue response, we reduced the thickness of the $Al_xGa_{1-x}As$ window from ~ 450 Å to ~ 300 Å. The reduction in window thickness, keeping x in the window ~ 0.75 , led to an improved J_{sc} of ~ 24.5 mA/cm².

Further reduction in window thickness from 300 Å to ~220 Å apparently does not improve the J_{sc} any more. Thus, a 300-Å-thick window appears optimum for a window doping level of $\sim 1 \times 10^{19} \text{ cm}^{-3}$. In order to further improve the J_{sc} , we considered the use of a thicker emitter as our other characterization studies have indicated ample electron diffusion lengths in the p^+ -GaAs emitter. The J_{sc} improved from $\sim 24.5 \text{ mA/cm}^2$ to $\sim 25.5 \text{ mA/cm}^2$ with a thicker emitter. In addition, the J_{sc} improved to $\sim 26.3 \text{ mA/cm}^2$ by using a smaller emitter grid-coverage.

Towards the improvement of V_{oc} values, we considered optimizing the spacer thickness. A typical set of data is shown in Table 1. We believe, as long as the spacer is thick enough to avoid tunneling of carriers between the heavily-doped emitter and the heavily-doped base regions formed near the grain-boundaries, a thinner spacer could be advantageous for lowering the dark current. In high-bandgap materials like GaAs a thinner spacer would reduce the depletion layer width in the base region of the p^+ -n junction and therefore, would reduce the dark current density. Hence, the V_{oc} is likely to improve with a smaller spacer. We also considered the effect of emitter thickness and the amount of emitter-grid metallization on the V_{oc} of cells. This study suggested that a significant component to dark-current generation may be from the emitter-contact regions or from the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ window-GaAs cap heterointerface.

These studies have enabled us to improve the large-area GaAs cell efficiencies on mm and sub-mm grain-size poly-Ge substrates. The data shown in Table 2 indicates the progress made at various stages in the last two years. We note that the recent progress in cell results are in spite of smaller, sub-mm, grain-sizes in the starting poly-Ge substrates. The NREL-verified cell efficiency data on the 18.2% cell indicated in Table 2 is shown in Figure 4. The data in Table 2 indicates that large-area GaAs cell efficiencies in excess of 20% are achievable on mm and sub-mm grain-size poly-Ge substrates. It is noteworthy that in a small-area, 21%-efficient cell, a V_{oc} of as much as 1.04 Volt and a $J_{sc} \sim 27 \text{ mA/cm}^2$ have been observed, thereby approaching some of the best single-junction GaAs cell results on single-crystal GaAs substrates.

Summary

GaAs material and device structure optimization studies on millimeter-and-less grain-size poly Ge substrates were described. An experimental study of dark currents in GaAs junctions, with and without the spacer, as a function of temperature (77K to 288K) was presented; this study suggests that the spacer reduces the tunneling contribution to dark current. Device-structure optimization studies have led us to achieve an open-circuit voltage (V_{oc}) exceeding 1 Volt and an AM1.5 efficiency of $\sim 19\%$ for a 4-cm^2 -area GaAs cell and an efficiency of $\sim 21\%$ for a 0.25-cm^2 -area cell on sub-mm grain-size poly-Ge, respectively.

Acknowledgments

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Fig. 1. Schematic of a p+n GaAs solar cell device structure on poly-Ge.

Fig. 2. Effect of an undoped spacer on dark current reduction in GaAs cells on single crystal Ge and poly-Ge substrates. All diodes have an area of 1 cm².

Fig. 3. Temperature dependence of saturation dark current in GaAs cells on poly-Ge, with and without the undoped spacer.

RTI GaAs on poly Ge

Sample: I-2505-a
Nov 22, 1995 9:00 AM
ASTM E 892-87 Global

Temperature = 25.0°C
Area = 4.011 cm²
Irradiance: 1000.0 W/m²

Figure 4. I-V characteristic of a 18.2%-efficient, 4-cm²-area GaAs cell on poly-Ge with a V_{oc} of ~1 Volt.

TABLE 1. Effect of spacer thickness, emitter thickness and emitter grid-coverage on V_{oc} of GaAs cells on mm grain-size poly-Ge.

Cell #	Spacer (μm)	Emitter (μm)	Grid Coverage (%)	V _{oc} (V)
2766	0.22	0.14	9	0.90
2763	0.14	0.14	9	0.96
2782	0.14	0.14	9	0.96
2786	0.10	0.14	9	1.00
2804	0.10	0.22	9	1.01
2809	0.10	0.28	9	1.01
2840	0.10	0.28	5	1.03

TABLE 2. Progress of GaAs cell efficiency on poly-Ge substrates

	Grain Size (cm)	Cell Area (cm ²)	AM1.5 Eff. (%)	Ref.
First Demo.	0.5	1	15.8	[4]
Phase 1	0.5	4	16.6	[9]
Phase 2 Begin	0.5	4	18.2	[5]
Phase 2 End	0.1	4	18.7	
Current	0.05-0.1	4	~19	
State-of-the-art	0.05-0.1	0.25	~21	

Title: Thin Film GaAs Solar Cells On Glass Substrates By Epitaxial Liftoff

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ABSTRACT. In this work, we describe the fabrication and operating characteristics of GaAs/AlGaAs thin film solar cells processed by the epitaxial liftoff (ELO) technique. This technique allows the transfer of these cells on glass substrates. The performance of the lifted-off solar cell is demonstrated by means of electrical measurements under both dark and illuminated conditions. We have also optimized the light trapping conditions in this direct-gap material. The results show that good solar absorption is possible in active layers as thin as 0.32 μm . In such a thin solar cell, the open circuit voltage would be enhanced. We believe that the combination of an epitaxial liftoff thin GaAs film, and nano-texturing can lead to record breaking performance.

INTRODUCTION

In recent years, III-V solar cell technology has been actively pursued for use in space applications. While GaAs has been regarded as a high-efficiency high-cost option, new developments in MOCVD growth reactors, epitaxial liftoff processing and substrate re-use can lead to low cost III-V epitaxial thin films [1]. As a result, III-V cells show significant potential for terrestrial use as well.

In this work, we describe the fabrication and operating characteristics of GaAs/AlGaAs thin film solar cells [2 -4] using the epitaxial liftoff (ELO) technique [5]. This technique allows the transfer of these cells onto glass substrates.

We also describe a way of enhancing light absorption by our solar cells through nanotexturing of the thin film after they have been transferred onto glass slides. This light trapping operation permits a much thinner than normal active layer which will allow a new higher voltage operating regime.

DEVICE FABRICATION AND LIFTOFF

The structure used in our experiment was grown using MOCVD. It consists of an n-GaAs active region sandwiched between n-In_{0.5}Ga_{0.2}Al_{0.3}P and p-Al_{0.3}GaAs window/passivation layers, and capped by a p⁺-GaAs contact layer. The entire structure is grown on top of a 500 Å thick sacrificial layer of AlAs, which is subsequently etched to release the device from its substrate. A thin GaAs layer above the AlAs serves to protect device layers during liftoff. This thin protective layer is removed after the structure has been lifted off and before it is bonded to a glass slide.

Devices were fabricated prior to epitaxial liftoff by first depositing Cr/AuZn/Au p-type contacts onto the sample, followed by a mesa etch down to the n-type active region. After the evaporation of AuGe/Ni/Au contacts onto the n-type layer, the sample was annealed at 380°C, to make both contacts ohmic. The material and junction quality were monitored after each process step using nondestructive room temperature photoluminescence [6- 8] and open-circuit voltage (V_{oc}) testing. No reduction in V_{oc} was observed during the process sequence, indicating that the material properties did not degrade during processing.

After device fabrication, the sample was covered with black wax. The thin-film GaAs solar cell was lifted off of its substrate by selectively laterally etching the buried AlAs layer in HF acid solution. Then the 100 nm thick GaAs protective layer between the InGaAlP window and AlAs epitaxial liftoff layer on the thin film is etched away using $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (1:8:500). Again, the device was monitored using absolute PL measurement before and after the removal of the GaAs layer to ensure the etching does not damage the cell. Finally the thin film is attached to a glass substrate with UV-curing polyurethane. The black wax was then dissolved and conductive copper wires were attached to the p- and n-type contacts by means of silver paint. The ELO process is summarized in Figure 2.

ELECTRICAL MEASUREMENTS

Electrical measurements were then performed on the lifted-off solar cell. The dark current-voltage (I - V) characteristic is shown in Figure 3. This plot exhibits a diode factor of $n = 1.93$ for voltages between 0.45 V and 0.9 V, which corresponds to nonradiative recombination current in the junction. The I - V curve is virtually identical to that obtained before liftoff, indicating little material degradation during that step. It is desirable for the operating point of the cell to occur in the $n = 1$ radiative recombination current regime, which is encountered at higher voltages. In this I - V curve, however, higher voltage regime is obscured by series resistance.

We also obtained I - V curve under an illumination condition of ≈ 1 sun. The above solar cell is bifacial, in that it can be illuminated either through the glass slide (the “front” side) or from the contact (“back”) side. The illumination was adjusted slightly above 1 sun to compensate for the absence of an anti-reflection coating between the InGaAlP window layer and the polyurethane adhesive layer. The result of the measurement is shown in Figure 4. Illumination from the front yields $V_{oc} = 0.995$ V and a short-circuit current I_{sc} of 30.7 mA/cm^2 . At an operating voltage of 0.85 V, the fill factor of this I - V power curve is 77%. The superior performance in front illumination is of course due to the fact that incident light is not obstructed from the active region by metal contact pads. Moreover, reflection from the pads on the backside may enhance performance by recycling unabsorbed photons.

DISCUSSION

Referring to Figure 3, it can be seen that the operating point lies in the undesirable $n = 2$ region of the I - V curve. This can be attributed edge leakage as has been thoroughly explored by the Purdue group [9]. Another factor is the bandgap of the $\text{In}_{0.5}\text{Ga}_{0.2}\text{Al}_{0.3}\text{P}$ window layer. This layer was made with only 30% Al-content, in order to resist the HF acid. In principle a higher Al concentration can be used allowing more of the short wavelengths to be transmitted, but this is probably unnecessary since the InGaAlP window layer is only 20 nm thick. We believe that these results indicate good performance is possible in an epitaxial liftoff thin-film GaAs solar cell with a 500 nm active layer.

NANOTEXTURING

Now we describe a process to enhance light absorption by our solar cells. Yablonovitch [10] showed that total randomization of light leads to an enhancement of absorption by a factor of $4n^2$. This result was confirmed experimentally by Deckman et al [11] by applying natural lithography technique to amorphous silicon solar cells. Our nano-texturing process applied to very thin GaAs/AlGaAs double heterostructure has achieved 90% of the enhanced absorption in the near band edge region. The structure of GaAs/AlGaAs sample used in our experiment is shown in Figure 5.

The double heterostructure sample is nano-textured by “Natural Lithography” using commercially available carboxylate modified $0.953 \mu\text{m}$ polystyrene spheres as ion etching mask. The spheres are diluted in 5.56% methanol such that we obtained 10.5% of spheres by volume. The diluted sphere solution is then spun onto the sample at 1700 rpm. The random close-packed array of polystyrene spheres act as a

mask on the sample surface. Then the sample is etched using reactive ion etching to impose the randomly closed packed sphere pattern onto the surface. The depth of the imposed pattern is 250 nm. After etching, the epitaxial liftoff is performed to separate the thin film from the substrate and then it is bonded to a glass slide with the untextured side against the glass.

The spectral dependence $R(\lambda)$ of reflectance of the textured and untextured films is then measured with respect to a white reference surface using a standard integrating sphere setup. Figure 6 shows the result of our measurement. The indicated 80% maximum attainable absorption is due to the reflection of the incident beam off the glass and the semiconductor adhesive interface.

Figure 7 shows the comparison between our data and theory. It indicates that our experimental data nearly reaches to 90% of the absorbance predicted by the theory based on the $4n^2$ expected absorption enhancement for light trapping (10). The absorbance oscillations which appear for energies above the band gap is due to Fabry-Perot oscillations which arise within the untextured sample. Residual Fabry-Perot oscillations occur also for nano-textured GaAs thin-films. This is the first time light trapping has been applied to a direct gap semiconductor of the order of one optical wavelength thick.

CONCLUSION

In summary, we have integrated a working thin film GaAs solar cell onto a glass substrate, using the epitaxial liftoff technique. This configuration allows illumination through the non-contact side of the cell. The cell exhibits $V_{oc} = 0.995$ V and fill factor of 77%. We also present new light trapping parameters which are unique to an ultra thin direct bandgap solar cell. We believe that this combination of low cost through ELO, and high performance through light-trapping in ultra-thin films shows promise for terrestrial photovoltaics.

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Figure 1. Structure of the solar cell after liftoff and bonding.

Figure 2. Epitaxial liftoff process

Figure 3. Current-Voltage characteristic in the dark.

Figure 4. Current-Voltage characteristic under ≈ 1 -sun illumination from the front side of the solar cell.
Voc=0.995 Volts F.F.=77%

Figure 5. Structure used in nanotexturing experiment.

Figure 6. Absorption of a textured and untextured films.

Figure 7. Comparison between experimental data and theory.

Advanced Characterization Techniques In-House Research

Title: **Material and Interface Characterization of PV Devices**

Organization: NREL

Contributors: Mowafak Al-Jassim, Sally Asher, Falah Hasoon, Kim Jones, Alice Mason, Rick Matson, David Niles, Robert Reedy, and Amy Swartzlander.

Introduction

The *Materials Characterization* task has provided extensive and crucial support for both our in-house and subcontract groups. A wide variety of techniques was used to characterize PV materials and devices. Compositional measurements are performed by fully computerized electron probe microanalysis (EPMA) using either energy dispersive or wavelength dispersive X-ray analysis. Structural and defect analyses are carried out by transmission electron microscopy (TEM). Additionally, scanning electron microscopy (SEM) in its various modes, such as secondary electron, CL and EBIC imaging, is providing a very wide support for measuring the topographical, luminescent and microelectrical properties of PV materials and devices. Furthermore, we have acquired a new X-ray diffractometer. This instrument, in its various modes, has already proved to be of great service to the PV program.

In addition to these measurements, the *Materials Characterization* task encompassed a powerful array of surface and interface analysis techniques. This includes scanning Auger spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), ultra-violet photoelectron spectroscopy (UPS), and secondary ion mass spectrometry (SIMS). XPS and AES spectroscopies are related techniques for determining the composition and chemistry of surfaces. The new field-emission AES and small-spot XPS systems were commissioned last year and have been used extensively this year to support the CdTe and CIS device development tasks. Furthermore, a new time-of-flight (TOF) SIMS instrument was commissioned during 1996. Capabilities of this instrument include improved sensitivity for trace element analysis, better mass resolution, and significantly improved secondary ion imaging capabilities.

Most of the research activities carried out by this task are planned through other in-house and subcontractors activities. The following is a brief description of some of the highlights of our work during 1996. These will be divided according to the material technology.

CIS

The *Materials Characterization* task continued to support in-house as well as outside research and development on CIS with a large number of analytical studies on various material aspects. More than 650 analyses were performed by EPMA, and over 200 devices and films were analyzed by SIMS, XPS, AES, SEM and TEM.

Aside from short-term characterization of CIS material-related issues, much time was concentrated on more fundamental aspects of material growth. One example of such a study is the investigation

of the effects of the concentration of Ga on junction formation in thin-film $\text{ZnO/CdS/CuIn}_x\text{Ga}_{1-x}\text{Se}_2/\text{Mo}$. These were studied using scanning electron-beam-induced current (EBIC) microscopy. The charge-collection efficiency profiles of cleaved devices on glass substrates were revealed for the cases where x was varied between 0 and 100%. We observed considerable variation in the EBIC peak position, the uniformity (between and within devices), and overall charge-collection profile of the junction as a function of Ga concentration. Whereas using only CuInSe_2 absorber material (Fig. 1a, $x=0$) results in a rather wide and buried junction in the CIS (Fig. 1d), the systematic addition of Ga to the p- CuInSe_2 matrix affects the conductivity type of the material, thereby creating an increasingly abrupt, uniform, and shallow junction near the heteroface (Figs. 1 b [30% Ga substitution for In], c[50%], d[100% - pure CGS]).

Figure 1. Comparison of the JEBIC profile for the (a) 0%, (b) 30%, (c) 50% and (d) 100% Ga substitution cases superimposed on their corresponding topography.

The figures to the right in each case display a Y-modulated map of the EBIC response of the device on a local scale, thereby indicating both the position of the electrical activity within the device and its spatial uniformity. The device efficiencies, FF, V_{oc} , Jsc, quantum efficiencies, and scanning Auger chemical depth profiles of the same devices all corroborated the EBIC results. These results are also quite consistent with earlier single-crystal CIS and CIGS studies. Basically, the study shows that perhaps one of the most important roles of the substitution of Ga for In in CIS thin film devices is dramatically changing the chemistry of the film throughout the film and especially as a function of film depth, of moving the junction closer to the heteroface where the light is absorbed, creating a more uniform response and an increasing V_{oc} , but lower FF and Jsc.

CdTe

An area of focus for this task in the CdTe arena has been the investigation of the chemistry of CdS thin films. This was done in support of the in-house CdTe Task. Low levels of O contamination have been found in CdS thin films grown by the chemical bath deposition (CBD) method. XPS was used to investigate the chemistry of the O impurity atoms in the CBD CdS for the CdTe and CIGS device development tasks. The results show that O is likely present as water incorporated from the bath during growth of the film.

XPS survey spectra were used to determine that O was an impurity in CBD CdS films; however, its chemical state was unknown. Sputter depth profiling showed that the O was present at a level of ~3.8 at.% throughout the film. Analysis of the high-resolution lineshapes revealed that the chemistry of the O was altered by the sputtering process used for depth profiling. Figure 2 shows the lineshape of the O KLL Auger and O 1s photoelectron peaks in the unsputtered CdS film. These peaks are consistent with peaks from Cd(OH)₂. After sputtering, both the O KLL and the O 1s peaks show a second component which is consistent with CdO. Figure 3 shows a similar series for the Cd MNN Auger and Cd 3d photoelectron lineshapes. Neither of the Cd peaks from the film match the ones for Cd(OH)₂ or CdO; however, the presence of CdS is clearly seen. The lack of Cd-O bonding indicates that the OH is likely bound to something other than the Cd. No other contaminants were identified through the survey spectra. From this it was concluded that the O present in the CBD CdS was bound to H in the form of water, H₂O.

Another topic of study in this area is the investigation of compositional uniformity in CdTe films. The nucleation and growth of CdTe by the closed-space sublimation (CSS) method is enhanced by the presence of oxygen in the deposition chamber. However, oxygen also has several detrimental effects including oxidation of the source materials. CdTe films grown from oxidized sources frequently exhibit particles on the surface which are detrimental to subsequent device processing. The particles were thought to originate from CdO in the source material. In this study, high-resolution scanning Auger electron spectroscopy (AES) was used to determine the composition and thus probable origin of these particles.

The high lateral specificity of the AES microscope was used to acquire information from the CdTe surface and from particles before and after sputtering. A typical particle is shown in Figure 4. Prior

Figure 2. O KLL Auger and O 1s photo-lines for relevant materials.

Figure 3. Cd MNN Auger and Cd 3d photo-lines for relevant materials.

to sputtering, little difference was observed between survey spectra. After sputtering into the particle, however, oxygen was found in the particle and not on the surface. Figures 5 a. and b. are survey spectra from the particle before sputtering and after sputtering, clearly showing the presence of oxygen inside the particle. Figure 6 is a depth profile taken from the particle showing the disappearance of oxygen as the particle is sputtered away. This work discovered that the particle began as CdO, probably emitted from the oxidized source. The CdO was then covered with CdTe during growth. Auger analysis helped to determine the optimum growth conditions and how the source plates should be oriented for best deposition conditions.

III-Vs

Our efforts in this area were concentrated on the microstructure of ordered and phase-separated alloys. We have examined double-variant CuPt ordered structures at the initial stages of MOCVD growth of GaInP alloys. The resulting network of interwoven variants resembles an orientational superlattice, showing modified optoelectronic properties. We have also examined the microstructures of double-variant GaInAs films and correlated the results with transient photoconductivity experiments. This revealed an extended carrier lifetime

in ordered material that appears to result from charge separation caused by the ordered/disordered domain structure. In a collaboration between NREL and Sandia National Laboratories, we have investigated lateral spontaneous composition modulations in GaAs/InAs and AlAs/InAs short-period superlattices grown by MBE. This work also revealed weak CuPt-ordered structures in AlInAs buffer layers that may explain the optical anisotropy that has been measured in these samples.

Figure 4. SEM of particle on CdTe film surface.

Figure 5. a) AES survey spectrum from particle before sputtering showing no oxygen signal, b) AES survey spectrum from particle after 75 minutes of sputtering, showing the oxygen signal.

Figure 6. AES depth profile from the particle showing the disappearance of oxygen as the particle is sputtered away.

Figure 7. Electron diffraction patterns from GaInAs samples: (a) disordered, (b) strongly ordered, and (c) partially ordered.

Si

The deposition of amorphous Si (a-Si) by the hot-wire method has been shown to produce device quality material which exhibits a reduced Staebler-Wronski effect. To produce the best material it is necessary to conduct the deposition with high substrate temperatures. However, efforts to fabricate devices from this material have been complicated by the high temperatures. Secondary ion mass spectrometry (SIMS) depth profiling showed that there was a substantial loss of hydrogen from the a-Si film. The loss of hydrogen correlated with low fill factors for the finished devices. The SIMS result led to the investigation of various methods of surface treatment to replace the H. Figure 8 shows depth profiles from two different a-Si films with different surface treatments. The lower hydrogen content film is without any special surface treatments and produced a low FF device. The

higher hydrogen content film received a special surface treatment, which resulted in a significant improvement in the FF for the device. SIMS results have been used to further optimize the processing for these devices.

Figure 8. SIMS depth profiles of H in two a-Si hot-wire-deposited films with different surface treatments.

The amorphous Si program within NREL has recently shown that the usually high elastic loss mechanisms characteristic of all amorphous solids are absent in Hot-Wire CVD (HWCVD) deposited a-Si:H. This was shown by measuring the damping of a-Si deposited on special oscillators made out of high-purity crystalline silicon. TEM and SEM were used to characterize the thickness, structure, and morphology of a-Si:H and a-Si thin films produced by a variety of techniques. Subsequent to cross-sectional TEM analysis of HWCVD films deposited on intrinsic Si for paddle oscillation measurements, a unique structural characteristic was discovered in this material. Figure 9 is a high-resolution TEM lattice image showing the Si substrate and the hot-wire CVD a-Si:H-deposited thin film. The inset is a selected area electron diffraction pattern identifying the amorphous structure of the deposited film. As a result of implementing an initial low-temperature growth step to improve the a-Si: adhesion to the Si substrate, cross-sectional TEM examination revealed that thin 10 to 20 nm epitaxial Si layers are being formed during the low-temperature growth step. The reproducibility of growing these thin epi layers by low-temperature HWCVD has been confirmed and continued efforts to improve the structural properties and possible device applications are being investigated.

1996 NREL patent filing: "Rapid Low-Temperature Epitaxial Growth Si Using Hot Filament Decomposition of Silane." E. Iwaniczko, K.M. Jones, R.S. Crandall, B.P. Nelson and A.H. Mahan.

Figure 9. High-resolution TEM lattice image showing the Si substrate and the hot-wire CVD a-Si:H-deposited thin film.

Title: **Electrooptical Characterization**

Organization: Center for Measurements and Characterization
National Renewable Energy Laboratory
Golden, CO 80401

Contributors: R.K. Ahrenkiel, Principal Investigator; F. Abulfotuh, P Diplo,
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Objectives

The overall objective of the electrooptical characterization task is to develop and provide electrical and optical measurement support for both in-house and subcontract photovoltaic (PV) device research, so as to accelerate commercialization of the respective technologies. Included in this objective is development of new techniques that will improve our understanding of the important parameters of PV materials. Also included is continued support to the PV program using the currently available measurement techniques. Finally, we will continue the technology transfer of new measurement techniques to industry so as to assist in quality control of manufacturing processes.

Technical Approach

1. Provide recombination and minority-carrier lifetime measurement support of in-house and subcontract programs using time-resolved photoluminescence (TRPL) and radio frequency photo-conductive decay (RFPCD) for all classes of PV materials.
2. Provide femtosecond TRPL and pump/probe characterization measurements of fast processes in PV materials.
3. Provide photoluminescence characterization of a wide variety of PV materials over a temperature range of 4 K to 300 K. This technique is applicable to all NREL programs.
4. Provide Fourier transform infrared (FTIR) spectroscopic analysis of PV materials including Fourier transform transmission, reflectance, and photoluminescence.
5. Provide deep-level transient spectroscopy (DLTS) measurements of PV materials in order to identify electrically active impurities.
6. Provide plasmon Raman scattering studies of heavily doped semiconductors, such as tunnel junctions, to provide measurement of dopant level.
7. Provide spectroscopic ellipsometry measurements to obtain optical constants of thin films.

Results

The following describe contributions of the above measurement technologies to the principal device technologies of the national PV program.

CdS/CdTe thin-film solar cells

We provided over 600 energy-resolved PL and TRPL measurements on CdTe and CdS. The lifetime studies related grain quality and morphology to photovoltaic activity. Also, we did innovative pump/probe measurements on the CdS thin films that are currently an integral part of this technology. These studies helped identify the role of CdS in the device activity during photovoltaic processes. FTIR microspectroscopic analyses of spots visible on CBD-deposited CdS films on CdTe layers were analyzed. The spots in the CdS films were identified as thiocyanates and cyanamides using FTIR library searching, and are products of the CBD reaction. Initial results were obtained using SimWindows software to analyze the CdS/CdTe solar cell. Numerous CdTe and CdS thin films were analyzed by energy-resolved photoluminescence, on a routine basis, at temperatures from 300 K to 4 K. DLTS measurements were made on a number of CdTe solar cells for defect identification.

Highlights include :

- Golden Photon Incorporated, Golden, CO: Time- and energy-resolved photoluminescence for CdTe/CdS thin-film materials characterization.
- Solar Cells Incorporated, Toledo, OH: Consultation on in-line, photoluminescence-based materials quality monitor for PV device manufacturing. Time- and energy-resolved photoluminescence for CdTe/CdS thin-film materials characterization. Developed, designed, and constructed a nondestructive technique for measuring CdS thin-film thickness. This technique is currently being used at Golden Photon and a similar system is being built at Solar Cells, Inc.
- University of Delaware, Institute for Energy Conversion, Newark, DE: Collaborative research project on interdiffusion across the CdTe-CdS interface.
- University of Toledo, Toledo, OH: Collaborative research project on photoexcited carrier relaxation and recombination mechanisms in the CdS window layer of CdTe/CdS PV devices.
- Colorado School of Mines, Golden, CO: Collaborative research project on the effects of growth and treatment conditions on carrier trapping and recombination in CdS.
- NREL CdTe Team, Golden, CO: Collaborative research projects on 1) effects of oxygen during growth and post-growth treatment of CdTe/CdS thin films, 2) effects of varying the extent of the CdCl₂ post-growth treatment, 3) effects of deposition conditions and post-deposition treatments on the electrooptical properties of chemical-bath-deposited CdS, and 4) effect of back-contact application on the electrooptical properties of CdTe thin films.

CIGS thin-film solar cells

Principal goals of this task for the CIGS program were:

- Investigation of the role of CdS, ZnO, and components of the chemical bath solution in affecting CIS material quality. Evidence of reduced surface recombination was observed. This was reported in 1) the CIS Junction Team Report and 2) the NREL/Sandia PV Review Meeting.
- In response to needs of the CIS program, changes were made to the FT-PL system that now allow acquisition of complete CIS spectra, regardless of the Ga content.

DLTS measurements were made on a number of CIGS solar cells for defect identification. Numerous CdS/CIGS thin films were analyzed by energy-resolved photoluminescence, on a routine basis, at temperatures from 300 K to 4 K. Minority-carrier lifetime measurements were made on CIGS films by RFPCD. Excitation density parameters for the FT-PL studies of CIGS passivation were determined by minimizing band-filling effects in the spectra of CIGS films and devices. The grazing angle accessory for the FTIR microscope was used to measure the C-H stretching modes of a C₁₈ alkanethiol monolayer on a silver surface, confirming the sensitivity of the accessory in measuring contaminants on silver grid lines. Twenty room-temperature and cryogenic (86 K) FT-PL spectra of CIGS films subjected to various steps and methods of the CdS junction process were collected in support of the NREL/industry CIGS junction team. In addition to the 12 spectra collected last month, the data represent a comprehensive investigation of the effects of different junction-forming process and excitation power on the PL spectra of CIGS films. The FTIR microspectroscopic analyses of CdS films on CIGS and tin oxide (TO) substrates continued. A new scanning and contaminant mapping capability for FTIR microspectroscopy was demonstrated using the carbonate-containing CdS/CIGS films from Energy Photovoltaics, which show clear correlation between the visible yellow inclusions and the maps of carbonate absorbency.

A series of CIS and CIGS samples from K. Ramanathan and from Washington State University were analyzed using FT-PL. The object of this work is to study the passivation effects of different buffer layers. After the analyses, these samples will be coated (or stripped) and reanalyzed.

Measurements and modeling of CIS materials and films were performed using scanning ellipsometry. The thickness and optical constants of the top chalcopyrite defect layer (which is considered crucial to the CIS device performance) were estimated from the data analysis. The results were reported in the Institute of Electrical and Electronics Engineers (IEEE) conference in Washington, D.C., in May 1996.

Crystalline silicon solar cells

A great deal of activity developed during the year using the new RFPCD technique to provide information on the minority-carrier lifetime in silicon materials. Measurements were made on silicon materials provided by a number of device research groups at AstroPower, Solarex, SUNY-Buffalo, Georgia Institute of Technology (A. Rohatgi), and the NREL in-house group.

Because the RFPCD technique provided the only known accurate measurement of lifetime in the AstroPower material, a proprietary agreement was made with the latter to set up a production line diagnostic system using the Phase II RFPCD technique. The Phase II RFPCD technique is currently subject to being written as a patent application. A comprehensive study of the effects of processing parameters on N and O levels and inclusions in EFG silicon was completed using FTIR spectroscopy and microspectroscopy for AstroPower (proprietary). Work continued, in collaboration with the in-house silicon group, on detection of implanted hydrogen in silicon. The bonded hydrogen which is visible via FTIR spectroscopy is more evident.

DLTS studies were initiated to study the iron impurity in silicon as a function of various heat treatments and hydrogenation processes.

High-efficiency III-V devices

- Provided measurements of material quality that are vital to the development of high-quality polycrystalline GaAs devices on various substrates (i.e., glass) in collaboration with the in-house group.
- Provide lifetime measurement support for the group at Research Triangle Institute that is growing epitaxial GaAs devices on polycrystalline germanium substrates.

Technique development

- A Phase II RFPCD lifetime measurement system was developed that offers greatly improved performance over the Phase I system. A patent application is in progress.
- Established new, state-of-the-art capabilities for optical characterization of semiconductors with the completion of NREL's Femtosecond Optical Spectroscopy Laboratory.
- The FTIR Center significantly upgraded its photoluminescence facilities to enable FT-PL measurements to be made on CIGS samples at temperatures as low as 85 K, and to enable excitation using a helium-neon laser as well as the Nd:YAG laser used previously.
- The scanning ellipsometry facility has added the software option to analyze multiple layers and surface roughness. It is now necessary to use more advanced programs for more complicated materials that include multiple layers; therefore, different analysis programs were tested during the year.

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Title: NREL Clean Room / Device Fabrication Team Activities

Organization: NREL Center for Photovoltaics and Electronic Materials

Contributors: T.A. Gessert, Senior Scientist and Team Leader, L. Roybal, M. Cudzinovic, J.S. Ward, A. Duda, S. Kurtz, D. Friedman, W. McMahon, C. Kramer, J. Olson, J. Alleman, M. Landry, S. Tsuo, M. Contreras, J. Keane, P. Parilla, X. Li, X. Wu, B. Mulligan, D. Ginley, T. Wangenstein, A. Cahill, J. Thiesen, and C. Allman

Objectives

The Clean Room/Device Fabrication Team provides the tools and procedures necessary to produce state-of-the-art test structures and devices from semiconductor materials synthesized by NREL or its subcontractors. The team also provides a "crossroads" at which researchers working on various technologies can mutually benefit from shared information and experience related to device fabrication. The team maintains an integrated, multidisciplinary facility comprising ~3500 square feet of Class 1000 clean room space and housing ~\$1M of processing equipment. Major equipment includes photolithographic processing, vacuum metallization, electrolytic metallization, and thermal processing. The team also maintains characterization equipment and techniques appropriate for related process monitoring and/or advanced process development. The team is presently composed of 23 team members from various "home" teams in the PV&EM, Basic Sciences, and Measurements and Characterization Centers. More than half the team membership use the team facilities on at least a weekly basis.

Technical Approach

Members of the Clean Room/Devices Fabrication Team use the SERF Clean Room facility and related characterization equipment to fabricate devices from semiconductor materials produced by their home teams or subcontractors. Process activities can also be performed for non-team members either by mutually beneficial collaborations between Team and non-Team members or by providing project-specific funds. Although the individual Team members work with a wide variety of material systems and related technologies, the procedure used to develop processes for device fabrication is similar. This will often involve review of related literature/documentation, design and production of required photomasks, preliminary process experimentation to optimize individual processing steps, process feasibility studies to determine how steps interact, and use of an entire process sequence to produce desired devices or structures. The time required for process development sequence can range from hours to months, depending on the complexity of the process and availability of related information. Because of this extensive effort to develop individual process, team members are encouraged to maintain awareness of other activities, and share information and/or experiences when appropriate. Team organizational functions are aimed at facilitating this transfer of process information. Within guidelines established by the team, a team member is free to use the Clean Room facilities on an as-needed basis. Team members that charge to Clean Room/Device Fabrication task (presently 0.3 FTE plus postdoc) perform functions related to developing team organization, maintaining facility equipment, providing training in the use of process equipment and procedures, acquiring and providing

process and ES&H documentation, performing business development activities, and providing long-term planning for the team and facilities.

Studies and Accomplishments

Following is a partial summary of studies and accomplishments resulting from work by Clean Room Team members and related collaborations. The list is organized by citing the home team of the researcher that performed the work, or the home team of the collaborating partner.

III-V Materials and Devices Team (Center for PV & EM)

- * Routine processing of III-V devices included use of plated Au for back contacts, photolithography and vacuum evaporation for processing of Ti/Pd/Ag top contacts. Photolithographic and chemical etching for device isolation and to enable profilometry of epi-layer thickness.
- * Advanced process activities included development of an improved metallization for high-concentration devices. This multilayer metallization involved high-profile grid lines (3 μm wide x 9 μm high). The contacts demonstrated low resistance, good adhesion, and compatibility with the selective etch used to remove GaAs capping layer. Because these metallizations are formed with gently sloped sidewalls, external-loss modeling indicates that obstruction loss may be much smaller than the contact area would suggest. Feasibility studies related to potential advantages of Al vs. Ag metal for this contact are currently proceeding.
- * Studies were performed to investigate the use of very thick photoresist layers for the production of thick depositions of plated Au. If successful, this procedure could allow for the economical production of chemically inert metallizations (Au) with high aspect ratios.

CdTe Team (Center for PV & EM)

- * Developed process to photolithographically define contact area of graphite-based contact using patterned polyimide layer.
- * Developed photolithographic/chemical etch process to isolate CdTe devices fabricated with sputtered ZnTe back contacts. Because this process produces reproducible contact characteristics and active areas, it allowed for spatial analysis of junction reproducibility and effect of parameters such as CdTe-layer thickness on device performance.
- * Use of Clean Room automatic ellipsometer to assist in development of CVD SiO_2 and SnO_2 layers. Because this instrument can produce numerous measurements of optical index and layer thickness very quickly, it is an invaluable tool for analyzing CVD deposit uniformity and thickness.
- * Deposited MgF_2 films of optimum thickness for use as antireflection coatings on CdS/CdTe devices.

CIS Team (Center for PV & EM)

- * Used clean environment for routine production of Mo-coated substrates for CIS growth. It was found previously that pinholes through the Mo back contact can detrimentally affect device performance. By cleaning the substrates in the Clean Room (Class 10 hood), and locating the Mo sputtering system in an adjacent area (Class 1000), pinhole formation is reduced.

- * Fabrication of photomask set for use in CIS concentrator studies. The goal of this study is to investigate if the open-circuit voltage can be improved significantly by saturating carrier traps through mild concentration. The design of the new mask set/process is based on preliminary studies conducted by the Clean Room Team in which 0.1 cm^2 CIS devices were produced for analysis at ~ 20 suns. This work tested both vacuum-deposited and electroformed Ni contacts and confirmed that photolithographic processing and chemical etching could be used to form multilevel grid patterns in CIS. The mask set produced during FY 1996 takes the process development one step farther by using a grid spacing that is compatible with an integral prismatic cover (22-Sun Optimization) produced by ENTECH, and optimizes the metallization for the expected current. The process design employs interdigitation and significantly reduces the series resistance of both the front and back contacts. The ENTECH prismatic-cover process technology was previously brought to NREL by the Clean Room Task.

Amorphous Si Team (Center for PV & EM)

- * Preliminary studies aimed at using liquid-spin processing to produce films of insulating polymers on glass for use by the a-Si Team.

TPV Team (Center for PV & EM)

- * This externally funded activity performed several routine processes aimed at developing photovoltaic devices with band gaps required to convert the thermal radiation directly into electricity. The activity developed and used several novel processes that are now part of the Clean Room Team's experience base, and available for the PV Program. Indeed, some of these have already been used by other teams within the PV Program (e.g., see fabrication of "free-floating films" for the Spectroscopy Team).
- * Process development resulting in first working NREL example of a monolithic interconnected module (MIM process). This process can be adapted to other PV devices and affords a method to interconnect small submodules into a larger module with high voltage but the short-circuit current of a single submodule.
- * Demonstrated fabrication process for inverted device structures using substrate removal procedures. Developed essential handling procedures for these ultra-thin films and devices.
- * Proof-of-concept studies related to Cd_2SnO_4 processing (NREL-developed TCO material) resulted in a demonstration that photolithographic process and chemical etching can be used to produce narrow conduction lines ($80\text{-}\mu\text{m}$ wide) in this material. This is an important process advantage to the thin-film display [TFD] industry, and is now part of an NREL patent.

Crystal Growth and Devices Team (Center for Basic Sciences)

- * Processed thin-film Si on metallurgical-grade Si wafers. Processing involved diffusion of emitter layer, fabrication of Al back contact, back contact annealing, and lift-off photolithography of multilayer top contact metallization (Ti/Pd/Ag). Results from this preliminary work provided a benchmark for the quality of the Si thin film.
- * Used Clean Room diffusion furnaces to study effect that cooling rate (after B dopant diffusion) has on the minority-carrier lifetime of high-purity Si. Analysis reveals changes in the PL peaks due to cooling rate, and these may be related to B-vacancy complexes.

- * Detailed study of effect of various heat treatments, including optical processing, on high-quality Al metallizations on crystalline Si. This work involved use of dedicated Al E-Beam evaporator to deposit numerous high-quality Al films, and thermal processing of these samples. The work resulted in a Ph.D. thesis.
- * Collaborative processing of 1-cm² Si devices with ITRI (Taiwan). Processing included wafer cleaning, diffusion, back and front contacting, AR coating, and device performance testing.

Energy Storage Team (Center for Basic Sciences)

- * Investigate use of spin processing to produce polymer films containing quantum dots onto mica and graphite substrates. Determine if an appropriate polymer and process will allow the spatial dispersion of quantum dots required for fundamental analysis of individual dots. Study represents joint project with Chemical Sciences Team of Center for Basic Sciences.
- * Clean Room Team members developed process to deposit stress-free Ti films on Si₃N₄ AFM cantilevers. Coatings of conductive films were required to enable AFM to be used for conductivity spatial mapping of surfaces. Technique potentially useful for polycrystalline and nanocrystalline PV films.

Spectroscopy Team (Center for Basic Sciences)

- * Clean Room Team members fabricated "free-floating films" of GaP and GaInP for PL analysis. The ability to remove these ~2- μ m-thick epitaxial films from the GaAs substrate enabled improved PL analysis that was helpful in understanding "ordering" in III-V materials. Study has led to two publications in FY 1996.
- * Clean Room Team members fabricated front and back contacts onto double heterostructure devices (GaAs/GaInP/GaAs) to enable studies of the effect of an electric field on the optical properties of this ordered III-V material.

Chemical Sciences Team (Center for Basic Sciences)

- * Performed routine processes on GaAs structures grown by OMCVD. The first structure was a OMCVD-grown GaAs homojunction device and was processed with a plated Au back contact, a photolithographically defined Au top-grid contact, and mesa etching. The second device was a metal-semiconductor Schottky barrier device incorporating a plated Au back contact and a top contact formed by photolithographic lift-off of an evaporated Ti/Pd/Ag metallization.
- * Clean Room Team members produced Pt metallizations on various glass substrates for use in dye-synthesized solar cell research. To produce required film adhesion, a previously developed alkaline-cleaning procedure was used to prepare the substrate. This was followed by a multilevel E-beam metallization using a Ti adhesion layer (400 Å) and Pt (600 Å). Approximately 200 Pt-coated substrates were produced for this effort during FY 1996. The cost of process development and precious metal consumption was shared between the Clean Room and Chemical Sciences Teams.
- * Deposited thin-film TiO₂ onto ITO-coated substrates. These coatings were successfully used to study the feasibility of a TiO₂ layer to reduce pinhole shunting in dye-synthesized solar cells.

Electro-Optical Characterization Team (Center for Measurement and Characterization)

- * The automatic ellipsometer in the clean room was used routinely to calibrate the wavelength-scanning ellipsometer. The automatic ellipsometer is well suited for this application because the Clean Room Team maintains ellipsometric standards for calibration of the instrument.

Conclusions and Future Directions

The Clean Room / Device Fabrication Team was created in 1996. Therefore, much of the past year's effort focused on providing process capability critical to the PV program while also developing longer-term objectives within the framework of available personnel, equipment, and program support. This involved identifying team members, identifying the collective capabilities, identifying which members required which capabilities, developing a method to assign critical responsibilities, identifying beneficial collaboration, and learning how to share and transfer the team's information base effectively. As indicated by the preceding list of the team's studies and accomplishments, these efforts have led to some significant accomplishments and synergistic collaborations. However, several important team objectives remain undeveloped, and it is here where a portion of next year's efforts will be placed. Some of these objectives are outlined below.

Business Development Activities

Because the equipment capabilities and processes expertise is valuable to many researchers both within and outside of NREL, it is believed the team has significant potential for income generation and/or potential to assist other teams in work-for-other activities. To this end, the Clean Room task supports 0.1 FTE, who is designated to assist the team in business development. These activities have focused on education and goal-development discussions within the team. Agreement has been reached to pursue the following goals: 1) Work with NREL staff and develop a Web site for the Clean Room, 2) Produce a brochure of capabilities, 3) Agree to a list of capabilities that can be effectively marketed, and a potential cost structure. It has also been determined that coordination of the team's capabilities with submission of process-related FIRST proposals is another important avenue to assist in the potential success of FIRST projects, and to further leverage the Team's value.

Facility Development

Capabilities that will be further discussed/developed during next year include: Multi-user diffusion-furnace laboratory, improvements to the Team's ability to produce multilayer antireflection coatings, and the potential for production and study of screen-printed contacts.

Exploratory Materials and Devices In-House Research

Title: Photochemical Solar Cell Development and Optimization

Organization: NREL Center for Basic Sciences, Chemical Sciences Team
Golden, Colorado 80401

Contributors: B. A. Gregg (Senior Scientist); A.J. Frank (Senior Scientist); A. Zaban (Postdoctoral Research Associate); S-Y Huang (Postdoctoral Associate); B. O'Regan (Graduate Student, subcontract to U. Washington); A.J. Nozik (Team Leader)

Objectives

The objective of this work is to develop very low-cost, durable, and efficient (>10%) photochemical solar cells; this new type of solar cell is based on the dye-sensitization of nanocrystalline films of titanium dioxide (TiO₂). The research focuses on defining and solving the problems that limit the efficiency and commercial viability of dye-sensitized nanocrystalline TiO₂ photochemical solar cells.

Technical Approach

This project is part of an integrated program of basic and applied research and development jointly funded by the Energy Research (ER)/Basic Energy Sciences (BES)/Chemical Sciences and Advanced Energy Projects Divisions and the Office of Energy Efficiency and Renewable Energy (EE)/PV program to explore, understand, and develop photochemical solar cells for both electricity and hydrogen production from water. This new type of cell offers the possibility of very inexpensive manufacturing and materials cost, with projected module costs of \$55/m² and \$0.60/pkW.

The cell is formed upon adsorbing a monolayer of an appropriate dye molecule on a 10- μ m nanocrystalline film of TiO₂ particles (30 nm diameter), which is supported on transparent conducting oxide glass, filling the void space between the particles in the thin nanocrystalline film with a non-aqueous electrolyte containing iodine and iodide ions, installing a counter-electrode, and sealing the edges of the cell to contain all the components. The program is designed so that basic research on the mechanisms and fundamental properties supported by the ER/BES/Chemical Sciences program will support and underpin the cell development program supported by the EE/PV program.

Our overall approach for the EE/PV program is to develop the skills and experience at NREL to produce photochemical solar cells that match the best-reported PV performance for such cells. We also plan to improve the performance and long-term stability, and lower the cell cost to make photochemical solar cells economically competitive. One of the strategies to achieve this is to reduce the back electron transfer rates from the TiO₂ particles to the redox electrolyte to achieve higher open-circuit photovoltages, optimize the dye to maximize the photovoltage and photocurrent, replace the liquid electrolyte with a solid-phase ionic conductor, and develop techniques for fabricating monolithic, parallel- and series-connected dye-sensitized cells to form large-area photovoltaic modules. We will also evaluate the long-term performance and reliability of the cells, and delineate the fundamental factors controlling the photovoltage and efficiency.

Results

We have reproducibly achieved conversion efficiencies at the 7% level (AM 1.5) for small-illuminated-area cells (0.7 x 0.7 cm²). One cell showed a conversion efficiency of 7.5% (AM 1.5), which is the

highest value reported for a U.S. laboratory. (A Swiss-made cell displayed a conversion efficiency of 8.5% at NREL.) The efficiency drops off for a single large-size solar cell ($10 \times 10 \text{ cm}^2$) owing to resistive losses of the conducting glass substrate ($10 \Omega/\text{SQ}$). To overcome this problem, we are fabricating, using various design configurations, modules consisting of interconnective small cells. Furthermore, for improved charge collection, in the case of the panel with a parallel-connected configuration, a metal-grid pattern will be deposited onto the conducting glass to lower the sheet resistance. Also, new counterelectrode materials based on graphite or other high-surface-area materials are being explored as a substitute for platinum, which is currently used. We are also investigating the stability of the cells. One laboratory reports that its accelerated-aging test indicates that the dye-sensitized nanocrystalline cells will be stable for up to 20 years. Others report very short-term stability. We are currently constructing a computer-controlled workstation to address this issue. Initially, the performance of continuously illuminated cells (photocurrent, photovoltage, and fill factor) will be examined. We are delineating the major factors limiting the conversion efficiency and photovoltage as well as exploring how various surface-modification treatments of TiO_2 particle electrodes affect these parameters. Specifically, as part of a collaborative effort with OER/Chemical Sciences, we are investigating charge-recombination and charge-transport processes in the cell and are studying the effect of surface-modification reagents (amines, polymeric materials) in controlling these processes. A paper demonstrating how such reagents can markedly enhance the photovoltage has been accepted for publication in *The Journal of Physical Chemistry*.

We also discovered that the oxidation potential of the sensitizing dye becomes pH-dependent when adsorbed onto the TiO_2 electrode, although it is not pH-dependent in solution. This unexpected result has important implications for the optimization of dye-sensitized solar cells, suggesting that it will not be possible to change the rates of the electron injection and recombination reactions simply by shifting the semiconductor flatband potential. IMVS data show that surface modification of TiO_2 in nonaqueous solutions shifts the band edges.

A solid-state analog of the dye-sensitized solar cell is expected to be more rugged and less sensitive to temperature extremes than the electrolyte-containing cells. Two approaches are being considered. One involves replacing the electrolyte with a conducting polymer that will transport the holes from the dye to the counter electrode. The other approach involves replacing the existing dye with 10-20 monolayers of a sensitizing pigment that we have previously shown to be an effective sensitizer of TiO_2 . The pigment layer absorbs a greater fraction of the solar spectrum than the current dye in a cell only 10% as thick as the existing ones. The thinner cells alleviate hole-transfer limitations, allowing either a conducting polymer or another sensitizing pigment to contact the back electrode. Both approaches eliminate the need for a catalytic platinum coating on the back electrode and make the solar cells more compatible with existing manufacturing methods. Factors affecting the efficiency, as well as the long-term performance, of the cells are also being evaluated.

Major Spin-off Discovery (B. Gregg and C. Bechinger)

A novel and potentially very important spin-off application of the jointly funded ER/EE Photochemical Solar Cell Project is for a smart window that darkens when exposed to sunlight; this invention has been named a *photoelectrochromic window*. The window is simply derived from the photochemical solar cell by replacing the counterelectrode with a thin film of WO_3 deposited on transparent conducting glass and adding Li^+ ions to the electrolyte. A patent has been applied for and the discovery has been written up in *Nature*. Many inquiries have been received at NREL on this invention and discovery.

Several companies have expressed interest in Photochemical Solar Cells, and have visited NREL for discussions:

- **Direct Gain**, NY: Has initiated a cooperative research and development agreement (CRADA) application involving NREL, NY State R&D Authority, and Direct Gain.
- **BHP, Ltd**, Australia: This is the largest company in Australia. They market metal roofs and are interested in incorporating photochemical solar cells into their roofing products. They visited NREL to discuss technical issues.
- **Superconductive Components, Inc.**, Columbus, Ohio: This company is very interested in a CRADA in which they would supply \$300K/yr for at least two years to NREL for a joint project to develop photochemical solar cells.
- For the Photoelectrochromic Window application of dye-sensitized TiO_2 cells, many companies and research organizations have contacted Dr. Brian Gregg (co-inventor) to explore opportunities and relationships with NREL. **Zeiss** (in Germany) has expressed an interest in licensing this technology, as has **Anderson Corp.**, the largest manufacturer of windows in the U.S. Representatives of both **Monsanto** and **Thermo Electron**, who recently visited NREL, have also expressed a strong interest in the technology.

Conclusions

Photochemical solar cells have the potential to develop into a new low-cost and commercially viable PV alternative. After a little over one year of research the efficiency of NREL-produced devices is approaching 8%. Our near-term goal is 10%; the ultimate attainable efficiency for photochemical solar cells is currently not known. NREL research is focused on improving the cell efficiency, developing interconnect strategies to produce large-area modules, developing solid ionic conductors to replace the liquid electrolyte and characterizing and improving cell lifetime. A potentially important near-term spin-off application from the EE/ER Photochemical Solar Cell Project in the form of a photoelectrochromic window has been discovered, and industrial relationships to develop and market this new invention are in progress.

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2. Zaban, A., Ferrere, S., Sprague, J., and Gregg, B.A., "pH-Dependent Redox Potential Induced in a Sensitizing Dye by Adsorption onto TiO_2 ," *J. Phys. Chem.*, 1997, in press.
3. Huang, S.Y., Schlichterl, G., Nozik, A.J., Graetzel, M. and Frank, A.J., "Charge Recombination in Dye-Sensitized Nanocrystalline TiO_2 Solar Cells, *J. Phys. Chem.* (in press).

Title: SOLID STATE THEORY OF NOVEL PHOTOVOLTAIC MATERIALS AND DEVICES

Organization: National Renewable Energy Laboratory, Golden, CO
Basic Sciences Center

Contributors: Alex Zunger, Research Fellow
S.-H. Wei, Senior Scientist
S. B. Zhang, Senior Scientist

This report provides a succinct summary of the PV research activities of the Solid State Theory Group on:

1. Defect physics of CuInSe_2
2. Silicon-based nanostructures
3. Ordering and surface effects in GaInP_2
4. PbS , PbSe , PbTe : new TPV systems?

The reader interested in further detail can consult the original journal article publications cited at the end of each section.

1. Defect Physics of CuInSe_2 [1]

CuInSe_2 is a prototype member of the family of I-III-VI₂ chalcopyrite semiconductors. Solar cells based on CuInSe_2 have developed rapidly from 5% efficiency in 1974 to about 17% at present. However, further increase of the solar cell efficiency requires better understanding of defect physics in this system. CuInSe_2 shows three unusual *defect-related effects*:

(a) Unlike GaAs or ZnSe, CuInSe_2 tolerates a large range of off-stoichiometry (i.e., samples with a few percentage Cu-poor and /or In-poor stoichiometries are stable). The extreme limit of "off-stoichiometry" manifested in this system is the existence of a series of compounds with unexplained integer stoichiometries (CuIn_5Se_8 , CuIn_3Se_5 , etc.).

(b) Unlike GaAs or ZnSe, CuInSe_2 can be doped to a low-resistivity p or n type merely via introduction of *native* defects, without extrinsic impurities.

(c) While in Si and in ordinary III-V semiconductors, polycrystallinity leads to a high concentration of electrically active (grain-boundary) defects that have a very detrimental effect on the performance of optoelectronic devices. Polycrystalline CuInSe_2 is as good an electronic material as its single-crystal counterpart, even though it has many non-stoichiometry defects.

Previous analysis of the "defect chemistry" in CuInSe_2 involved some assumptions which we now find questionable:

(i) The relative concentration of point defects was assumed by defect chemists to follow their formation energies as computed by a very simple model of Neumann and Rincon. This model predicts that it's harder to make a vacancy in CuInSe_2 than in a II-VI. The relative defect concentration that emerges from the model is

$$In_{Cu} < Cu_{In} < V_{Se} < V_{Cu} < V_{In} < Cu_i,$$

where V_α denotes a vacancy of atom α , α_i denotes an α -type interstitial, and α_β denotes an antisite of atom α on site β . We now find that this order is incorrect. The correct orders are

$V_{Cu} < Cu_{In} < V_{In} < Cu_i < In_{Cu}$	(Cu-rich; In-rich; n-type)
$V_{Cu} < Cu_{In} < Cu_i < In_{Cu} < V_{In}$	(Cu-rich; In-rich; p-type)
$V_{Cu} < In_{Cu} < V_{In} < Cu_{In} < Cu_i$	(Cu-poor; In-rich; p or n-type)
$Cu_{In} < V_{In} < V_{Cu} < Cu_i < In_{Cu}$	(Cu-rich; In-poor; p or n-type)
$V_{Cu} < V_{In} < Cu_{In} < In_{Cu} < Cu_i$	(Cu-poor; In-poor; p or n-type)

(ii) The formation energies were assumed by defect chemists to be constant. We now find that this is incorrect, as formation energies depend strongly on the position of the Fermi level and on the chemical potentials. For example, in the Cu-poor and In-rich region, V_{Cu} has the lowest formation energy, while in the Cu-rich and In-poor region, Cu_{In} has the lowest energy (see above).

We calculated the formation energies and electronic structures of the point defects in $CuInSe_2$ using the first-principles, self-consistent electronic structure method [1]. Our results show that it is *easier* to form cation vacancy in $CuInSe_2$ (i.e., V_{Cu}) than in II-VI's. The formation energy can be further lowered by forming charge-compensated defect pairs [e.g., two Cu vacancies ($2V_{Cu}$) plus one In-on-Cu antisite (In_{Cu})] and arrays. The three unusual effects (a)-(c) mentioned above are explained as follows:

(a) The existence of the off-stoichiometric ordered compounds is identified as a repeat of m units of $(2V_{Cu}^- + In_{Cu}^{2+})$ for every n units of $CuInSe_2$. This gives, for example, the observed $m=1$, $n=4$ phase $CuIn_4Se_8$; the observed $m=1$, $n=5$ phase $CuIn_5Se_5$, etc.

(b) The *shallow* acceptor level in $CuInSe_2$ is identified as the V_{Cu} acceptor (0/-) transition, while the shallow donor level is identified as $(In_{Cu} + V_{Cu})$ donor (+/0) transition. Our calculated cation defect levels are compared with available experimental data and previous theoretical estimation. Previous misassignments of the defect levels are corrected.

(c) The electrically benign character of the large defect population in $CuInSe_2$ is due to an electronic passivation of the easily-formed $2V_{Cu}^-$ by its attraction to In_{Cu}^{2+} . We find that the pair is electrically neutral, has no gap "defect levels", and that the ordered defect arrays, e.g., $CuIn_5Se_8$, $CuIn_3Se_5$, and $Cu_3In_7Se_{12}$ have larger band gaps (1.38, 1.29 and 1.23 eV, respectively) than $CuInSe_2$ (1.04 eV).

These results await experimental testing.

1. A. Zunger, S. B. Zhang, and S.-H. Wei, "Why Is $CuInSe_2$ Tolerant to Defects and What Is the Origin of Ordered Defect Structures," in *Proceedings of the 14th NREL PV Program Review*, edited by C. E. Witt, AIP, New York (1997).

2. Silicon-Based Nanostructures [2-4]

With the new drive to investigate *low-dimension* Si structures (e.g, thin-films), and with the advent of light-emitting Si systems, we started looking at the basic theory of Si *nanostructures*. The objective was to develop the theoretical tools able to predict the optical and materials properties of such structures, as they pertain to PV. To this end, we have developed a systematic approach to the study of the electronic structure of thousand-atom (nanometer-scale) Si structures. This approach uses the empirical pseudopotential method to approximate the Hamiltonian and a plane wave basis to expand the wavefunctions. Two complementary, newly developed methods are used to calculate

the electronic structure of the system. The first method calculates the valence band maximum and the conduction band minimum. Its computational time scales *linearly* with the size of the system. The second method calculates *statistically* the electronic density of states and optical absorption spectra. The combination of these two methods is used to study the electronic and optical properties of up to a thousand Si atom quantum dots passivated by hydrogen. The properties studied include: (1) band gap vs size; (2) band gap vs shape; (3) analysis of band edge states in terms of bulk Bloch functions; (4) total electronic density of state and optical absorption spectra; (5) dielectric constant vs size; (6) photoluminescence radiative lifetime vs luminescence photon energy. Comparison with experimental data is made whenever possible. Good agreements with experiment are obtained for photoluminescence lifetime and for the ratio between conduction band shift and valence band shift.

2. L. W. Wang and A. Zunger "Pseudopotential Theory of Nanometer Silicon Quantum Dots" in *Nanocrystalline Materials*, edited by P.V. Kamat and D. Miesel, Elsevier Science, p. 161, (1996).
3. A. Zunger and L.W. Wang, "Theory of Silicon Nanostructures," *Appl. Surf. Sci.* **102**, 350 (1996).
4. A. Zunger, "Pseudopotential Theory of Semiconductor Quantum Dots," in 23rd Int. Conf. Physics Semicond., edited by M. Scheffler and R. Zimmermann, *World Scientific*, Singapore Vol. 2, p. 1341 (1996).

3. Ordering and Surface Effects in GaInP₂ [5-9]

We have now formulated a list of experimentally testable predictions of the consequences of ordering on the optical (and thus, PV) properties of GaInP₂. The analysis was published (see below) in a way that emphasizes the experimental aspects, rather than theoretical intricacies [5-6].

In a related work, we have now developed a method [7] that predicts the thermodynamic stability/instability of various surface reconstructions [$\beta 2$ (2×4); (2×2); C(4×4) and $\beta 2$ (4×2)] of III-V substrate materials, and another method [8] that predicts the STM image of given defects on such surfaces. These developments could open the door to electronic nanoscale engineering of semiconductor surfaces [9].

5. S.-H. Wei, A. Franceschetti, and A. Zunger, "Dependence of Optical Properties of Semiconductor Alloys on Long Range Order, Strain, and Pressure," *Materials Research Society*, **417**, (1996).
6. A. Franceschetti, S.-H. Wei, and A. Zunger, "Prediction of New Fingerprints of Ordering in GaInP₂," *Materials Research Society*, **417**, (1996).
7. S. B. Zhang and A. Zunger, "The Method of Linear Combination of Structural Motifs for Predicting Surface Step Energies: Application to GaAs (001)," *Phys. Rev. B.* **53**, (1996).
8. S. B. Zhang and A. Zunger, "Structure of the As Vacancy on GaAs (110) Surfaces," *Phys. Rev. Lett.* **77**, 119 (1996).
9. S. B. Zhang, S. Froyen, and A. Zunger, "Theory of Surface Dimerization-Induced Ordering in GaInP Alloys," *Materials Research Society*, **417**, 43 (1996).

4. PbS, PbSe and PbTe: New TPV Materials? [10]

The rocksalt-structure lead chalcogenide narrow-gap semiconductors PbS, PbSe, PbTe and their alloys have been applied in thermophotovoltaic (TPV) energy converters (T.K. Chaudhuri, *Int. J. Energy Res.* **16**, 481 [1992]). A close examination shows that these systems pose some peculiar electronic and structural properties relative to the more conventional zinc-blende II-VI and III-V compounds and alloys, including the occurrence of direct gaps at the L point, anomalous order of band gaps and valence band maximum energies versus anions, negative optical bowing, negative band-gap pressure coefficients, and the occurrences in the random alloy of two distinct bonds for each anion-cation pair.

Using a first-principles, all-electron method, we show that the seemingly unrelated electronic anomalies noted above have a common origin: they can be explained by noting that the Pb 6s band lies *below* the top of the valence band, while in conventional II-VI and III-V semiconductors the cation s band is unoccupied. The existence of an occupied cation s band leads to strong level-repulsion between the valence states at the rocksalt L point of the Pb chalcogenides. We further find that the topological properties of octahedral coordination lead to the occurrence in the random alloy of *two* distinct bonds for each anion-cation pair, and to the predicted stabilization of ordered $(\text{PbX})_1(\text{PbY})_1 < 111 >$ ("rocksalt CuPt") structure.

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Exploratory Materials and Devices Subcontracts

Title: Solar Energy Conversion at Dye Sensitized Nanostructured Electrodes Fabricated by Sol-Gel Processing

Organization: The Johns Hopkins University, Baltimore, MD 21218

Contributors: P. C. Searson and G. J. Meyer, Principle Investigators
F. Cao and J.M. Stipkala

Objectives

In this program we are exploring the use of nanostructured materials as substrates for dye-mediated light-to-electricity conversion in a photoelectrochemical cell. The objective of current work is to develop new materials, electrolytes, and molecular sensitizers which increase solar energy efficiency and stability. Materials processing and synthesis is carried out in conjunction with characterization of cell performance, detailed investigation of operating mechanisms, and modeling of charge transfer and transport in these systems.

Results

In our continuing work on solar energy conversion at dye sensitized nanostructured electrodes fabricated by sol-gel techniques [1-5], we recently reported an alternative sensitizer-to-semiconductor linkage based on a derivative of acetylacetonate (acac) [6]. Acac was chosen for the known chelate rings formed with Ti(IV) and Ti(III) metal centers. The ligands shown in Scheme 1 were coordinated to *cis*-Ru(4,4'-(CH₃)₂-bpy)₂Cl₂ and bound to TiO₂ thin films for use in regenerative solar cells. Significantly, the bpy-acac based sensitizer binds to TiO₂ in high surface coverage. In alkaline water the stability of this sensitizer-semiconductor adduct is dramatically higher than that observed for sensitizers anchored to TiO₂ through carboxylic acid groups. Photoelectrochemical studies revealed a surprisingly high monochromatic light-to-electrical energy conversion, IPCE = 0.30, despite the n-propyl spacer between the chromophoric ligand and the surface anchor. Since this spacer is flexible, it is possible that the sensitizer is proximate to the TiO₂ surface.

In an attempt to achieve molecular control of the sensitizer orientation we prepared the bimetallic sensitizer shown in Scheme 2 and a linkage isomer [7]. The facial geometry of the Re center holds the Ru polypyridyl sensitizer proximate to the TiO₂ surface. The Re chromophoric unit absorbs light in the UV region, so visible light excitation almost exclusively excites the Ru chromophore. The photoelectrochemical properties of these sensitizers also reveals a high photocurrent efficiency. Further, recombination of the injected electron with the oxidized sensitizer was significantly inhibited when compared to sensitizers bound to TiO₂ through 4,4'-(COOH)₂-bpy ligands. This result suggests that an undetermined optimal sensitizer-semiconductor orientation exists wherein interfacial charge separation is efficient yet the energy wasting back

reaction to ground state products is further inhibited. We expect such orientations will increase the power output in an operational solar cell. At a minimum, these results indicate that a covalent linkage between the semiconductor and the chromophoric ligands is not a strict requirement in the design of efficient sensitizers for this application.

To produce a higher open circuit photovoltage in a regenerative solar cell, we prepared the sensitizer shown in Scheme 3 [8]. The strategy in the design of this sensitizer is as follows: Light excitation of $\text{Ru}(4,4'-(\text{CO}_2\text{H})_2\text{-bpy})_2(4\text{-CH}_3,4'\text{-CH}_2\text{-PTZ,-bpy})]^{2+}$, anchored to TiO_2 results in rapid interfacial and intramolecular electron transfer that efficiently translates the "hole" away from the chromophoric unit to the pendant PTZ group. The net result is the formation of a remarkably long-lived charge separated pair that lives for ~ 300 microseconds and directly results in an increased open circuit photovoltage when compared to a model compound. Attempts to use phenothiazine derivatives in place of iodide result in very low photocurrent production, $\text{IPCE} < 0.01$. Spectroscopic studies demonstrate that this is due to rapid recombination of the charge separated pairs $\{\text{e}^-(\text{TiO}_2), \text{PTZ}^+\}$, which results from their high concentrations within the mesoporous TiO_2 network. New strategies designed to block recombination are currently being investigated.

A limiting factor in photoelectrochemical cells is the presence of a liquid electrolyte. We have shown that ionically conducting polymer gels can be used in the fabrication of quasi-solid state cells employing a dye sensitized, nanocrystalline TiO_2 electrode [10]. The cells show open circuit voltages close to 0.6 V and short circuit currents larger than 3 mA cm^{-2} under 30 mW cm^{-2} white light illumination. Fill factors and open circuit voltages of the cell are comparable to those of similar cells with liquid electrolytes. An overall energy conversion efficiency of 3-5% has been achieved.

A characteristic feature of photoelectrochemical energy conversion at porous nanocrystalline electrodes is the long photocurrent rise times associated with illumination. Since nanometer sized particles are too small to sustain significant electric fields, charge separation is dominated by carrier diffusion rather than by drift. For the case of dye sensitization, electron injection from the sensitizer occurs on the order of nanoseconds, or faster, whereas the photocurrent transients have time constants on the order of milliseconds to seconds, depending on the light intensity. We have used photocurrent transient measurements and intensity modulated photocurrent spectroscopy to characterize the transient response of these films [11,12]. Figure 1 shows a typical photocurrent transient for a dye sensitized TiO_2 cell and Figure 2 shows the rise time (time for the current to reach half the steady state value) plotted against the light intensity. In recent work we have shown that the transient photocurrent response can be explained by the thermally activated hopping of electrons through the particle network [12] where the diffusion coefficient is proportional to the electron density. The fast component of the transient response (Figure 2) is related to the build up of a peak in the electron concentration close to the back side contact whereas the slow component is due to the progressive build up of the electron density in the outer part of the film.

Scheme 1

Scheme 2

Scheme 3

Figure 1. Photocurrent transient under monochromatic illumination ($\lambda = 514$ nm) at 4 mW cm^{-2} .

Figure 2. Photocurrent rise time (o) and IMPS time constant (◇) for a cell biased at 0 V. $\lambda = 514$ nm.

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Title: New Approaches for High Efficiency Solar Cells
Selenium Doping of GaInP by Atomic Layer Epitaxy

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Objective

One of the remaining problems in multi junction solar cells is to achieve a connecting junction (Tunnel Diode) in material system with $E_g = 1.9$ eV or larger. Limited success has been reported mainly due to the lack of achieving high levels of doping, specially n-type, in these high band gap materials. We will report on our effort to use Se as a dopant to achieve doping levels in InGaP approaching the 10^{20} cm⁻³ range.

Approach

Selenium (Se) is a common-type dopant in III-V compounds due to its low activation energy and high solubility. Since selenium has a high vapor pressure at elevated temperatures, for the effective Se incorporation into the epitaxial layers, it is necessary to reduce the growth temperatures. Atomic layer epitaxy (ALE) can be a good choice because it permits lower temperature growth of III-V compounds, including GaInP than MBE or MOVPE. Low temperature growth is possible even outside of the self-limiting regime, providing the ALE application with more flexibility.

In this report, we show the ALE growth of Se-doped GaInP. The dependence of the n-type carrier concentration of Se-doped GaInP on growth temperature was studied and compared with that of GaAs. Variation of the n-type carrier concentration of Se-doped GaInP with the Se source flow rate was also studied.

Results and Discussion

Atomic layer epitaxial growth of GaInP was performed in a modified atmosphere pressure MOVPE system described earlier (1,2). The growth system can also perform conventional MOVPE growth. The group III precursors were trimethylgallium (TMGa) and trimethylindium (TMIn). These group III sources were introduced on the column III side of the reactor. AsH₃ (100%) and PH₃ (100%) were the group V source materials and were introduced on the column V side of the reactor. H₂Se (45ppm in H₂) was used as the n-type dopant source and introduced on the column V side mixed with PH₃. Chromium-doped semi-insulating GaAs (100) substrates were used.

The ALE growth consisted of the simultaneous exposure of the substrate to TMGa and TMIn fluxes followed by rotation of the PH₃ side to complete one cycle (1,2). The composition of Ga_xIn_{1-x}P was controlled by the TMGa/(TMGa + TMIn) molar ratio in the column III stream and was determined from x-ray diffraction. The growth temperature

was varied from 400 to 500°C. The exposure time to TMGa and TMIn fluxes was 0.2 s. However, it was necessary to keep the sample under PH₃ flux for 3 s due to the low decomposition rate of PH₃ at the temperatures used in this experiment. In our growth system, since PH₃ and H₂Se were mixed before they were introduced in to reactor, it was impossible to expose the sample separately to PH₃ and H₂Se fluxes. Although samples with better quality were obtained with longer exposure to PH₃ in the case of undoped GaInP, an exposure time of 3 s was used for Se-doped GaInP. Longer exposure of the sample to the mixture of PH₃ and H₂Se resulted in the degradation of the surface morphology probably due to the formation of high concentration of selenium compounds.

Figure 1 shows the variation of n-type carrier concentrations of Se-doped GaInP with growth temperatures. N-type carrier concentrations of Se-doped GaInP showed a strong dependence on the growth temperature. In our experiment, growth temperatures for Se-doped GaInP were varied from 400 to 550°C, and the H₂Se flow rate was kept at 10sccm. All the samples showed gallium composition around 51%, as determined from x-ray diffraction.. As the growth temperature was reduced from higher temperatures to 450°C, the carrier concentration increased quite rapidly, which is expected to be due to the high vapor pressure of Se at elevated temperature. In the growth temperature range of 400-450°C, the carrier concentration increased only slowly with decreasing growth temperature.

Se-doping of GaAs was also carried out using our experimental setup, it is obvious that there are differences between Se-doping behavior of GaInP in our experiment and that of GaAs as shown in Fig.(1). The current GaAs results are consistent with that reported earlier (3), and it maybe due to the difference between the properties of the two materials. In order to investigate the possible reasons for the difference between Se-doped GaInP and GaAs, we performed growths of Se-doped InP and GaP at 420 and 460°C. Due to the slow growth rate, thicknesses of InP and GaP were limited to ~100 and ~40 nm, respectively. Carrier concentrations of Se-doped InP were as high as $9.05 \times 10^{19} \text{ cm}^{-3}$ at 420 °C and $8.78 \times 10^{19} \text{ cm}^{-3}$ at 460°C, respectively, while carrier concentrations of Se-doped GaP were not high enough to be measured for the epitaxial layers as thin as ~40 nm. From the results of Se-doping of InP and GaP by ALE, it could be suggested that, while a large portion of Se atoms incorporated in GaP sublattices of the $\text{Ga}_{0.51}\text{In}_{0.49}\text{P}$, they do not act as an efficient donors, as in the case of Se-doped GaAs grown at lower temperatures. However, Se atoms incorporated in InP sublattices contribute to n-type conduction, thereby not resulting in the decrease of the carrier concentration of Se-doped GaInP grown at low temperatures. The difference in the Se-doping behavior of GaP and InP can be due to the relative stability of "second phases of selenium" in GaP and InP such as gallium selenides and indium selenides at the growing surface respectively. More stable gallium selenides consume the selenium source more readily, at the growth temperatures, thus reducing the selenium incorporation as ionized impurities during the growth of GaP. It is also possible that indium selenides are more difficult to be formed in InP, and, therefore, more selenium atoms from the selenium source are consumed as shallow donor atoms in InP. More experiments such as secondary ion mass spectroscopy (SIMS) are needed to clarify the Se incorporation process in GaInP. At growth temperatures lower than 450°C, $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ films have carrier concentrations in the range of $4\text{-}6 \times 10^{19} \text{ cm}^{-3}$. These are considered to

compound semiconductors.

Figures 2a and 2b are the x-ray diffraction spectra of GaInP films grown at 440 and 400°C, respectively. Lattice mismatches between the epilayers and the substrates are 4.6×10^{-4} and 4.5×10^{-4} for (a) and (b), respectively. The ratio of peak intensities of the deposited GaInP film and the GaAs substrate is higher in Fig. 2a than in Fig. 2b, implying a higher quality for the sample grown at 440°C. The degradation in the crystal quality of the samples grown at these low temperatures can be due to the second Se-phases in the epitaxial films. Selenium atoms which form these Se-phases such as GaSe and Ga_3Se_3 may act as defects in the epitaxial layers rather than donors. It should also be mentioned that GaInP can be deposited in ordered or disordered structures depending on the growth conditions. With these fairly high levels of doping, the disordered phase will be dominant as has been previously reported (4).

The variation of n-type carrier concentration of Se-doped GaInP with respect to H_2Se flow rate was also investigated at two growth temperatures, 420 and 460°C, as shown in Fig. 3. At 420°C, as H_2Se flow rate was increased, the carrier concentration increased and then nearly saturated for H_2Se flow rates above 10 sccm. At 460°C, the carrier concentration stayed at the value of $2.5 \times 10^{19} \text{ cm}^{-3}$ with a H_2Se flow rate of 10 sccm. A higher flow rate of 20 sccm did not increase the carrier concentration. Under this growth condition, an opaque surface was observed. This indicates that in order to achieve high doping levels in GaInP using H_2Se as the dopant source, it is crucial to reduce the growth temperature, which is made possible with the atomic layer epitaxy approach.

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Fig. 1. Dependence of n-type carrier concentrations on growth temperatures in Se-doped GaInP, GaAs, InP, and GaP. although carrier concentrations of GaP samples grown at 460 and 420°C were too low to be put on the same scale with those of GaInP, GaAs, and InP samples, they were included for the ease of comparison.

Fig. 2. X-ray diffraction patterns from Se-doped GaInP grown at 440°C (a) and 400°C (b).

a

Fig. 3. Variation of n-type carrier concentrations in Se-doped GaInP with H_2Se flow rates. Se-doped GaInP was grown at 420 and 460°C.

Title: Fundamental Studies of the Effect of Crystal Defects on CuInSe₂/CdS Heterojunction Behavior

Organization: Department of Materials Science and Engineering
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Contributors: J. Benner, program manager; A. Rockett, principal investigator; Jose Luis Hernandez, K. Granath, visiting scientists; D. Schroeder, G. Berry, John Belanger, graduate research assistants; Benjamin French, Terrence Yeoh, and Jessica Nelson, undergraduate research assistants.

Objectives

The project seeks to determine the source of sample-to-sample variability in CuIn_{1-x}Ga_xSe₂ (CIGS)-based solar cell performances and the mechanisms restricting carrier collection at large voltages in CIGS/CdS heterojunctions. The detailed objectives involve determining the relative importance of structural and chemical defects in the material and how they affect electronic properties and hence device performances. A byproduct of the project is fundamental data on the properties of CIGS alloys as a function of processing conditions and composition. This is important to improving device modelling. Finally, as a university research program the goals include the training of graduate students and post-doctoral researchers and the exposure of as many individuals as possible to renewable energy research (see contributors list).

Approach

The basic approach is to grow the highest quality CIGS under a variety of conditions and to measure the morphology, microstructure, and properties of the resulting layers. Electrical properties have been measured extensively this year for correlation with compositional and structural data. Except as noted, the results described were recorded for CIGS deposited in a single step from magnetron sputtered Cu and In fluxes and evaporated molecular Se. The single crystal CuIn_{1-x}Ga_xSe₂ layers were deposited directly on "epi-ready" GaAs (001) or (111)_{As} wafers. Deposition temperatures were ~650°C. In addition, a collaborative study of polycrystalline CIGS grown by Lars Stolt and coworkers at the University of Uppsala in Sweden was undertaken. The samples were grown by open boat multiple source evaporation on soda-lime glass or other substrates. Some substrates were coated with Al₂O₃ as a diffusion barrier to prevent Na from passing from the substrate into the film. Na could also be intentionally added to the films.

Microstructural studies were carried out by X-ray diffraction and by scanning and transmission electron microscopies. Composition analyses used secondary ion mass spectrometry (SIMS), and by energy-dispersive spectroscopy. Scanning ion images were also obtained using the Cameca IMS-5f SIMS. Hall-effect measurements were obtained as a function of temperature. Electroluminescence measurements were made on solar cells from the University of Delaware, the National Renewable Energy Laboratory (NREL), and Siemens Solar Industries. Emission from forward-biased solar cells was studied as total intensity and as a function of wavelength and bias current. Spectral response was also measured for each device in the same instrument.

In addition, during this year we have begun a collaboration with other members of the NREL CuInSe₂ Team studying Mo back contacts for CIGS devices. Our part of the team activity has included obtaining Mo samples from various laboratories and analyzing them by SIMS.

Results (10/1/95 - 9/30/96)

Characterization of hole transport in CIGS

During the past year we have completed a detailed analysis of the electronic conduction properties of p-type CIGS.[1] We have demonstrated in detail the doping behavior of single crystal epitaxial CIGS layers, grown under conditions similar to those used to grow polycrystalline CIGS for solar cells. Specifically, we have shown that there are at least two electrically active acceptor states with depths of 167 ± 20 and 42 ± 8 meV above the valence band edge and present at concentrations of 10^{18} and 10^{16} cm⁻³, respectively. In addition, there is a donor state present at concentrations varying over a wide range from 10^{12} to 10^{15} cm⁻³. We have shown that the expected majority defects in the material which control stoichiometry are electrically inactive and that the active defects are not dependent on film composition. Hence, we conclude that they are not the same defects. It seems likely that the deeper, higher concentration, acceptor is the result of Cu_{In}⁻ antisite defects, while the shallower, lower-density state is the result of vacancies on one of the metal sublattices. If this is the case, there should be another acceptor level caused by Cu_{In}⁻ near the intrinsic level in energy and with a density of $\sim 10^{18}$ cm⁻³. The films have the highest hole mobilities ever recorded. We have fit the hole mobilities with a detailed model and confirmed our previous result that the mobility near room temperature is dominated by phonon scattering and not by defect states. Unlike in group IV or III-V semiconductors, the acceptor concentration does not substantially affect the room temperature mobility. This implies that the mobility at room temperature should be insensitive to the concentration of intrinsic or extrinsic point defects until very high concentrations are reached, as observed here. An abrupt decrease in hole mobility at widely varying temperatures was modelled and shown to result from compensation due to the donor states giving rise to impurity band conduction. [See also the discussion of preliminary results on Na in CIGS, below.]

Ga Diffusion in CIGS

We have completed a study of the composition dependence of diffusion of Ga in CIGS single crystals this year.[2] This was measured using SIMS as a function of the Cu/In ratio in the CIGS and modeled with Fick's Second Law. All films studied had Cu/(In+Ga) ratios greater than 1.0 as is typical of device-quality CIGS. The Cu/In ratio was controlled by the deposition conditions. The Ga diffusivity was a minimum near a Cu/In ratio of 1.0 and increased rapidly for both higher and lower values of this ratio, see Fig. 1. The diffusivity ranged from a minimum of 2.7×10^{-13} cm²/s at Cu/In=0.94 to 5×10^{-11} cm²/s at Cu/In=1.41 and 7×10^{-12} cm²/s at Cu/In=0.43. It was concluded that Ga diffuses on metal vacancies on *either* the Cu or In sublattice. The diffusivities are in good agreement with results for Ga diffusion in polycrystalline CuInSe₂/CuGaSe₂ diffusion couples, which yielded diffusivities of between 3×10^{-13} and 5×10^{-12} cm²/s at temperatures between 400 and 600 °C.[3] This suggests that diffusion in polycrystals is intragranular rather than intergranular. The range of diffusivity is significantly larger for the single crystals than was found in polycrystalline CIS and indicates that the film composition is a more important factor than is temperature in controlling the diffusivity of Ga in CIS.

The Effect of Na on CIGS

CIGS-based solar cells deposited by vapor phase techniques show significant improvements in performance when Na is present at the growth surface. During this year, we have completed characterization of the distribution of Na in CIGS in as grown device-type films, in Na-free films implanted with Na, and the effects of annealing of these layers.[4] The films were analyzed before and after annealing at 420°C. Na was found to segregate rapidly out of CIGS at normal physical vapor deposition temperatures. No Na diffusion at room temperature was observed in samples after six months. The segregation drives Na both to the surface of polycrystalline layers and into the Mo substrate. The segregation ratio for the CIGS/Mo interface is ~ 10 at 400 °C and

~100 at 600°C. Small Na-rich regions can also occur inside the CIGS layers. In spite of a preference to segregate out of CIGS, Na leads to a strong (112) CIGS preferred orientation and apparently improves the performance of devices.

Preliminary work has begun on the effect of Na on hole transport in single crystals of CIGS. Na was introduced into CIGS epitaxial layers on GaAs by coating the sample surfaces with NaHCO_3 or Na_2Se and annealing under various conditions. The details of the annealing cycle determined the final Na concentration in the CIGS. All Na concentrations were uniform in the CIGS. The results suggest that Na is not a dopant in CIGS but does reduce compensation significantly. Furthermore, dc photoconductivity of the samples was increased. Experiments are currently underway to understand the detailed mechanism by which Na influences CIGS.

Electroluminescence from CIGS Solar Cells

Observations of electroluminescence from forward biased solar cells, begun in 1995 was continued during 1996.[5] This year, studies as a function of temperature and Ga content were initiated. Results obtained to date suggest that at low temperatures a significant fraction of the carriers recombine radiatively. The width of the luminescence is large indicating a range of states contributing to radiative recombination. In some devices, subsets of these states can be resolved as distinct populations with different temperature dependencies, see Fig. 2. The effect of temperature is also different for the radiative recombination process and the carrier generation process responsible for spectral response. This implies that radiative recombination occurs between states near the band edge but does not follow the usual temperature dependence observed for the band edge.

CIS Team Activities

This year we have participated actively in the NREL CIGS Team working on the properties of Mo back contacts for CIGS solar cells. Our responsibility has been primarily SIMS analysis and heat treatment in the presence of Na. In addition to our heat treatments, Mo samples were selenized by two processes at two different industrial laboratories. In addition to these studies, samples produced at Uppsala University in Sweden were analyzed. These latter samples included controlled oxygen additions and some were implanted with Na. Preliminary data indicates that Na does not diffuse in the Mo grains and that Na diffusion in the Mo grain boundaries depends strongly on the oxygen concentration in the thin films.

Conclusions

The results obtained this year have provided details concerning several major effects critical to operation of CuInSe_2 -based solar cells. Characterization of hole concentration, defect states in the energy gap, and mobility of carriers is fundamental to a detailed understanding of the operation of CIGS solar cells. Furthermore, this knowledge is a necessary prerequisite for interpretation of data on important impurities in CIGS such as Na. The preliminary work done this year on the influence of Na in CIGS begins to clarify the detailed mechanism by which Na acts in CIGS devices. The detail of the diffusion of Na in Mo and CIGS layers is critical to this understanding and to control of this impurity during device production. Finally, we have continued to increase our knowledge of the operation of CIGS devices through electroluminescence characterization.

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Figures

Figure 1: SIMS data showing outdiffusion of Ga and an error function curve fit for a near stoichiometric CuInSe₂ epitaxial layer on a GaAs substrate.

Figure 2. Comparison of the electroluminescence (individual data points) and spectral response (solid curves) obtained from an ~14% efficient solar cell fabricated at NREL. The electroluminescence was obtained at 0.1 A/cm² current.

Title: Electronic Processes in Thin Film PV Materials

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Objectives

The major objectives of this subcontract are (1) to identify metastabilities caused by carrier recombination or by frozen-in departures from equilibrium, and to determine if the metastabilities that plague devices are "intrinsic" and therefore not correctable or "extrinsic" and therefore capable of being eliminated in future devices, (2) to characterize the important defects and impurities in the bulk and at surfaces and interfaces because interfaces are becoming more important with the advent of tandem cells with several heterojunctions, and (3) to measure the motion of hydrogen in a-Si:H and related alloys on a microscopic scale because the motion of hydrogen is thought to play an important role in many of the metastable effects that occur in a-Si:H and related alloys and the microscopic mechanism for this motion is not known.

Approaches

Three new approaches, that have not been employed in the past, have been emphasized: (1) below-gap spectroscopy, such as optical absorption, photoluminescence (PL), PL excitation, electron spin resonance and other spectroscopies using primarily a tunable Ti sapphire laser system to excite carriers well below the optical gap (down to ~ 1.1 eV). (2) novel nuclear magnetic resonance (NMR) techniques such as measurements of the spin-lattice relaxation in a dipolar field (T_{1D}), to probe local hydrogen motion in doped and intrinsic a-Si:H and selected alloys. (3) doping with group VI; elements that introduce new metastabilities into a-Si:H and related alloys.

Research Results

The subcontract is divided into several tasks. One task is the growth and characterization of doped and undoped a-Si:H and related alloys. Alloys with small sulfur concentrations have been found to exhibit n-type doping due to the presence of the sulfur.^{1,2} In some cases these dopants are passivated by the presence of hydrogen. The sulfur in a-SiS_x:H alloys is thermally very stable.³ Sulfur does not diffuse out of the films at temperatures below 600 C.³ These results are summarized in Fig. 1. Films of μ c-Si:H, that were grown at different plasma deposition frequencies, have been characterized.⁴ In these films the hydrogen is incorporated in both clustered and dilute phases, just as in a-Si:H, but some of the hydrogen is moving even at 300 K. We have speculated that this motion is due to tunneling or rotating of Si-H₂ groups.⁴

A second task concerns below gap spectroscopy in a-Si:H and related alloys. We have been using Photoluminescence (PL) excitation spectroscopy (PLE), time resolved PL and optically detected magnetic resonance (ODMR) to probe defects which produce absorption below the gap in a-Si:H.⁵ Photoluminescence in a-SiS_x:H has been investigated using optical excitation energies E_x varying from 0.95 to 2.0 eV. These measurements show that, as far as the recombination processes are concerned, they are identical with those observed in intrinsic a-Si:H for sulfur molar fractions less than about 10^{-3} . Above this sulfur concentration the PL exhibits different behavior.

A third task involves studies of local diffusion of hydrogen in a-Si:H using NMR techniques. We measured T_{1D} , the dipolar spin lattice relaxation time, whose inverse (T_{1D}^{-1}) gives a measure of the local motion of hydrogen.⁶ The T_{1D} values for doped and undoped a-Si:H exhibit trends that are similar to the variation of the macroscopic diffusion of hydrogen with respect to various doping levels. Although the details of the local motion are very different from those of the macroscopic diffusion, we have speculated that the local motion either involves rapid, long-range motion of bond centered hydrogen or local tunneling modes at bonded hydrogen sites. The precise interpretation remains unclear.

A fourth task involves the study of interfaces, defects and impurities in a-Si:H and related alloys, including the metastabilities that are related to such interfaces, defects and impurities. The measurement of PL and ESR in nitrogen-rich hydrogenated amorphous silicon nitride (a-SiN_{1.6}:H) films has provided a probe of optically-induced metastabilities in these films.^{7,8} ESR experiments have discovered a new nitrogen-related defect in a-SiN_{1.6}:H. We extracted the signal due to the nitrogen-related center from the overlapping K center by performing experiments at low temperatures (4 K) and high microwave powers. PL detected magnetic resonance (PLDMR) and absorption detected magnetic resonance (ADMR) experiments⁹ have investigated the spin coupling of photo-excited electron-hole pairs in a-Si:H. The PLDMR and ADMR lineshapes are shown in Fig. 2. These results represent the first observation of the $g = 4$ resonance in ADMR.

As mentioned above sulfur acts as an inefficient donor in A-SiS_x:H alloys. There is some evidence that these sulfur doping effects may reduce the degradation in solar cells¹⁰, but final conclusions await further experiments.

Conclusions

Major accomplishments of the previous year include (1) demonstration of the thermal stability of sulfur in a-SiS_x:H alloys, (2) the measurement of various optical processes in a-SiS_x:H using excitation energies well below the optical band gap (down to 0.8 eV), (3) development of models for local motion of hydrogen in doped, compensated and intrinsic a-Si:H, and (4) the observation of a new nitrogen-related defect in a-Si_xN_{1-x}:H alloys, (5) the discovery of inefficient sulfur doping in a-SiS_x:H which can be modified by optical activation of passivated donors and may contribute to better stability of solar cells. Future directions for the research include (1) measurement of local hydrogen motion in hot-wire samples of a-Si:H and (2) further investigations of the metastabilities introduced into a-Si:H by the presence of group VI impurities (sulfur and selenium).

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Fig. 1. Dependence of sulfur-to-silicon S/Si ratios in a-SiS_x:H (x = 0.06) on annealing temperatures, T_a, using ESCA. Circles and triangles are S/Si ratios obtained by S 2p and S 2s_{1/2} peaks, respectively. S/Si ratios of the samples as deposited are plotted at T_a = 0°C.

Fig. 2. The PLDMR (a) and the PADMR (b) spectra as function of magnetic field for a-Si:H at 10 K for magnetic fields up to H = 2000 G. The three resonances are designated A, B and C.

Title: **Electrochemical Fabrication of Dye Sensitized Heterojunctions for Solar Energy Conversion**

Organization: Department of Chemical Engineering, University of Washington,
Seattle WA 98195-1750

Contributors: D. T. Schwartz, principal investigator; and Brian O'Regan

Objectives

The general goal is to demonstrate the feasibility of replacing the liquid layer in dye sensitized photoelectrochemical cells with a solid hole conductor. This is undertaken to solve a potential problem in dye sensitized photoelectrochemical cells and, more generally, to attempt to incorporate the advantages of dye-sensitization of wide band gap semiconductors into the realm of solid-state devices. The specific goal is to show that it is possible to achieve a high quantum efficiency for dye sensitized charge separation at a wide band gap n-p heterojunction where the n-type material is TiO_2 .

Fabrication of Dye Sensitized Heterojunctions

The fabrication of a solid-state device containing dye monolayers sandwiched between two semiconductors requires deposition conditions that do not degrade any previously-formed dye/semiconductor interfaces. The necessity for mild deposition conditions has, so far, ruled out the more common wide-band-gap p-type materials such as GaP and SiC. This constraint on the p-type layer, and the need for transparency, has led us to focus on CuSCN, whose semiconducting properties have been only recently elucidated. CuSCN is a wide band gap, p-type semiconductor whose use in dye sensitization has been pioneered by Tennakone and co-workers.

We have found that CuSCN can be electrodeposited from solution in a manner that does not disturb the dye/ TiO_2 interaction and we have confirmed that CuSCN is a good substrate for dye sensitization in photoelectrochemical cells. Photoelectrochemical measurements have confirmed the p-type nature of the electrodeposited CuSCN under both band gap illumination and dye sensitized conditions. The low work function places the valence band edge at an energy (~ 6 V vs SCE) accessible to hole injection by dyes also suitable for sensitization of TiO_2 . TiO_2 always displays n-type behavior in dye sensitization cells, due to photodoping by injected electrons. These characteristics have allowed the deposition and testing of the TiO_2 /dye/CuSCN dye-sensitized heterojunctions (DSH's) described below.

The deposition steps were as follows. Transparent conductive substrates were cleaned by heating at 450°C for 15 minutes. A thin film ($\sim 50\text{nm}$) of TiO_2 was deposited by spray pyrolysis using $0.2\text{ M Ti(IV)isopropoxide}$ and $0.4\text{ M acetoacetone}$ in ethanol with a substrate temperature of 450°C . Dyes were deposited from ethanol, with the addition of 10^{-3} M HNO_3 in the case of rhodamine dyes. The substrates were placed in the dye solutions while still above 100°C and remained in the solution at least 1 hour. The deposition of CuSCN followed the published procedures^{1,2} except that an initial voltage pulse was necessary to initiate the electrodeposition on the TiO_2 film. Briefly, CuSCN was cathodically electrodeposited from an ethanol solution of $0.1\text{ M CuBF}_4 \cdot x\text{H}_2\text{O}$ ($x \approx 3.5$) and 0.025 M KSCN that had been aged ~ 4 days. Aging improves the homogeneity of the electrodeposited film. A few seconds after immersion of the dyed TiO_2 film, electrodeposition was started with a -400 mV (vs SCE) pulse ($\sim 1\text{ sec.}$) and carried out at -200 mV . The graphite contact was made by pressing graphite powder onto the surface, under an

aluminum foil contact, with a glass slide and clamp. In most cases the active area was $\sim 1 \text{ cm}^2$. All the fabrication steps were carried out in unfiltered laboratory air using solvents and salts as received. Water, up to a few percent, in the electrodeposition solution does not have deleterious effects although deposition from pure water results in a coarser film morphology and DSH's that function poorly.

After deposition of the CuSCN the interface was activated for charge separation by either heating, in the case of the organic dyes, or by exposure to UV light for the ruthenium dyes.

For the quantum efficiency calculations we measured the quantity of dye present at the interface by desorbing the CuSCN and the dye. Desorption of known quantities of dye from high surface area TiO_2 films, and other checks, such as dye stability and lack of adsorption to cuvette surfaces, have shown this method to be accurate despite the small quantity of dye involved.

Results

UV activation

During FY96 we have found that the final heating step previously developed for the Rhodamine DHPE DSHs was not fully effective for DSHs containing ruthenium polypyridyl dyes. We have found that 30 mins of exposure to UV light, at short circuit, brings the ruthenium polypyridyl DSHs from an initial APCE (absorbed photon to current efficiency) for dye-sensitization of 10-20%, up to near 100%. We have found that this effect is caused by the UV excitation of the TiO_2 and the subsequent transfer of a hole across the interface. We believe at this time that the hole transfer results in the oxidation of adsorbed water or of SCN^- . In the case of water, the removal of water from the interface by its oxidation may directly increase the quantum efficiency because the dyes used are known not to function in aqueous electrolyte. On the other hand, the oxidation of SCN^- may give rise to a poly-SCN layer at the interface which may limit the back reaction. Both processes may be occurring simultaneously. The UV activation is increased by positive bias and reduced by negative bias. The enhancement of the dye sensitized photocurrent is transient for low UV exposures but becomes permanent for exposures longer than 30 minutes. The IV characteristics are also affected by the UV illumination. During the first few minutes of UV, the diode characteristics improve. Further UV illumination causes an increase in the dark current and thus results in a decrease in the open circuit potential. The UV activation procedure cannot be used on organic dyes because of photodegradation, however the ruthenium polypyridyl dyes, especially "N3",³ are stable to this treatment.

Photocurrent Generation Efficiency

For the ruthenium dyes tested, if the injection into TiO_2 is efficient in a photoelectrochemical cell, the APCE is also high in the DSH. In each case the action spectra is similar to the absorption spectra of the dye adsorbed on transparent high surface area TiO_2 . A positive deviation of the action spectra at short wavelengths is due to a tail of photocurrent activity that is created during the UV exposure. For N3, the IPCE of the DSH was considerably larger than the absorbance of the dye at the interface. The implied "APCEs" are thus larger than 100%, which will be discussed below. The high value of the APCE for monolayer coverage indicates that none of the loss mechanisms present can compete with charge injection and collection in the external circuit. Specifically, "wrong way" charge transfer, e.g. electron injection into the CuSCN, must be absent or minimal. Also, at zero bias, the recombination of electrons and holes across the interface must be much slower than the escape of the charge carriers into the bulk. The high quantum efficiency shows that it is possible to simultaneously optimize both the dye/n-type and dye/p-type interface for efficient forward charge injection and slow charge recombination in a solid-state device.

Stability

We have exposed one N3 DSH to 2 months of intermittent illumination on an overhead projector. For the first period, illumination was carried out with the entire spectrum of the lamp, which contains some UV. After an initial increase in short circuit current, and decline in open circuit voltage, both the voltage and photocurrent remained stable for approximately one month. After a 1 month storage in the dark, the second illumination period was carried out with only light above 470 nm. Approximately the same decline in voltage occurred showing the voltage drop does not result from holes excited in the TiO_2 . These results show not only that N3 is very stable in this DSH, having undergone 12 million turnovers, but also that the photocurrent is not consuming the CuSCN. The total charge passed, ≥ 200 Coulombs, is enough to consume the 0.25 C of CuSCN present more than 800 times.

Cu(II) Quenching

A concern in using CuSCN as the hole conducting layer in a DSH is the well known ability of Cu(II) to quench the excited state of many dyes. Moreover, Cu(II) binds to the S terminal of a the SCN ligands that are present in many good sensitizing dyes.. This binding occurs immediately when the dye coated TiO_2 films are placed in the Cu(II) containing electrodeposition solution. The binding can easily be detected by a spectral blue shift. For N3 in solution, a 1:1 solution of Cu(II) and dye is enough to cause strong quenching of the luminescence, even at concentrations as low as 10^{-5} M. For another dye which has no SCN ligands, no spectral shift is observed, and no quenching of photocurrent occurs. In addition, the luminescence, although extremely weak, appears not to be quenched by Cu(II) until the concentration exceeds 10^{-4} M

The spectral shift that occurs upon Cu(II) binding can be compared to the spectral shift that occurs between the dye adsorbed on TiO_2 and the action spectrum of the dye incorporated in the DSH; i.e. adsorbed on TiO_2 and covered with CuSCN. The action spectra in the DSH turns out in most cases to be almost identical to dye bound to TiO_2 without Cu(II) binding. Presumably, the bound Cu(II) is reduced to Cu(I) during the electrodeposition of the CuSCN.

High Surface Area Interfaces

The dye-sensitized heterojunctions we have fabricated contain only one planar dye monolayer and thus absorb $<3\%$ of the incident light. Optically dense dye-sensitized devices intended for high light absorption require multiple dye-sensitized interfaces that are stacked in some fashion. This problem has been solved in DSPEC solar cells by the use of a porous, transparent, n-type electrode filled with a transparent liquid electrolyte. The dye monolayers in this case are adsorbed on the internal surface area of the electrode. In this kind of device both the electron-transport and hole-transport materials must be transparent so that photons not absorbed in the first dye layer may be absorbed in the second and so on. We have begun fabricating TiO_2 /dye/CuSCN DSHs with different degrees of interpenetration of the TiO_2 and the CuSCN. For surface roughness up to 10, we have seen increasing photocurrent as the degree of roughness increased. This has been observed on TiO_2 films made from colloids and also by electrodeposition. For much rougher films, a decrease in the photocurrent is seen. At this time our maximum IPCE has been for a colloidal film of approximately 6-8 layers of particles. After 30 minutes of UV exposure at a positive bias of 600 mV, the IPCE stabilized at 8.1% at 480 nm.

Discussion

As mentioned above, the IPCEs for the DSHs are larger than the absorbance of the dye at the interface. Although the currents are small, the similarity of the action spectrum and the absorption spectrum shows that the currents arise from the dye, and not from bulk defects or

surface states of the TiO_2 or CuSCN . The "enhancement factor" for the IPCE in the DSH is reproducible although the factor varies from 1.4 to 2.5 depending on the CuSCN deposition and UV exposure. As the CuSCN films scatter some light, some of the increase can be ascribed to photons back scattered from the CuSCN /air interface. We have made measurements on several identical sensitized films to see if there is sufficient scattered light to account for the larger IPCE. For example, a typical flat TiO_2 film showed a peak photoelectrochemical IPCE of 0.6%, corresponding to a $\geq 90\%$ APCE. When incorporated in a DSH, the same film, sensitized with the same quantity of dye, gave an IPCE of 1.5%; a factor of 2.5 times larger than in the photoelectrochemical cell. The transmission and reflectance, at 490 nm, were 70% and 6% respectively. The SnO_2 film absorbs about 8% at this wavelength, thus only 16% of the light is scattered from or absorbed by the CuSCN . If one assumes no absorption occurs in the CuSCN , then, in order for scattered light to result in a 150% increase in the IPCE, the scattered photons must have a ten times higher chance of being absorbed by the dye than the incident photons. For this to be true, there must be some form of wave guide confining the scattered photons and causing multiple intersections with the TiO_2 / CuSCN surface.

Other possible sources for the increased IPCE exist. One might be that the dye has a much larger peak absorption coefficient at the interface, however the lack of any narrowing in the action spectrum argues strongly against major increases in the absorption coefficient. An intriguing third possibility for the source of the increased current is the phenomena of current doubling. Current doubling at semiconductor electrodes occurs when the product of an oxidation reaction occurring at the electrode is itself sufficiently reducing to inject an electron into the conduction band. Oxidation by photo induced holes in TiO_2 has been reported to give rise to current doubling in, alcohols, propane, CN^- , and others. Current doubling however often results in irreversible electrochemistry. For example the product of CN^- is thought to be CNO^- . The fact that the CuSCN is not consumed, as demonstrated above, indicates that the current doubling, if any, must result in a species which is mobile and can undergo a two electron reduction at the graphite contact. Presumably the hole in CuSCN is some kind of "bipolaron" similar to that found in conductive polymers.

Summary

Our results show that it is not difficult to construct a functioning dye-sensitized solid-state interfaces using inexpensive procedures. The fact that it has been possible to reach quantum efficiencies near unity with relatively impure starting materials shows the advantage of using a "majority carrier" scheme such as dye-sensitization. In FY96 we have extended the range of dyes which we have shown to be capable of sensitizing efficient charge separation at a solid/solid interface. We have shown that the TiO_2 , dye, and CuSCN are at least fairly stable to illumination and photocurrent at open circuit. There is some evidence, not yet compelling in our view, that current doubling may be occurring in these DSHs, which, if true, is probably the first time this effect has been observed in the solid state. Application of these findings to practical devices still requires development of a high surface area architecture for the TiO_2 /Dye/ CuSCN interface.

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Historically Black Colleges and Universities

1994-1995
1995-1996
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1999-2000

Title: Photovoltaic Applications in Developing Countries

Organization: Office of Sponsored Research, Central State University, Wilberforce, Ohio

Contributors: C.W. Fuller, Principal Investigator;
H. Evans, Student Research Associate

Background

The National Renewable Energy Laboratory's Historically Black Colleges and Universities (HBCU) Photovoltaic Associates Program provides undergraduate support for photovoltaic energy research and education at HBCU's. The aim is to attract qualified science, engineering and business students toward pursuing a career in these areas with emphasis in photovoltaic technology. Central State University currently has one student participating in a three year program entitled, "Photovoltaic Applications in Developing Countries".

OBJECTIVES

The Central State University program requires its participant to do the following:

1. Survey literature, participate in seminars and lecture sessions, and review principles regarding photovoltaic applications;
2. Incorporate the testing of interconnected and mutually supporting wind and solar electricity generating systems on the Central State campus;
3. Compare and analyze statistical and performance data of windmill water pumping systems observed and collected by Central State University in the Louga and Thies Regions of Senegal;
4. Observe and analyze environmental and mechanical data from renewable energy products already constructed in Senegal by Central State University as part of the Northern Senegal Water Management Project;
5. Compare and analyze statistical and performance data of photovoltaic systems emplaced by World Vision international in Senegal, of which the expected results will indicate the marketing realities and the sustainability of photovoltaic energy systems in Senegal.
6. Participate with Central State University, FOPEN-Solaire and World Vision International in the installation of photovoltaic systems in Senegal and Mauritania, by which this experience will give the student a real-world experience regarding photovoltaic applications in Developing Countries and present the challenges of marketing photovoltaic materials in West Africa, particularly batteries, regulators and solar panels;
7. Write a detailed trip report regarding a four to six week overseas training experience in West Africa.

Approach

Mr. Evans has been a former student participant in the Central State University directed "Northern Senegal Water Management Project" in Senegal, West Africa. This natural resources project is designed to develop self-sufficiency among Senegalese villagers by providing them with the expertise and materiel to install and maintain their own windmill water pumping systems. While under the sponsorship of the NREL scholarship program, Mr. Evans has focused his research on ways in which photovoltaics can provide new and supplemental energy sources to address the critical shortage of water in many Developing Countries. Mr. Evans completed the first year of his research associates program by traveling to Senegal, West Africa during March and April, 1996 for the purpose of continuing his research and to practically apply the photovoltaic principles he studied in the United States. As he has only completed the first year of a three year program, Evans' results are preliminary and are not yet complete.

RESULTS OF TRAINING/RESEARCH PLAN, SENEGAL/MAURITANIA

Mr. Evans research in Senegal and Mauritania was reinforced by combining the advantages of Central State University ongoing projects with training/research arrangements with experienced, local NGO's (non-governmental organizations). The purpose of this arrangement was to take advantage of the experience in renewable energy and photovoltaics already known in West Africa by CSU and local organizations. Mr. Evans basic training/research plan overseas consisted of the following:

- Week One: Renewable energy and photovoltaic Interface with World Vision International and the Northern Senegal Water Management Project, Thies and Louga Regions, Northern Senegal.
- Week Two: Photovoltaic principles and hands-on photovoltaic construction activities in small villages with FOPEN-Solaire, Dakar Region, Senegal.
- Week Three: Photovoltaic fabrication, marketing, and development activities with small businesses, Nouakchott, Mauritania.
- Week Four: Interaction with governmental research institutions and foreign investment firms, Dakar Region, Senegal.
- Week Five: FOPEN-Solaire photovoltaic marketing and system construction, Casamance Region, Southern Senegal until departure.

(1). Background, Central State University Technology Transfer and Language Training Program in West Africa.

Since July 1991, Central State University (CSU) has been conducting a water management and development program in West Africa to address critical shortages of safe drinking water. The primary project (designated the **NORTHERN SENEGAL WATER MANAGEMENT PROJECT**) is a pilot project designed to develop self-sufficiency among Senegalese villagers by providing them with the expertise and materiel to install and maintain their own windmill water pumping systems. The project links Central State University and an Ohio manufacturer with the U.S. Agency for International Development, World Vision International, and the government and people of Senegal.

A parallel and supporting project simultaneously managed by Central State is a three year program from the U.S. Department of Education, Fund for the Improvement of Post-Secondary Education (FIPSE). The project (called the **FOREIGN LANGUAGE/AREA STUDIES ENHANCEMENT PROJECT**) began in 1992 and supports an experience-centered, cooperative education program that gives students on-site training in language, culture, and technology. The main thrust of this program is to increase the knowledge of Central State University students and faculty regarding the language, culture, history and economics of selected West African countries through a project of personal interaction in overseas work-study projects - particularly in Senegal. French and Wolof language and culture training is achieved through a combination of in-country and overseas classroom instruction that culminates in the practical application of language skills by participation in a major developmental project with a common goal of improving the health and agricultural production of the region.

During the initial phases of the joint projects, more than twenty-six (26) rural villages directly benefited from the program. New boreholes, new windmills, and new water storage and water distribution systems were installed in ten (10) of the rural villages. Sixteen (16) additional villages saw their old and broken windmill facilities and wells improved and made functional again. In each of the villages, local technicians were provided with maintenance tools and were trained in the proper methods to repair and maintain the new facilities.

Hakim Evans research in photovoltaics was developed as a parallel and reinforcing effort to these two programs.

(2). Interface of the West Africa Program with the HBCU Photovoltaic Research Associates Program.

CENTRAL STATE--The Central State staff/faculty and student technical teams are responsible for coordinating the construction and rehabilitation activities of the project and are instrumental in training local Senegalese technicians in the operation, maintenance, and repair of each of the water supply systems. It has given the participants a broad exposure to renewable energy systems. Central State students selected to participate primarily include majors from the Departments of Water Resources Management, Manufacturing Engineering, and Foreign Languages, while other departments are selectively represented. Students are expected to gain valuable, hands-on technical experience and an increased proficiency in the Wolof language by actively recording and evaluating windmill performance measures and assessing the viability of water councils in selected villages. As a previous project participant, Hakim Evans interacted with other students to seek additional information related to his 1996 photovoltaic research objectives overseas.

WORLD VISION/SENEGAL- World Vision/Senegal, an internationally known voluntary organization serving developing nations for more than 50 years, is the primary partner affiliated with health and agricultural issues and the borehole drilling operations in the countryside. World Vision/Senegal has extensive experience in photovoltaics and provides lighting system resources for several villages in the northern/central region. In addition to being involved with Central State in the overseas component of the Photovoltaic Research Associates Program, World Vision maintains and stocks replacement parts to insure continuous water and light service in many rural villages.

FOPEN-SOLAIRE- FOPEN-Solaire is a federation of eleven rural associations in West Africa that are based in 6 of the 11 regions of Senegal. As operating partners of the Senegal-German Solar Photovoltaic Energy project, these associations have carried out since the promotion, installation and maintenance of over 1,500 solar lighting systems throughout Senegal since 1989. FOPEN-Solaire has a well equipped workshop, a trained team of at least two solar energy technicians, an assortment of tools for its technical team, a solar lighting system to test malfunctioning components, and a mobile solar lighting system for demonstrations during village commercialization sessions. FOPEN-Solaire is instrumental in the research and training for Hakim Evans as part of the overseas component of the HBCU Photovoltaic Research Associates Program.

The outcome of Mr. Evans research will be reported at the end of next period, when he focuses on incorporating the testing of interconnected and mutually supporting wind and solar energy electrical generating systems based on his overseas experience. A hybrid wind and solar energy facility has been constructed on campus for use in the study of system capabilities.

Title: **An Assessment of the Operation of Photovoltaic Devices for Solar Energy Applications**

Organization: **Research Center for Science and Technology and Department of Physics, Clark Atlanta University, Atlanta, Georgia**

Contributors: **G. W. Grams, principal investigator; L. J. Lewis; D. Raubenheimer (Vista University, Port Elizabeth, South Africa)**

Objectives

The primary goal of this project is to determine the effects of atmospheric variability on the production of solar energy by photovoltaic sources. A combination of solar radiation measurements, meteorological observations, and computer modeling work will be used to carry out an assessment of the efficiency of operation of photovoltaic modules under different atmospheric conditions.

A secondary goal of this project is to promote the use of photovoltaic technology to provide electric power to remote areas in developing countries. The research is thereby being carried out as a joint effort involving Clark Atlanta University and Vista University in Port Elizabeth, South Africa.

Approach

This project will emphasize the need to improve our understanding of how the atmosphere affects the performance of solar energy systems. In particular, changes in atmospheric variables such as cloud cover, water vapor content, and/or aerosol loading can affect the proportion of direct and diffuse radiation reaching the earth's surface. Our solar radiation measurements are based on the use of a relatively small, rugged, self-powered, stand-alone solar monitoring instrument manufactured by Ascension Technology, Inc., of Lincoln Center, Massachusetts. The Ascension Technology rotating shadowband pyranometer (RSP) measures total horizontal, direct normal and diffuse horizontal irradiance by analysis of data obtained by rotating a shadowband once per minute over a single light sensor. The system includes the RSP head, an air temperature sensor, a Campbell Scientific datalogger with 1200 baud telephone modem, a photovoltaic power supply, instrument enclosure, and software to control the RSP and determine the global, direct, and diffuse irradiance. This single instrument replaces the solar tracker, pyrheliometer, and pyranometer used to obtain the same measurements with conventional radiation monitoring systems.

We had the instrument modified by the manufacturer so that simultaneous meteorological data such as wind speed, atmospheric pressure, temperature, and relative humidity could be digitized and recorded by the multi-purpose datalogger already included as part of the standard RSP system. Additional sensors were provided with the RSP to measure and record watt-hour meter pulses and transducer outputs for watts, volt-amperes, and current from an operational PV

system. The data set obtained with the modified RSP instrument thereby allows comparisons between the *measured* and *estimated* efficiency and hourly output of an operational PV system.

Our joint research project involves the operation of identical versions of the modified RSP instrument by both Vista University and Clark Atlanta University. One instrument would be installed and operated on the platform for an Atmospheric Optics Observatory located on the rooftop of the Research Center for Science and Technology at CAU. The platform was originally constructed as the base for a Brewer ultraviolet spectrometer operated as part of the Environmental Protection Agency's National UV Monitoring Network. The platform was designed to be large enough to accommodate a complete set of instruments for monitoring UV, visible, and infrared radiation at our location. Figure 1 shows a photograph of the platform as it was being installed in Spring 1996 for operation of the UV spectrometer. The RSP instrument provided by this project provides an ability to monitor visible radiation at the site. The CAU investigators will use the observations made at the Atmospheric Optics Observatory, including the RSP data and supporting data from the meteorological sensors, to evaluate the performance of the RSP instrument under a wide variety of atmospheric conditions. This will be used to evaluate the overall accuracy of the instrument itself. On the other hand, Vista University will use their instrument to monitor the solar insolation as a function of time of day at representative locations in South Africa. In future years, it might be possible to acquire other instruments and establish a network of solar monitoring sites throughout Southern Africa. Vista University's work will complement that of Clark Atlanta University in that Vista's effort will be directed toward the application of knowledge developed under this program to the South African atmosphere and its effects on PV system performance.

Results

The RSP instrument modifications to add the meteorological sensors and the sensors for monitoring the performance of operational PV systems were carried out by the manufacturer during the first six months of this year. One instrument was completed and shipped to Vista University in July 1996. The other instrument was received at CAU in August 1996. Figure 2 shows a photograph of the RSP instrument mounted on the Atmospheric Optics Observatory platform.

At the present time, the RSP systems have been installed and are being used to collect data on the solar irradiance and meteorological parameters at both the CAU and the Vista University sites. Figure 2 shows a photograph of the RSP instrument mounted on the instrument platform at our Atmospheric Optics Observatory. Examples of data obtained with the modified RSP instrument are available. Figure 3 shows the solar radiation data at the CAU site for the week of December 8, 1996. Data are recorded and plotted as 15-minute average values of the total horizontal irradiance (W/m^2) as measured with the RSP instrument. Figures 4, 5, and 6 show values of the atmospheric pressure, temperature, and relative humidity for the same time period. The irregular fluctuations of the solar irradiance on day 1 and days 4, 5, and 6 are associated with clouds. The smooth curves for the solar radiation data displayed in Figure 3 for Days 2, 3, and 7 represent data taken with the clear, cloudless skies associated with high pressure conditions.

Figure 1: Installation of platform for Atmospheric Optics Observatory.

Figure 2: Photograph of rotating shadowband radiometer.

Radiation and Meteorological Parameters for Week of December 8, 1996

Figure 3: Total horizontal radiation (W/m^2)

Figure 5: Atmospheric Temperature ($^{\circ}\text{C}$)

Figure 4: Atmospheric Pressure (mbar)

Figure 6: Relative Humidity (percent)

Title: HBCU Photovoltaics Associates Program

Organization: Department of Physics
Clark Atlanta University
Atlanta, Georgia

Project 1: Deposition of Protective Films on Photovoltaic Cells

Contributors: C. A. Papageorgopolous (principal investigator), J. Collins*, K. Goodman*, and L. Richardson*, Adero Corner, and D. Mosby

Objectives

The general goals of the project are to study the mechanisms and surfaces that lead to passivation and metallization of semiconductor surfaces. Our interest is in silicon and III - V (GaAs, InP) compound semiconductor surfaces. These semiconductors, besides their potentially wide use in high speed electronics and long wavelength optical circuits (optoelectronics), have demonstrated great value as solar cells.

Approach

To prevent damage to the surfaces of PV devices without reducing their efficiency, the above semiconductors are covered by protective thin films. This is done by depositing the protective films (dielectric window layers), such as chalcogenides: sulfur, selenium and their compounds gallium sulfide, indium sulfide, etc. In-situ analysis of the initial stages of the interface formation in ultra-high vacuum (UHV) is necessary for the understanding and subsequent improvement of the deposition process. Thus we will start with the deposition of elemental sulfur and selenium on silicon (100)2x1 in UHV. Coadsorption of alkalis with chalcogenides on the above will take place to study the mutual influence on the adsorption process and electronic structure of the adsorbates. Subsequently, we will continue with the deposition of cubic GaS and tetragonal InS on GaAs and InP, respectively.

Results

All NREL Photovoltaic Associates were made aware of all of the goals of the program. Although each of the three associates were assigned to a specific project in the original proposal (as required), it was deemed appropriate that all associates should obtain a fundamental understanding of both projects. To accomplish this, the students were

assigned reading materials involving all areas of the projects. During this year, the students concentrated on project 1. Each student chose or was assigned a particular analysis technique [UHV, Auger Electron Spectroscopy (AES), work function analysis (WF), scanning tunneling microscopy (STM), quadruple mass spectrometry (QMS)] for in-depth study. The students assisted in the acquisition of data by two graduate students (Adero Corner and D. Mosby) doing work on their Master theses. Twice weekly meeting of the CAU PV Group took place where progress and concerns were discussed. Students were required to make presentations to the group concerning some aspect of the project to help hone presentation skills as well as to communicate findings. Students were exposed to NREL PV Program materials to come up to speed on issues, resources, and people concerned with PV technology. They were also required to use the internet for both email and literature searches. Prof. C. Papageorgopolous left CAU in January to return to Greece for the semester and returned during the summer. However, he will not remain at the University during the Fall 1996 semester.

Summary

The PV Associates increased their basic understanding of analysis techniques for studying surfaces and interfaces and the necessary skills needed to do research in this area. Two of the Associates were also enrolled in the course Phy 422 Undergraduate Research where they received credit for work on this project.

Project 2: Atmospheric Variations and Their Effects on the Operation of Photovoltaic Devices.

Contributors: L. J. Lewis (principal investigator), G. W. Grams (principal investigator), J. Collins*, K. Goodman*, and L. Richardson*, O. Gibson, and K. Ingram

Objectives

The overall goals of this project are to carry out a study of the effect of variations in atmospheric parameters such as changes in humidity and changes in the direct and diffuse radiation caused by changes in aerosol loading on the operation and performance of sensors that incorporate photovoltaic devices. A further goal is to improve our understanding of how the atmosphere affects the performance of solar energy systems. In particular, changes in cloud cover and/or aerosol loading will affect the proportion of direct and diffuse radiation reaching the earth's surface. A final goal is to initiate a study of the effects of changes in the atmospheric radiation field on the performance of systems that make use of photovoltaic devices in solar panels or solar concentrators.

Approach

Two students are assigned to this project. One will work on the effects of the atmosphere on the accuracy of solar radiation monitors that incorporate photovoltaic sensors. The other student will work on the effects of the atmosphere on the performance of solar panels or solar concentrators used in solar energy systems. Each student would begin with literature surveys of his/her topic in the first year. This would be followed by the development of computer models to make predictions regarding their respective areas. In the final year, experimental verification of their predictions would be carried out using facilities at CAU or elsewhere.

Results

All NREL Photovoltaic Associates were made aware of all of the goals of the program. Although each of the three associates were assigned to a specific project in the original proposal (as required), it was deemed appropriate that all associates should obtain a fundamental understanding of all the projects. To accomplish this, the students were assigned reading materials involving all areas of the projects. During the year, the students concentrated on project 1. Twice weekly meeting of the CAU PV Group took place where progress and concerns were discussed. Students were required to make presentations to the group concerning some aspect of the project to help hone presentation skills as well as to communicate findings. Students were exposed to NREL PV Program materials to continue to come up to speed on issues, resources, and people concerned with PV technology. They were also required to use the internet for both email and literature searches. Two additional students (O. Gibson and K. Ingram) were involved with the project during the Spring 1996 semester by enrolling in the course Phy 422 Undergraduate Research. Topics related to solar radiation and its measurement were discussed in the twice weekly meetings. They were exposed to simple devices that teach and lead to an understanding of sun - earth relationships and the tracking of the sun. These relationships are vital for an understanding of solar radiation measurement, data, and utilization by PV devices. We acquired a solar radiation (radiative transfer) model which uses GOES satellite data to calculate ground fluxes. The model was retrieved over the internet. We are familiarizing ourselves with the model and learning how to input data and change parameters. The PV Group continues to collect UVB data using a handheld monitor. Some data is shown in Figure 1. PV associates assisted in the planning of the CAU Solar Radiation and Atmospheric Optics Observatory being established on the roof of the Research Center for Science and Technology.

Summary

The PV Associates increased their fundamental understanding of solar radiation basics including sun-earth relationships and how to track the sun. New skills were acquired in the use of the internet and a new solar radiation model was acquired for use. They became familiar with the standard solar energy literature such as Solar Energy, Solar Today, Sun World as well as more technical journals. Two of the Associates were also enrolled in Phy 422 Undergraduate Research where they received credit for work on this project. Failure to allocate a portion of the funds for travel prevented us from attending some interesting conferences, e.g., Solar 96 in Ashville, NC.

Figure 1. Solar UVB Radiation Index vs. Day of the Month for Atlanta, Georgia taken at Clark Atlanta University

PV Applications in Building Design

Department of Architecture
Hampton University
Hampton, Virginia 23668

Sallie A. Hood, Ronald Sakal, Norma Sellman - Faculty Investigators
Natalie Bunkley, Santora McKinney, Toren Williams - Student Researchers

At the end of the first year of our subcontract, the three student researcher-designers are continuing their studies of PV technology, and all three have begun investigations of PV applications in their individual building designs. At the same time, the three student researchers are also serving as role models to younger students in the Architecture Department. NREL's support is enabling us to include PV technology in the broader curriculum. The Faculty Investigators are now introducing photovoltaics in all their second-year classes: Design Studio (see sketches below), Building Systems, and The Physical Environment.

Next semester, each of the three student researchers will complete a fully developed building design incorporating PV technology. The entire second-year design studio will further investigate photovoltaic applications in urban design and renovation, campus planning, and housing design projects.

Thomas O'Neal

Bryan Thomas

Brandi Stevenson

Amanda Pillo

Melanie Archer

Second-year students in Hampton University's architecture program are now investigating building-integrated photovoltaics in their designs for a small campus art gallery and sundial-stair tower.

Jamal Wells

Charles Woods

Leshelle Morton

Reuben Hameed

Synfoni Bailey-Green

Melvin Mitchell

Explorations of Building-Integrated Photovoltaics

Department of Architecture
Hampton University
Hampton, Virginia 23668

Toren Williams - Student Researcher

In today's revitalization of urban communities, there are numerous opportunities to introduce photovoltaics into public spaces. Fountains, seating areas, and even bus stops can be creatively enhanced and powered by photovoltaic arrays. When implemented, such designs will introduce the public to new ways of generating power and also serve as energy conservation marketing tools for the future.

I am currently working on my thesis project -- an investigation of photovoltaic technology and its application to the design of my proposed John Biggers Museum of African American and American Indian Art for the Hampton University campus. My design, scheduled for completion in May 1997, responds to the existing physical context, allows for easy access to the building, and provides for a maximum south face exposure to capitalize on the sun's energy. Next semester I will continue implementing the ideas and information from my photovoltaic research to produce a creative, energy-efficient design that responds to the environment in an aesthetically pleasing and responsible manner.

Applications of Building-Integrated Photovoltaics for Hampton University

Department of Architecture
Hampton University
Hampton, Virginia 23668

Santora McKinney - Student Researcher

Introducing photovoltaics at a more human and intimate scale could greatly increase the public's awareness of this technology. In the conceptual design of the gazebo (below), a PV array is used to provide power for illuminating the gazebo at night and also to provide power for small electronic devices. When carrying this concept a step further, one can begin to see other creative uses for PV technology in everyday objects. For example, in the conceptual design of the public clock (right), PV modules are used as sculptural elements. These sculptural elements are both aesthetic and functional -- enhancing the architectural landscape while providing power for a variety of exterior amenities. Employed in this manner, photovoltaics greatly advance their own cause in the public eye. As I continue my study of photovoltaics, I plan to explore still more ways to creatively incorporate PV technology into our everyday environment.

**Applications of Building-Integrated
Photovoltaics for Hampton University's
Fine and Performing Arts Building**

Department of Architecture
Hampton University
Hampton, Virginia 23668

Natalie Bunkley - Student Researcher

The objective of this project is to design a new building for the School of Fine and Performing Arts at Hampton University, integrating PV arrays so they and the building compliment each other technically and aesthetically. Next semester, with continuing research, I will refine and enhance this design as I further investigate options for panel size, arrangement, and solar orientation.

The challenge of this project was to apply PV technology -- specifically the 1600 Power Wall by Kawneer Company, Inc. -- to optimize solar energy on a site which receives moderate sun in the winter, and at the same time to create a building in harmony with Hampton's historic and eclectic campus. Passive solar design is maximized to enhance the effectiveness of the PV technology. The building has a south orientation with a curvilinear form to follow the sun's path, thus enabling the arrays to receive maximum exposure. Aesthetically, the building's form announces its function as the center for fine and performing arts. The rectilinear panels are arranged to both compliment and contrast with the curvilinear form of the building, creating a more dynamic elevation.

HISTORICALLY BLACK COLLEGE and UNIVERSITY PHOTOVOLTAIC (PV) ASSOCIATES PROGRAM

MISSISSIPPI VALLEY STATE UNIVERSITY
Department of Natural Sciences and Environmental Health
14000 Hwy 82W, Itta Bena, MS 38941.

B.S.Balam, Director; T.P.Pillai, Principal Investigator.

Objectives

The major objectives are: (1) to expose to and involve minority students to Photovoltaic (PV) energy as the energy of the future (2) to train them to acquire in-depth knowledge of the fundamental scientific principles, technology of manufacturing, and operation of PV cells and panels, to produce energy on a smaller scale to suit individual or special needs [1-3] and that on a large scale [4-5] to supply like a public utility system (3) cost effectiveness of use of PV at present and in future (4) to disseminate the knowledge to public through seminars and community outreach programs.

Approach

Three highly motivated and potentially qualified science majors were selected, based on their interest and future career objectives. These individuals were required to take all fundamental science courses and then do literature search to have an in-depth knowledge of PV fundamentals and technology. Individual students made their literature search from various sources - books, publications [6-7] and Internet. Discussions have been carried out five hours, every week. Group discussions were conducted to strengthen the understanding and review the findings. Group discussions were targeted to learn (a) quantum mechanical principles of photo-electric phenomenon with satisfactory explanations (b) enumerating PV materials and chemicals and their efficiencies to produce electricity (c) stability, reliability and cost effective approach to production and use of PV panels. Since the participating students had a little difficulty to understand the quantum mechanical approach to the problem of photo-electric effect the discussion is limited to the basics only. A study and tabulation of most PV materials was made for their effectiveness to stability, reliability and cost effectiveness and usefulness. Three seminars were conducted on PV studies. The topics were "Our energy problem and solution from PV technology", "Unlimited source and Pollution free Energy", and "Energy of the new Millennium" [8].

Results

While the energy related problems of the future are real, ordinary citizens can not solve these problems unless they are given clear directions by the Scientists and Technologists, to alternate sources of energies, followed by manufacturers to meet the demands of the alternate sources of energy. Presently, the PV technology is a clear means and direction for the future demands of alternate, pollution free energy. Manufacturers are producing at a rate of the present

demands although in the near future the demand will increase at a faster rate. Technology is always ahead of the comprehension of the ordinary citizens; this is especially true for the Black-American communities of the Mississippi Delta which Mississippi Valley State University (MVSU) primarily serves. Hence a special approach and effort must be made to expose the relatively new PV technology to minority citizens. The approach to the problem at MVSU is just doing this purpose.

Our next phase of the work is to initiate hands-on experiments with PV materials and to study their reliability, stability, and efficiency during Spring and Fall of 1997. Silicon and non-Silicon based PV panels will be investigated.

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Title: Study of Development and Utilization of Photovoltaic Materials

Organization: Southern University
Baton Rouge, LA 70813

Contributors: P.K. Bhattacharya and Rambabu Bobba

This research report is being submitted following our work conducted at NREL and Southern University. The research review report covers the research work carried out for the period of May 15, 1996 to May 15, 1997. The research summer internship of Ms Tameka Page with Dr. McMahan and Ms. Danisha Williams with Dr. Bob McConnell was successfully completed at NREL and both the students submitted a detailed report of working on two different problems at the advanced facilities they were working with. Now they are close to graduation from Southern University and some of them have disconnected themselves from the program due to load of work. Ms Danisha Williams dropped out in October and had to be replaced by Mr. Tam Thai who had been keen to work with and devoted a lot of time and effort, but is graduating. He has solved all existing problems of completion of configuration of LABVIEW 4.0 for process monitoring and control software and has hooked it up to our Diffusion and Thermal annealing Furnaces.

We have also installed and tested an ultrasonic surface cleaning system within a separate hood including a hepa filter system. This was bought from Title III money. We have installed and tested an a headway spinner capable of spinning up to 6" Si wafers, on the

patterning side. One reactive etching front we are still struggling to repair a Tegal 701 plasma etcher and have at present got stuck with testing leaks in the MFCs. The Turbo V70 dry pumping station was obtained from Title III funding. we have tested its uniformity and flexibility of spinning various photo-sensitive organic materials including polyimides. A big miscellaneous hood for the purpose was borrowed from the Physics department moved and installed in the J. B. Moore Hall with proper exhaust system, at a cost of \$ 3,000.00 paid as a sponsored grant buy Motorola.

The experiments conducted were basically aimed at calibration experiments for study of all the hardware and research experiments on annealing of MOSFET devices fabricated using 1.0 μm design rule. Since MOSFET devices were characterized to study radiation exposure studies of synchrotron radiation lithographic processing, annealing was an important process to study with all its interdependencies to various process parameters. We presented a paper in ASEE (GSW) Conference entitled, " I-V Characterization of Gate Oxides by Studies of X-ray Induced Defect Distribution in IGFETs", held from March 23rd to March 25th 1997 in Houston Texas. We also attended an EFAD conferences and interacted with all the attendees in doing strategic planning of our future work.

We have also presented a paper in a SPIE Sensor Fusion Conference on , " Primary Response of High Aspect Ratio Thermoresistive Sensors" held in Orlando, Florida from April 22nd to 25th, 1997. Dr. P. K. Bhattacharya visited Cleveland, Ohio to talk to

NASA and other Allied Companies working with NASA to investigate the role of micromachining of polyimides and study of polymer metal composite, and participated in their HITEMP Conference. The aim of this trip supported by SEA - CAMD project was to discover new materials for aerospace applications. Focus was on high temperature metal matrix composites (MMC), polymers and polymer matrix composites (PMC). Since my work is related to polymers being close to the Center of Advanced Microstructure and Devices, a DOE established 20 million dollar Synchrotron Facility, and especially high temperature treatment of polyimides, it was interesting to see the usage of high temperature polyimides. Our interest is due mainly investigate the usage good conducting polyimides which are useful for renewable energy sources in aerospace applications. Microfabrication of circuits on the HITEMP polyimides is another application of great importance in modern aviation industry.

On the average about four Afro-American students get trained on the new equipment that gets set up in the microelectronics laboratory. This year these students were: Mr. Robert Osborne, Ms. Tiffany Monroe, Mr. Derrick Bell and Mr. Pham Luan. Mr. Tam Thai (NREL Scholar) has already got two offers from HARRIS and Texas Instruments, respectively. Other students have got offers ranging from \$36,000- 46,000 to join companies such as Delco, Hughes, Texas Instruments and Harris Semiconductors etc.

Title: Discovering Solar Energy at TSU

Organization: Department of Technology, School of Technology, Texas Southern University (TSU) Houston, Texas

Contributors: Dr. Joshua Hill, principal investigator and student Oral LaFleur, PV Research Associate

Objectives

To present the contributions that Texas Southern University has made to ultimately strengthen the research and education capabilities of HBCU's in photovoltaic (PV), enlarge the scientific and technical knowledge and resource base in PV technology and attempt to develop through a hands-on approach, highly qualified scientific and technical personnel to meet current and future national needs in PV.

Approach

There is a great need for the development of energy efficiency and renewables in America . Involving our youths at the high school level by teaching them the value of solar energy and the contribution it can make toward keeping our environment safe, is one goal of the photovoltaic program in the School of Technology. The development of a photovoltaic demonstration and testing lab is in progress. Data generated from photovoltaic applications will be used in programs designed to educate students and the public on solar energy.

The School of Technology participated in a PV training project in South Africa and also assisted with the successful functioning of South Africa's program, Renewable Energy for South Africa (REFSA) during the summer of 1996. The School's involvement in the development and implementation of the Rural Electrification program in South Africa which includes electrifying 16,000 schools with PV systems, will greatly advance the PV industry in South Africa. TSU's participation is the result of a NREL-sponsored collaboration with Port Elizabeth Technikon in South Africa , for the further development of their PV program.

Solar Energy and America

Solar energy is a term used to identify a broad range of energy forms which are classified as renewable energy. The sun's energy profoundly affects the world's wind patterns, causes ocean water to evaporate as part of the hydrologic cycle, and is essential for plant growth. The winds may be used to turn windmills; the hydrologic cycle makes Hydroelectric Power possible; and vegetation, which grows in the presence of sunlight, may be burned directly--for instance, as wood in a stove or fireplace--or processed into fuels, such as the fermentation of grain to produce ethyl alcohol, which can be used alone or mixed with gasoline to power an internal-combustion engine. Solar energy also makes it possible to harness Ocean Thermal Energy, which uses the temperature difference between sun-warmed surface water and cold water from the ocean depths to produce power. Although all of these indirect means of using energy from the sun are considered solar technologies, the term solar energy most commonly refers to direct use of the sun's energy: by means of photovoltaic Solar Cells, which convert sunlight into electricity.

Texas Southern University subscribes to the concept of solar energy development, by which America and other nations seek to meet current energy, economic, and environmental needs.

America needs solar energy to help U.S. industry contain costs. By the end of this decade, U.S. industries will be spending nearly \$200 billion each year to control pollution.

America needs solar energy to help ensure our national security. Today, we import more oil than any other time in the nation's history. Oil imports contributed \$50 billion to the U.S. trade deficit in 1993, and leave our economy vulnerable to increases in oil prices.

America needs solar energy to eliminate money wasted on health care. American families spend \$50 billion each year on health care as a direct result of air pollution. The elderly are vulnerable to hypothermia and malnutrition due to budget cuts in home energy assistance programs.

America needs solar energy to compete in the global economy. By the year 2000, the world market for environmental technologies will reach billions annually.

Therefore, Texas Southern University understands that the opportunities for new global markets in both energy supply and energy demand technologies in the coming years is staggering. These challenges present opportunities to create an educational bridge for a future labor force to new markets.

School of Technology Summer Program (REEP)

In 1995, Texas Southern University entered into an agreement with the National Renewable Energy Laboratory as part of their Historically Black Colleges and Universities (HBCU) Photovoltaic (PV) Associates Program. Since then, the School of Technology at TSU has taken to the sun.

At TSU's School of Technology, we have made strong efforts to put our mark of contribution on the solar industry. The first of our effort was achieved this summer when TSU hosted fifty high school juniors and seniors from around the state of Texas. The program was called REEP or Renewable Energy & Environmental Protection. REEP came about as a way for the University to introduce its program in energy conservation, environmental protection and renewable energy (with improved access to science and technology) to inner city youths who are otherwise less likely to gain exposure to renewable energy and environmental studies as a career.

Results of REEP:

- 82% of the students felt that the summer institute presented a challenge.
- 97% said that their awareness of the need for more education and experimentation in solar energy and other renewables were increased.
- 95% saw the field trips very appropriate for the course outline.
- 80% of the students rated the quality of teaching they received as excellent or good and 16% noted it fair.
- 80% rated the lab activities were excellent or good and 16% rated them fair.

The program gained support from some of our major industries such as the Energy Conservation Office of Texas, Houston Lighting & Power, Houston Industries Incorporated, the Electric Power Research Institute (EPRI), Sandia National Laboratories, NASA and the National Renewable Energy Laboratory (NREL). The involvement of these companies and the young men and women in our society is the first giant step toward the development of solar energy in the School of Technology.

Photovoltaic Demonstration & Experimentation Laboratory:

The goals of this project are to: (1) demonstrate the technical potential of using commercially available photovoltaic equipment to generate electric power for off-grid applications in the small commercial sector. (2) evaluate issues such as the use of low-voltage appliances versus standard voltage appliances with an AC-DC inverter and the related battery requirement for each.

The project will install two 2-kW photovoltaic systems at the School of Technology's main building with an adjacent room / lab to house the project's monitoring equipment and appliances

The first 2-kW system will be converted to 120 volts AC in an approximately 2000-W peak battery output delivery system. This system will test the applications of commercially available, standard voltage equipment and appliances. Equipment will include 120-volt florescent lighting, a refrigerator / freezer with manual defrost, a small color TV (about 13 in.) a radio, and a clothes washer.

The second 2-kW system will supply power at low voltages of 12 to 24 volts DC in an approximately 2000-W peak battery delivery system. This system will test the low voltage DC (typically 12 volt) florescent lighting, a refrigerator / freezer with manual defrost, a small color TV (about 13 in.), a radio, and a clothes washer (if available).

The project will also install a 1-kW photovoltaic system that will have the flexibility to supply power at either low-voltage dc or switch to 120-volt ac. This system will also be installed on campus, in a garage apartment / lab located adjacent to the University's Mickey Leland Center on World Hunger. The photovoltaic modules and batteries of this system will be configured so that the power can be split to test two applications simultaneously. This system, will test the application of commercially available small-type appliances for commercial sector applications, such as a medical-type refrigerator, individual water-pumping system, and stand-alone outdoor lighting and/or an emergency call box. The end-user will equipment will be primarily low-voltage dc, typically 12 volt.

The School of Technology is developing this project in partnership with Houston Lighting & Power (HL&P). The TSU campus is near the HL&P headquarters building and will provide the utility company a convenient place to show customers and employees a working photovoltaic system. On the other hand, the School of Technology will be educating its students and the community on the contributions they can make to society by becoming educated in this technology.

TSU & Solar Energy; an International Perspective:

These writers were sponsored by NREL this past summer on behalf of TSU School of Technology to travel to Port Elizabeth, South Africa to participate in a training project in South Africa and also assist in the successful functioning of South Africa's solar project called Renewable Energy for South Africa (REFSA). Additionally, the TSU team was impressed in P.E. Technikon's program to train majority South African contractors to install and maintain PV systems.

These interactions and processes have enabled the Port Elizabeth Technikon (PE Technikon) and Texas Southern University's School of Technology to work collectively in improving the PV training program. For example, this past summer exchange and field exploration in South Africa highlighted a need for end-user training, PV water purification and pumping and the development of installation standards, in addition to the enhancement of the current contractor PV training program. PE Technikon has been conducting this type training program in conjunction with ESKOM for the past year. This training program is gaining a wide reputation in South African rural communities. So, it is expected that this collaboration between TSU and the PE Technikon will become a model for transferring and distributing

appropriate technology.

This opportunity for TSU to interact with the PE Technikon's training staff this summer provided a tremendous advantage in the development of our own PV program here at home.

Results:

- it provided face-to-face interaction on curriculum;
- the opportunity to explore the environment and conditions our program seeks to address and improve was made possible;
- the backgrounds and skills profiles of the trainees were reviewed both in written form and in interviews;
- the end user of the PV systems were interviewed, which provided essential feedback;
- the national utility, ESKOM, was engaged in interview and review of the training program.

As a result of the relationship developed in PV between Texas Southern University and the Port Elizabeth Technikon, TSU is prepared to assist with the further development of the Technikon's PV program. Two of P.E. Technikon faculty and PV research and training staff will visit TSU during the month of January. This visit affords an expanded opportunity to share information of work on mutual PV projects.

We will work in partnership to :

1. Assist in the continued assessment and development of the P.E. Technikon's PV contractor training program and curriculum development in areas such as conduit sizing and installation, estimating cost and materials, concrete mixes, cash flow projections, basic finance and money management.
2. Develop a training curriculum that will prepare rural school personnel to operate the PV system and to recognize systems failures before they reach the point of total system impairment. Our field work during the summer and interviews with rural school personnel concluded that this type of training would be very meaningful and will complete the training loop. P.E. Technikon staff agrees with this assessment and recommendation. ESKOM also acknowledged that this added feature will be helpful.

Texas Southern University feels very strongly that the School of Technology is on the right track in the development of this solar industry. The school will continue to broaden the scope of learning in this field while working in collaboration with national and international educational institutions and industries to improve this technology.

**Title: The HBCU Photovoltaic Research Associates Project
at Wilberforce University**

Organization: Division of Natural Science, Wilberforce University
Wilberforce, Ohio 45384

Contributors: Dr. Herbert C. Smitherman, principal investigator

Objectives

The overall objectives of this project are to improve the University's capability to teach the fundamentals of photovoltaic science to Wilberforce students and to develop in the participating students an enthusiasm for this area of science through participation in photovoltaic research.

The HBCU Photovoltaic Research Associate Project at Wilberforce University currently consists of three separate projects carried out by different student/faculty teams. By carrying out these projects, our faculty members are increasing their familiarity with the utilization of their discipline in photovoltaic research and the students are developing a special association with photovoltaic science which we are trying to nurture into a powerful enthusiasm for the subject. These three projects emphasize advancing our understanding of how to modify the surface properties of semiconductor materials for improved performance, model semiconductor performance and evaluate the electronic properties of semiconductor.

The specific objectives and the current status of the individual projects are described in the next three sections.

1. Chemical Etching of Germanium

Student Researcher: Tosha Cameron

Faculty Advisor: Dr. Tuhfeh Habash

Objective: To examine the etching properties of a series of etching solutions on germanium wafers and their effect on the performance of germanium in photovoltaic applications. Specifically, we are looking for etchants that produce a sawtooth (v-shaped groove) profiles on germanium wafers. Etched samples with a distinctive profile will be evaluated for their suitability for photovoltaic applications based on the energy conversion efficiency.

Approach: Chemical etching of single crystal semiconductors plays an essential role in microelectronic solid-state device technology. It is used in device manufacture to produce a shiny damage-free surface in preparation for diffusion or epitaxial growth procedures. The type of etchant and the method of its application is critical for obtaining the right surface properties. Anisotropic etching has been used to create square-wave and sawtooth profile structures on many semiconductor materials. These profiles are useful profiles for photovoltaic applications because the surface area is increased and light can be caught in the grooves. When light hits the surface of a v-shaped groove, the reflected portion can reflect to the other side of the groove

providing a second opportunity for absorption. Capturing the extra light increases the energy trapped which can increase the efficiency of solar cell devices made from etched semiconductors.

Results: KOH and 1:1 HBr:H₂O₂ etchants have been found to selectively produce v-shaped grooves on silicon and indium phosphide respectively. A number of etchants utilizing AgNO₃, H₂O₂ and HF in various concentrations were examined for germanium. The etched wafers were studied with a scanning electron microscope which showed that these etchants produce a variety of profiles including pits, round domes and hillocks but not the desired sawtooth profile. Interestingly, the addition of a small amount of alcohol to a 3:1:1:3 HNO₃; H₂O₂; HF:H₂O etching solution changed the resulting etch profile to a unique one that looks like a hole with a triangular base. This has added a line of inquiry to the study as the role of the alcohol and its concentration dependence is examined. Etched wafer samples were submitted to chemical vapor deposition growth of a semiconductor layer on the wafer, a common next step in the process of going from wafer to photovoltaic device. The deposition was also studied with a scanning electron microscope which indicated that the etch procedure produced a surface on which uniform crystalline growth was poor.

Summary: The series of etchants examined to date have produced a variety of etch profiles but not the desired sawtooth groove. Work is being conducted to develop an understanding of the interesting new etch profile that was observed. In addition, work is being done to consider ways to make the etched surface more amenable to consistent epitaxial growth. And finally, the effort to find etchants which produce the sawtooth profile on germanium will continue.

2. PC1D computer Modeling of Solar Cells

Student Researcher: Jeffrey Turner Faculty Advisor: Dr. Edward Asikele

Objectives: To apply the PC1D computer modeling program to the performance of one-dimensional photovoltaic device analysis on a personal computer. The initial focus is on the treatment of the solar cell as a diode. The simulation program is used to calculate n_p near the junction and this will be compared with a straight theoretical calculation. After this verification of the computer model, some common Si and CdTe solar cells are to be evaluated with PC1D.

Approach: Since a solar cell is basically a diode with light shining on it, a non-uniform doping profile is used to create an n+p asymmetrical diode. The forward-biased diode carrier concentration profile has been studied and electron (n) and hole (p) concentrations near the junction have been determined with the PC1D program. The value of n_p near the junction has been compared to the theoretical value and the peak electric field and current density were also evaluated.

Result: The results from a comparison of the simulation program output and the theoretical analysis are shown below.

1. From the simulation model: near the junction, $n=1.16E15 \text{ cm}^{-3}$ and $p=1.05E15 \text{ cm}^{-3}$.
 $n_p=1.16E15 \text{ cm}^{-3} \times 1.05E15 \text{ cm}^{-3} = 1.22E30 \text{ cm}^{-6}$

2. The theoretical analysis is based on the following equation:

$$np = n_i^2 e^{qV/kT}$$

where n is the electron concentration
 p is the hole concentration
 $n_i = 1.01 \times 10^{10} \text{ cm}^{-3}$ Intrinsic Concentration
(including bandgap narrowing)
 $kT/q = 0.02585 \text{ V}$ Thermal Voltage
 $V = 0.6 \text{ V}$ Base Voltage

Applying these values, $np = 1.23 \times 10^{30} \text{ cm}^{-6}$

Summary: There is excellent agreement between the computer simulation and the theoretical analysis. The next step is to apply the model to some common Si and CdTe solar cells.

3. The Design, Construction and Testing of a PC based Solar Cell Analyzer

Student Researcher: Raymond Haraway

Faculty Advisor: Dr. Ravi Nadella

Objectives: To design, build, test and refine a personal computer controlled system for the electrical characterization of photovoltaic devices.

Approach: This project consists of a program to design, build, test and refine an automated system for the electrical characterization of photovoltaic devices. The system is based on a personal computer (PC), plug-in boards, external circuitry with suitable transducers and an illumination source. The completed system will be capable of measuring I-V curves and extracting solar cell parameters including efficiency, fill factor, short-circuit current and open-circuit voltage from the measured I-V curves. The electronic hardware will be interfaced to the PC and the necessary software routines developed to enable the computer to measure the I-V curves of samples at different levels of illumination and over a range of temperatures. The system will be tested and calibrated using standards supplied by MASA Lewis Research Center's Photovoltaic and Space Environments Branch.

Results: The design of the solar cell and analyzer has been completed and component acquisition has begun. After carefully considering some solar cell analysis models from the literature, we have developed a design for our instrument system. A tungsten halide filament light was selected to be the illumination source for the system. Even though outdoor exposure is the ultimate test for photovoltaic devices, solar simulators provide valuable data on these devices because the irradiation levels can be controlled and compared with internationally accepted standards. And although xenon arc lamps are frequently used in solar simulators, the advantages over a tungsten halide filament does not warrant the additional cost of these light sources. What is more, the tungsten halide filament has a smooth spectrum and is very stable.

In our design, a combination of battery power and variable power supply will be used to simulate variable load to the cell. The cell voltage and current will be measured by a pair of multimeters

which will be interfaced to the computer. Once the current-voltage data has been collected by the computer, several calculations will be done using software routines to find cell parameters like short circuit current, series resistance, efficiency, fill factor, and parallel resistance. Testing the system against data from NASA's Photovoltaic and Space Environments Branch will help us fine tune the system for accurate measurements.

Summary: The design of the solar cell analyzer has been completed and its construction is underway. We anticipate completing construction before the end of 1997 leaving a semester for testing and refinement prior to completion of the project at the end of the 97/98 academic year.

Overall Summary: The education of Wilberforce students is improving in several ways as a result of our participation NREL's HBCU Photovoltaic Research Associates Program. First and foremost is the direct benefit to the student participants. They gain special knowledge, learn first hand about the nature of research and get to work closely with a faculty member on the research project. What's more, they are able to focus more on their studies because they are not distracted with the issue of how to pay for their college education. There is also a spillover effect as the students discuss and thus transfer some of their experiences to their peers. This results in a wider impact on Wilberforce students than the direct impact to the participants.

Because we see these effects of the program, we are pleased to have the opportunity to participate in this program. We believe that at our school, the effect of the program is to increase the awareness of the nature and scope of photovoltaic science and to encourage the study of this area of science.

3.0 THIN-FILM TECHNOLOGIES PROJECT—Introduction

Ken Zweibel, Project Leader

The Thin-Film Technologies Project includes in-house R&D in CIS, CdTe, and amorphous silicon as well as subcontracted R&D within the Thin-Film PV Partnership. Research is conducted by research teams within each organization and by cooperative National Research Teams in amorphous silicon, cadmium telluride, CIS, and Thin-Film ES&H.

Some of the highlights for the fiscal year include:

In CIS:

- NREL researchers added substantially to their world-record cell efficiency (see Figure 1) by reaching 17.7% efficiency on a CIGS cell.

In CdTe:

- Solar Cells Inc. fabricated a 9.1%-efficient very-large-area CdTe module (see Table 1), meeting several of our Annual Operating Plan milestones for the CdTe technology. This is the most efficient thin-film module of its size.
- Solar Cells Inc. CdTe systems (1-10 MW) demonstrated 1-3 year outdoor stability at various locations (e.g., NREL, PVUSA, Ohio Edison).
- Golden Photon fabricated the highest efficiency CdTe cells made on low-cost, soda-lime glass (14.8% efficient). They also produced a near-30-W CdTe module of about 3400 cm² area.
- Golden Photon identified stability as a critical issue for their approach to manufacturing CdTe modules.

In amorphous silicon:

- United Solar made a significant advance in the world-record efficiency for a-Si cells, reaching a NREL-measured stabilized efficiency (total area basis) of 11.8%. The previous best was about 10.9%. This is the first significant advance in a-Si cell efficiency in more than 5 years.

The thin-film technologies made progress toward commercial readiness. In amorphous silicon, both Technology Partners (Solarex and United Solar Systems Corporation) began construction of amorphous silicon production plants of sizes larger than had previously existed (United Solar, Troy, MI, 5-MW plant; Solarex, 10-MW Virginia plant). The two CdTe Technology Partners, GPI and SCI, delivered about 200 kW of product from pilot lines, including 25 kW each to a Navy-sponsored experiment at Edwards Air Force Base in California. Several of the CIS companies are experimenting with sub-MW pilot lines. Despite this progress, no thin-film technology has yet reached substantial commercial presence in PV measured by annual worldwide production. Further technological and transitional scale-up to manufacturing issues must be addressed on an ongoing basis.

Figure 1. The Best Polycrystalline Thin Film Laboratory Cells (1996)

Table 1. The Best Thin Film Modules (1996)

Material	Size (cm ²)	Efficiency (%)	Power (Watts)	Company & comments
CdTe	6728	9.1%	61.3 W	Solar Cells Inc.
CuInSe ₂ (CIS)	3859	10.2%	39.3 W	Siemens Solar Industries
Amorphous silicon	3906	7.8%	30.6 W	Energy Conversion Devices
CdTe	3350	8.7%	29.3 W	Golden Photon Inc.
Amorphous Silicon	3432	7.8%	26.9 W	United Solar Systems (USSC)
Amorphous Silicon	1200	8.9%	10.7 W	Fuji (Japan)
CuInSe ₂ (CIS)	938	11.1%	10.4 W	ARCO Solar (now Siemens Solar Industries)
CdTe	1200	8.7% (reported)	10.0 W	Matsushita (Japan)
Amorphous Silicon	902	10.2	9.2 W	USSC

Note: Efficiencies verified independently at NREL unless noted as 'reported'; for a-Si they are after 600 hours light-soaking.

Thin-Film PV Technologies In-House Research

Title: Development of Polycrystalline Cu(In,Ga)Se₂ Thin Films and Devices

Organization: NREL PV & EM Center

Contributors:

Full Time

R. Noufi, Principal Scientist and Team Leader
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K. Ramanathan, Senior Scientist
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Part Time

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R. Matson, Senior Scientist

Objective: Advance the development of CIS-based PV toward commercialization

Technical Approach: The following are the technical problems addressed:

- Improvement of the materials quality and modifying device structure to obtain high conversion efficiencies
- Development of Alternative CIS Absorber processing, by depositing Cu_xIn_ySe₂ precursors, at relatively low temperature and high rates, followed by recrystallization in a Se over-pressure. We emphasize the following delivery methods: sputtering, sublimation, and electrodeposition.
- Evaluation of the CIS/CdS/ZnO junction. We attempt to understand the role of the chemically deposited (CBD) CdS in CIGS devices. Why does CBD CdS give superior devices compared to vapor-phase deposition (PVD) CdS? What are the characteristics and prospects for a direct ZnO/CIGS junction?
- Absorber with high Ga concentration. What principal material properties are responsible for the performance enhancing and degrading of devices containing high Ga concentration? What device structure is better suited for devices with high Ga concentration?
- Back contact. We examined the interaction and effect the soda-lime glass (SLG) substrate and the Mo back contact have on the performance of the device. We also demonstrated an alternative substrate to the SLG.
- We address technical issues in partnership with industry through the CIS Thin Film Partnership team, and through cooperative research and development agreements (CRADAs).

Results

Device Development: We have fabricated high-efficiency, Cu(In,Ga)Se₂ (CIGS)-based photovoltaic (PV) devices by four different PVD processes. Each process may be characterized as either sequential or concurrent deposition of the metals with or without an activity of Se. A world-record, total-area efficiency of 17.7% (Fig. 1) has been achieved by the concurrent delivery of the metals in the presence of Se. Ga has been introduced into the device in such a manner as to produce homogeneous, normal profiling, and double-profiling graded band gap structures. This has resulted in an open-circuit voltage (V_{oc}) parameter of 680 mV and a fill factor over 78%. The quality of CIGS-based films and devices is becoming decoupled from the method of film delivery. This leads to novel, fast, and low-cost methods for absorber fabrications.

Figure 1. Current-Voltage characteristics of world-record CIGS-based thin-film solar cell.

Alternative Processing Development: A growth model describing the formation of CIGS absorbers from a Cu-rich precursor has previously been presented. (See Ref. 1) A consequence of formulating this model is an understanding of how to translate the results from the laboratory to the factory.

The next-generation CIGS-based thin-film device will ideally have the following characteristics. The back contact and substrate combination will offer superior reproducibility to the present Mo/SLG system through controlled introduction of required impurities (e.g., Na, O). This will expand the list of potential substrates and back-contact metals to those that may be more optimally suited to CIGS thin-film processing. The absorber will be fabricated in a manner that minimizes in situ process control and high-temperature processing. This will drastically reduce the cost of manufacturing equipment. Finally, the heterojunction partner will be formed in situ with the absorber to relieve the necessity for a vacuum break and a CBD process. This will improve reliability and throughput and will reduce cost.

The critical absorber process parameters have been considered and a generic flowchart developed for the fabrication of CIGS absorbers (Fig. 2). By breaking the process into three or four independent stages, there are clear opportunities to use a variety of deposition techniques, separate and reduce the time for high-temperature (High-T) process segments, and introduce intelligent process control.

Four source-material delivery techniques consistent with the processing scenario described above were investigated: **rapid evaporation, sputtering, electrodeposition, and sublimation**. Table 1 presents the best results to date using the first three techniques. In the sublimation technique, we first evaluated the sublimation dynamics/characteristics of In_xSe_y , Cu_xSe_y , and Ga_xSe_y , and demonstrated deposition control of the stoichiometry. To date, because the sublimation apparatus is not ready, we have simulated the technique in an evaporator. Device performance was encouraging: $V_{oc} = 0.59\text{V}$, $J_{sc} = 32\text{Ma.cm}^{-2}$, $\text{FF} = 0.72$ and the efficiency was 13.7%.

Evaluation of the CIGS/CdS/ZnO Junctions: Can we integrate the formation of the junction into the absorber fabrication? We have pursued three approaches to explore this: (1) deliver In-Ga-Se to the substrate at lower T_{sub} to produce an n-type $(\text{In,Ga})_x\text{Se}_y$ layer; (2) form a built-in junction between the <112> chalcopyrite phase and a defect-chalcopyrite phase (In-rich, n-type), and (3) modify the ZnO deposition process for the optimal new junction. The status to date is as follows: Devices from (1) and (3) yielded 11% and 12.7T, respectively.

A summary of the working of the standard junction can be found in the proceedings from the CIS national Thin Film Partnership team. (Results to be made public soon.)

Absorbers with High Ga Concentration: Why do devices based on CIGS absorber films with Ga/In ratio higher than about 0.3 perform much poorer than the lower Ga-containing devices?

We have shown that there are significant crystallographic differences between the bulk absorber $\text{Cu}(\text{In,Ga})\text{Se}_2$ and the defect chalcopyrite $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$ materials present at the surface. Lattice mismatch in the basal plane becomes <1% for Ga contents >30% (relative to In). Also, the n-type conductivity of the defect chalcopyrite is found to exist up to $x \sim 0.3$, and for higher Ga contents, it shifts to p-type. Uniform high-Ga-content absorbers are observed to behave more like true heterostructures, where the CdS/ZnO layers begin to play a more active role in junction formation.

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Fig. 2. Generic flowchart for fabrication of CIGS absorbers.

Table 1.

Process	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	η (%)	Comments
Rapid Evaporation	623	32.9	75	15.3	CIGS + (Cu,Se) + (In,Ga,Se)
Rapid Evaporation	605	31.4	73	13.9	CIGS:CS + (In,Ga,Se)
Sputtering	508	24.3	57	7.0	CIGS + Cu + Se + (In,Ga,Se)
Electrodeposition	689	27.65	71.6	13.6	CIGS:CS + (In,Ga,Se)

Considering the chalcopyrite/defect chalcopyrite junction model, we postulate that the traditionally poor device performance of uniform high-Ga-content absorbers ($x \sim 0.3$) is due to a relatively poorer character—both structural and electrical—at the chalcopyrite/defect chalcopyrite interface. We have demonstrated that improved efficiencies are attainable in high-Ga-content absorbers by properly grading the surface of such materials. To date, we have demonstrated <14% device based on this understanding.

The Back Contact/Substrate: One difficult issue that is being addressed in our laboratory is irreproducibility associated with changes in the Mo/SLG substrate system. The irreproducibility may be characterized by a long time-constant that is related to process variations from one source of Mo/SLG, or a very short time-constant resulting from parallel processing of substrates from different sources. This issue has been investigated by a combined effort of material and device characterization.

To date, we have developed the following understanding:

1. There is a level of inconsistency over time in the substrate obtained from different suppliers in terms of the Na migration from the substrate to the absorber film.
2. There is a relationship between the Na concentration within the absorber and the resulting carrier concentration and open-circuit voltage (V_{oc}) of the device.
3. That the nature of the Mo surface and its reactivity with Se can influence the characteristics of the absorber and the performance of the device.

We have also demonstrated the feasibility of substituting the SLG substrate by stainless steel. To date, the device performance demonstrated is 13.5%

Interaction with Industry: The CIS team interacts with industry using several vehicles of outreach:

1. Site visits where we consult with industry and transfer information related to the CIS technology, or participate in hands-on work on-site related to processing and/or hardware
2. We participate in the national CIS Thin-Film Partnership team where collectively we address issues related to the device junction, the substrate/Mo impact on the device, and the nature of transient effects.
3. We are performing on three CRADAs:
 - a. The Lockheed-Martin CRADA addresses the fabrication of CIGS solar cells as taught by the NREL processing patents, using LMA Dynamic Research System for scale-up.
 - b. The EPV CRADA also calls for validation of the NREL CIS processes using EPV pilot production hardware.
 - c. The CRADA with DayStar explores the feasibility of CIGS solar filament cells using the NREL processes.

References: The following publications describe the details of the research summarized in the preceding pages.

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2. "Defect Chalcopyrite Cu(In,Ga)₃Se₅ Materials and High-Ga Content Cu (In,Ga)Se₂-Based Solar Cells," M.A. Contreras, H. Weisner, D. Niles, K. Ramanathan, R. Matson, J. Tuttle, J. Keane, and R. Noufi, Proceedings of the 25th IEEE PV Specialists Conf., p. 809, Washington, D.C., May, 1996.
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9. "12.3% Efficient $\text{Cu}(\text{In}_x\text{Ga}_{1-x})\text{Se}_2$ Device from Electrodeposited Precursor by Two-step Process," R.N. Bhattacharya, H. Weisner, T.A. Berens, R.J. Matson, J. Keane, K. Ramanathan, A. Swartzlander, A. Mason, and R. Noufi, *J. Electrochem. Soc.*, in press.

Title: Hydrogenated Amorphous Silicon Device Research

Organization: NREL In-House Amorphous Silicon Research Team
National Renewable Energy Laboratory, Golden, CO

Contributors: H.M. Branz (Team Leader), R.S. Crandall, E. Iwaniczko, H. Mahan,
B.P. Nelson, Q. Wang, Y. Xu

Objectives

The NREL Amorphous Silicon Team pursues breakthrough advances in materials and devices in order to improve the stabilized efficiency of amorphous-silicon-based PV cells and meet DOE PV cost goals. We collaborate closely with PV industry and academic collaborators through participation and direction of the National Amorphous Silicon Teams. During FY 1996, the team's main focus was on development of hot-wire (HW) CVD amorphous silicon for use as a mid-gap cell in a triple-junction solar cell. We also study the physics of solar cell operation¹⁻³ and light-induced degradation,⁴ electronic defects,⁵⁻⁷ and hydrogen diffusion.⁸ Advances in processing technology are transferred to industry through the National Teams. For example, in 1996, Solarex Corp. achieved significant reductions in i-layer processing time⁹ by adapting NREL's strategy of H diluting only the i-layer interface region. In this report, we focus only on the hot-wire materials and device work done by the team in FY 1996.

Hot-Wire Materials Progress

The search for improved intrinsic amorphous silicon material to incorporate in devices has long been a principal goal of amorphous silicon materials research. At NREL, we have developed hot-wire a-Si:H and have shown that its properties are in many ways superior to those of conventional glow-discharge (GD) a-Si:H. By raising the substrate temperature (T_s) to about 350°C, device-quality a-Si:H could be deposited for the first time with bonded H contents as little as 1 at. %.^{10,11} The HW films with about 2 at. % H display improved stability against light-induced degradation compared to GD films. Saturated defect densities after prolonged light soaking measured by the constant photocurrent (CPM) technique,^{12,13} and by capacitance spectroscopy¹⁴ are found to be $1-3 \times 10^{16} \text{ cm}^{-3}$, significantly lower than GD densities. Ambipolar carrier diffusion lengths after light soaking are more than 1600 Å, again better than GD values. These HW a-Si:H films were deposited at deposition rates of 6-8 Å/sec, compared to typical GD rates of 1-2 Å/sec.

Studies during FY 1996 reveal still more clearly that HW material has fundamental differences from GD a-Si:H. Collaborators at Syracuse University observed¹⁵ that hole drift mobility is increased by a factor of about 5, suggesting that valence band tail is narrower by about 10% or roughly 5 meV. A narrower valence band tail is normally associated with improved structural ordering, and our preliminary x-ray diffraction measurements support this hypothesis. Collaborators at the University of North Carolina also observed¹⁶ a dramatically different H microstructure by nuclear magnetic resonance (NMR). These magnetic resonance results reveal that much of the material is devoid of H while large H clusters contain most of the H.

Hot-Wire Device Progress

Recent computer modeling suggests that incorporation of our present best HW i-layer would improve stabilized efficiency of single-junction a-Si:H solar cells by 1%-2% in *absolute* efficiency. It is clear that improved i-layer materials properties will be needed to achieve the DOE efficiency goals. As described below and in a more complete report elsewhere,¹⁷ we are collaborating closely with colleagues at United Solar Systems Corp. (USSC) and making good progress toward obtaining the stabilized efficiency improvement promised by modeling.

The principal difficulty in using optimized HW i layers in a solar cell is substrate temperature (T_s) of 350°C. Device-quality GD a-Si:H is normally deposited at 200° to 250°C. The higher HW deposition temperature leads to increased diffusion of dopants and H through the structure. Early NREL attempts to grow p-i-n solar cells were hampered by B diffusion from the p-layer during HW i-layer deposition.

In 1995, we began to fabricate SS/n-i-p/ITO substrate cells to reduce B diffusion problems. Before incorporation of a high T_s HW i-layer into a complete substrate solar cell, we also studied the closely related SS/n-i-Pd Schottky barrier structure. Results on the Schottky cells and on our first-generation n-i-p HW "hybrid" cells, made with HW n- and i-layers but a GD μ c-Si(p) layer (deposited at USSC), are described below.

We find that Schottky HW device fill factors (FF) do not depend strongly upon the HW i-layer thicknesses. This suggests that the Schottky device performance is not limited by the transport properties of the i-layers. We find instead that the device FF is governed mainly by the surface treatment of the HW i-layer before Pd deposition. Stopping the HW i-layer growth completely and cooling the SS/n-i structure in vacuum produces a device with a very low FF. Cooling the sample in silane atmosphere and then treating the exposed surface with an H_2 plasma at 200°C yields significant FF improvement.¹⁸ Fig. 1 shows SIMS H profile measurements on two devices with these very different treatments. It can be seen that our surface treatment inhibits H out-diffusion, and actually puts H back into the surface layer. This extra H increases the device FF from 0.28 to 0.60. It appears that H out-diffusion from the HW i-layer introduced defects that were responsible for the poor FF. Our best HW Schottky devices to date were made with a variant of this surface treatment and have a FF of 0.65 and a V_{oc} of 0.54. These values are superior to our best GD Schottky devices to date, which have a FF of 0.63 and a V_{oc} of 0.51.

Figure 1. SIMS profile of devices with and without H plasma treatment.

We deposited SS/n-i-p/ITO test devices that show remarkable stability under light soaking, but are not yet quite as good as similar GD devices. For a good i-p interface, these devices use the i-layer surface treatment described above. Table 1 shows device parameters for a typical HW device in its initial state and after having been light soaked for 887 h under 1 sun. The range in J_{sc} is representative of the spread in the 11 (out of 12) active devices which were measured. For comparison, a state-of-the-art GD SS/n-i-p/ITO device¹⁹ with a 4000-Å i-layer and no light trapping, has an initial efficiency of ~7.8% and degrades after 600-hour light soaking under 1 sun by ~16%, to an efficiency of ~6.5%.

Table 1. Light-soaking data for a SS/n(HW)-i(HW)- μ C-Si(p)(GD)/ITO device.

THDni113	as-grown	887-hr light soak
white FF	0.605	0.545
V_{oc} (V)	0.88	0.86
J_{sc} (mA/cm ²)	11.0 to 12.8	no change
efficiency (%)	6.81	6.13
% change		~ 10%

The biggest differences in the initial state between the GD and HW "hybrid" devices are in the values of V_{oc} (0.94 vs. 0.88 V) and FF (0.66 vs. 0.605). We believe that the lower V_{oc} for the HW device is due primarily to the lower band gap of the high T_s HW i-layers (1.65-1.70 eV), compared with GD i-layers deposited with H dilution (> 1.70 eV). Indeed, the V_{oc} was higher (0.93 eV) in a device we made with a higher band gap HW i-layer deposited at a lower T_s (280°C). The low HW gap will actually be useful for the mid-gap cell of a triple-junction device.

We believe that the fill factor is reduced in our HW devices by a loss of H at the back of the i-layer (n-i interface) that we observe in SIMS profiles (see Fig. 1). Defect studies also suggest that high defect densities do occur in the (back-surface) region. Because we saw dramatic FF improvements when we addressed this out-diffusion problem at the top surface (the surface most easily accessible to H treatments), we are now exploring techniques for controlling the H profiles in the region of the n/i interface.

Summary and Acknowledgments

Low H content, high deposition rate, hot-wire-deposited a-Si:H shows superior electronic properties after light soaking compared to GD a-Si:H and should lead to improved a-Si:H solar cells. However, the high HW deposition temperature makes incorporation in a solar cell quite challenging. During FY 1996, we incorporated an HW i-layer into a substrate solar cell for the first time and further developed our all-HW Schottky cells. We find that the treatment of the top surface of the HW i layer is crucial to device performance. The top-surface treatment is needed to keep sufficient H in this layer and improve the i-p or i-Pd interface. Although no light-trapping layer is used to increase the device current, we have obtained efficiencies of up to 6.8% for an n-i-p cell with a 4000-Å-thick HW i-layer. This cell degrades less than 10% after a 900-hour AM1 light soak, much less than GD solar cells of comparable thickness. In FY 1997, our work will focus on developing ways to keep H in at the back interface (n-i) to further improve device fill factor.

We are grateful to Drs. J. Yang and S. Guha of USSC, who supplied much valued advice and contributed to the device fabrication. We thank Prof. A. Gallagher of the University of Colorado for many stimulating discussions during the entire course of this work. We also acknowledge V. Dalal and S. Hegedus for QE measurements and T. Unold for ESR and CPM measurements.

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Title: Thin-Film CdS/CdTe Solar Cell Development

Organization: National Renewable Energy Laboratory
Golden, Colorado

Contributors: P. Sheldon (Team Leader), D.S. Albin, S.A. Asher, T.J. Coutts, R.G. Dhere,
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Team Objectives:

- To Develop Reproducible Processes for High-Efficiency CdS/CdTe Devices
 - *Continue to develop and improve a baseline CdS/CdTe device process*
 - *Develop a fundamental understanding of the physics and chemistry of critical interfaces and processes*
- To Explore Alternative Processes Which Lend Themselves to Improved Device Performance, Improved Device Understanding, Improved Reproducibility, and/or Improved Manufacturability
- To Provide Industrial Partner Support
 - *Through materials and device characterization and cooperative research and development agreements (CRADAs)*
 - *Through development and participation in the Thin Film Partnership program*

Technical Approach:

In FY96 the CdTe team focused on a wide variety of research projects which support the objectives outlined above. Research activities pursued fit into one of three tasks: (i) Baseline Process Development/Improvement; (ii) Applied and Innovative Research-development of alternate processes which either improve device performance, understanding, reproducibility and/or manufacturability; or (iii) Industrial Partner Support.

Three projects were pursued under the "Baseline Process Improvement" task, which included:

- Studying SnO₂ stability effects and their impact on reproducibility and device performance¹
- Continuing investigation of the effect of oxygen on close-space sublimation (CSS) CdTe films and devices^{2,3,4}
- Completion of an infrastructure development plan with the installation and commissioning of a low-pressure chemical vapor deposition (CVD) system for SiO₂ and SnO₂ depositions

Four projects were pursued in the "Applied and Innovative Research" task, which included:

- Development of a new, high-performance transparent conducting oxide (TCO)^{5,6}
- Development of a unique CSS temperature profiling technique which yields enhanced material properties and device performance⁷
- An investigation of the effect of CSS substrate temperature and CdCl₂ treatment on CdS/CdTe interface alloying⁸

- Development of a novel all-dry ZnTe-based contact^{9,10,11}

Progress in each of these projects is outlined in the "Results" section below.

In FY96, the CdTe team also provided significant industrial partner support. In addition to actively participating in the Thin-Film Partnership program, we interacted closely with both Solar Cells, Inc. (SCI) and Golden Photon, Inc. (GPI) and assisted ITN. We submitted a final report to SCI for a CRADA which focused on developing a ZnTe-based contact and development of a PL-based diagnostic monitor. We also developed a CdS thickness monitor for GPI which they use routinely to analyze their production CdS films. Finally, we initiated a funds-in CRADA with GPI to develop and investigate nanoparticle inks for CdS/CdTe spray deposition.

Results:

Baseline Process Development/Improvement

Tin Oxide Stability Effects:

In FY96 we investigated the stability of SnO₂-coated substrates subjected to high-temperature processing in reducing ambients. CdS is reported to benefit from a brief (400°C) hydrogen anneal prior to CdTe deposition. However, we have shown that SnO₂ can be susceptible to reduction in H₂ and that the degree of susceptibility is dependent on the type of SnO₂ used. Chemical-vapor-deposited SnO₂ films (Solarex) show the most resistance to reduction while room-temperature-sputter-deposited SnO₂ films show the least resistance. We find that when films are annealed under reducing conditions, Sn from the SnO₂ reacts with S-containing impurities and oxygen in the as-grown chemical bath deposited (CBD) CdS films to form SnS (oxygen is the primary contaminant in CBD-grown CdS films). The formation of SnS in the CdS and possibly SnO in the SnO₂ layer also degrades the transparency of these films.

Typically after the H₂ anneal, CSS CdTe deposition is initiated at temperatures of 550-600°C in either a He or He:O₂ ambient. In pure He, CdS films lose both Sn and S due to evaporation of the SnS. In a He:O₂ ambient (an oxygen partial pressure of ~1-2 Torr is typical during CSS deposition), the SnS converts to SnO₂ allowing only the S to evaporate. Therefore, we find that Sn levels on the CdS surface, immediately prior to the deposition of CdTe, can be affected not only by the temperature of the H₂ anneal, but also by the amount of oxygen present during the CdTe deposition step. Modifications in the CdS/CdTe device fabrication process, including the use of more stable tin oxide layers (CVD-grown) and lower temperature H₂ anneals (300°C), produced devices with higher open-circuit voltages, fill-factors, and total-area efficiencies. By eliminating the insulating-sputter-deposited SnO₂ layer, we were able to achieve an average increase in V_{oc} of 34 mV over our baseline value.

The Role of Oxygen on CSS-Deposited CdTe and CdS/CdTe Devices:

CSS of CdTe in an oxygen ambient had been reported to be essential for fabricating high-efficiency CdS/CdTe solar cells by increasing the acceptor density in the absorber. In FY96, we continued to improve our understanding of the role of oxygen in CSS-deposited CdTe. We find that the presence of oxygen during CSS increases the nucleation site density of CdTe, thus decreasing pinhole density and the grain size. The latter is clearly shown in Figure 1, which is a plot of the grain size as a function of oxygen partial pressure during CSS deposition. Photoluminescence showed that increased

oxygen partial pressures also decreases material quality in the bulk of the CdTe film, but positively impacts the critical CdS/CdTe interface. However, through device characterization we were *unable* to verify an increase in acceptor density with increased oxygen. These results, along with the achievement of high-efficiency cells (13% AM1.5) without the use of oxygen at any stage of the process, has led us to conclude that oxygen during CSS CdTe deposition can be useful but is not essential.

Figure 1. Effect of oxygen partial pressure on grain size.

Infrastructure Development:

In FY94, the CdTe team initiated an aggressive infrastructure development plan. Our goal was to develop hardware that yields highly reproducible films and devices. In FY96 this plan was completed with the delivery, installation, and commissioning of a low-pressure CVD system. The system is configured to deposit both SnO₂ and SiO₂ thin films. Previously, the CdTe team had to rely on external vendors for SnO₂-coated substrates. Procuring substrates of consistent and acceptable quality was problematic. This new capability ensures that the CdTe team will have a steady supply of high-quality substrates. The system can accommodate 4" × 12" substrates and deposit films with excellent thickness uniformity. Initial development work has focused on optimizing the thickness uniformity for SiO₂ and undoped SnO₂ films. Thickness uniformity of better than ±0.9% has been achieved over 4" × 4" substrates for both SiO₂ and undoped SnO₂ depositions. SiO₂ will be used as a diffusion barrier and nucleation layer for SnO₂ depositions on glass substrates and provides a critical processing capability for the PV and Electronic Materials Center. Work in early FY97 will focus on developing a doped tin oxide process.

Applied and Innovative Research (Alternate Processes)

High-Performance TCO Development:

One goal of the CdTe team is to develop device structures capable of higher performance and improved manufacturability. Along this line, we have initiated a project to develop a high-performance TCO which could replace the conventional SnO₂ layer in a CdS/CdTe device structure. One promising candidate is cadmium stannate (Cd₂SnO₄). Cadmium stannate transparent conducting oxides have several significant advantages over conventional TCOs. They are more conductive, more transparent, have a lower surface roughness, are patternable, and are exceptionally stable. Figure 2 shows the

Figure 2. Comparison of the transmittance and absorbance between Cd₂SnO₄ and SnO₂ films.

transmittance and absorbance of both a Cd_2SnO_4 and a SnO_2 thin film. The Cd_2SnO_4 film has a much lower resistivity (Cd_2SnO_4 resistivity is >3 times lower than the SnO_2 resistivity). The improved transmission and absorbance of the Cd_2SnO_4 film is ideal for superstrate CdS/CdTe devices and should yield improved short-circuit currents.

We have integrated this into a device and produced the first Cd_2SnO_4 -based CdS/CdTe polycrystalline thin-film solar cell ($\eta = 13.7\%$). Cd_2SnO_4 -based CdS/CdTe cells have a higher fill factor and open-circuit voltage, and are less dependent on the CdCl_2 heat treatment than their SnO_2 counterparts. These preliminary results demonstrate that by replacing SnO_2 with Cd_2SnO_4 CdS/CdTe device performance can be enhanced. We believe that the performance of Cd_2SnO_4 -based CdS/CdTe cells is far from optimized. Future work will concentrate on improving the efficiency of $\text{Cd}_2\text{SnO}_4/\text{CdS/CdTe}$ cells through the optimization of Cd_2SnO_4 film preparation and cell fabrication procedures.

Enhanced CSS Temperature Profiling Technique:

Previously we have shown that high substrate temperatures (T_{sub}) improve both material and device properties. However, as T_{sub} increases beyond 610°C , device performance degrades due to increased pinhole densities. In order to maintain the improved material properties associated with the higher deposition temperatures, without suffering the detrimental effects (and to maintain processing temperatures $\leq 600^\circ\text{C}$, temperatures compatible with low-cost soda-lime glass), we have developed a modified temperature profiling technique. Temperature profiles were defined by separately controlling the source and substrate temperatures as a function of time. Although these profiles limit the high-temperature segment to only the initial nucleation stage of the film (approximately the first 20-40 seconds), the films retain many of the benefits associated with sustained high-temperature depositions (i.e., increased grain growth). This is clearly seen in Figure 3, an atomic force microscopy (AFM) image of a film nucleated and grown at 600°C (Fig. 3a) and a film that was nucleated at 645°C and then reduced to a growth temperature of 600°C (Fig. 3b). The final grain size is dictated primarily by the initial nucleating conditions. We find that improved material and device properties can be obtained while maintaining deposition temperatures compatible with commercially available substrates. This temperature profiling technique can be easily applied to a manufacturing environment by adjusting the temperature as a function of substrate position.

Figure 3. AFM images of CSS-deposited CdTe films grown at 600°C and nucleated at either 600°C (a) or 645°C (b).

All-Dry ZnTe-based Contact:

Typically, CdTe devices require a wet chemical etch to prepare the surface for application of the back contact. From a manufacturing standpoint, this is an undesirable step which most manufacturers would like to eliminate. In FY96, we produced a CdS/CdTe thin-film device with a conversion efficiency of 12.1% using a proprietary ZnTe-based back contacting process. This result is significant because the contact was produced using a completely *dry* process that is applicable to continuous-feed, large-volume module production. Sputter deposition was used to deposit the ZnTe layers and the outer metallization (Ni layer). All steps of the contacting process were performed at a deposition temperature of 300°C. The relatively high deposition temperature significantly improves adhesion of the outer metal (Ni) layer, and is believed to suggest enhanced contact stability (because diffusion of contact layers will have already occurred).

Future Directions:

In FY97, we will develop a doped SnO₂ process, providing a source of SnO₂-coated glass substrates for the CdTe team. We will also continue to develop and optimize the Cd₂SnO₄-based device structure initially developed in FY96. We will develop a dry CSS-based CdS deposition process and compare it to our baseline CBD CdS films, as well as dry vapor-based Citeatment to replace the wet CdCl₂ process we currently use. In FY97 we will also initiate stability studies on our ZnTe-based contacts, and continue work on collaborative projects initiated with our industrial and team partners through the Thin-Film Partnership program. In addition, we will apply our improved knowledge and processing expertise to producing high-efficiency CdTe devices. A detailed description of tasks is outlined in the CdTe FY97 Annual Operating Plan.

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Thin-Film PV Technologies Subcontracts

Title: **Light-Trapped, Interconnected, Silicon-Film Modules**

Organization: AstroPower, Inc.
Newark, Delaware

Contributors: R.B. Hall, program manager; D.H. Ford and J.A. Rand, principal investigators; A.M. Barnett, J.A. Adkins, J.R. Bower, J.E. Cotter E.J. DelleDonne and A.E. Ingram

PROGRAM OVERVIEW

AstroPower is developing a module manufacturing technology based on a film-silicon technology. AstroPower, as a Technology Partner in the Thin-Film Partnership, is employing its Silicon-Film™ technology toward the development of an advanced thin-silicon-based, photovoltaic panel product for use in power applications. This module will combine the design and process features of the most advanced thin-silicon solar cells with light trapping. These solar cells will be integrated into a low-cost interconnected array.

This advanced product includes the following features:

- silicon layer grown on a low-cost substrate,
- a 50-micron thick silicon layer with greater than 100 micron diffusion lengths,
- light trapping due to back-surface reflection,
- back surface passivation.

The 50-micron thick silicon layer achieves high solar cell performance and can lead to a sub-module conversion efficiency as high as 19%. These performance design features, combined with low-cost manufacturing using relatively low-cost capital equipment, continuous processing and a low-cost substrate, will lead to a panel cost of less than \$1.00/watt.

KEY RESULTS OF PHASE II

Previously, AstroPower reported an efficiency of 13.8%. This device, however, had an active layer thickness greater than 175 μm . The key thrust of our Phase II effort has been on reducing the active layer thickness thereby reducing the costs.

The key results of the second year program are:

- a confirmed 12.5% efficient, thin solar cell fabricated on a low cost substrate (Figure 1.),
- development of a new technique to achieve light trapping in thin layers of silicon based on pigmented, high-temperature glass materials,
- development of key sub-module fabrication processes, including contact grid design, sub-element isolation and screen printed interconnection,
- development of a screen printable barrier layers.

AstroPower Thin film Si

Sample: C	Temperature = 25.0°C
Dec 11, 1996 11:54 AM	Area = 0.4673 cm ²
ASTM E 892-87 Global	Irradiance: 1000.0 Wm ⁻²

$V_{oc} = 0.5657$ V	$V_{max} = 0.4614$ V
$I_{sc} = 13.71$ mA	$I_{max} = 12.66$ mA
$J_{sc} = 29.34$ mAcm ⁻²	$P_{max} = 5.841$ mW
Fill Factor = 75.30 %	Efficiency = 12.5 %

Figure 1. I-V characteristic of a thin (60 μ m) solar cell fabricated on a new barrier-coated substrate.

TECHNICAL APPROACH

The solar cell sub-element device structure (Figure 2b) consists of a thin (35–50 μ m) polycrystalline silicon layer which is grown on a low-cost substrate material. The thin layer/low-cost substrate approach results in lower cost by minimizing the use of relatively expensive silicon feedstock material. Diffusion lengths equivalent to twice the device thickness are required to assure high carrier collection throughout the bulk of the base layer, enabling the use of imperfect materials and increased doping levels for improved solar cell voltage and fill factor.

Thin films grown on an insulating substrate allow the fabrication of large-area, series-interconnected sub-modules (see figure 2a) [1]. The sub-module design incorporates a method of partitioning the thin-film photovoltaic layer into sub-elements and reconnecting them as a series connected array. The sub-module design also incorporates conductivity enhancement to minimize the power loss associated with lateral current flow through the thin base layer.

Figure 3 illustrates the general principle of light trapping through the use of pigmented materials. Adjacent to the back surface, the pigmented material acts as a reflector, scattering weakly absorbed light back into the thin silicon layer. Furthermore, the reflector scatters the light in a diffuse pattern, and the escaping light can be perfectly reflected again at the front surface, back into the silicon layer, by the phenomenon of total internal reflection. In this case, light will travel a much greater distance than the thickness of the silicon layer and the absorption of light will therefore be enhanced.

Figure 2. (a) Solar cell sub-module device structure and (b) sub-element device structures.

Figure 3. The concept of pigmented materials for light trapping in thin films of silicon.

Pigmented materials consist of two substances of different refractive index. The “pigment” is in the form of small particles, usually of high refractive index. The “medium” is a binder, usually of low refractive index, throughout which the pigment is dispersed. Paint is a good example of a pigmented material. If the particle size and refractive indices are carefully chosen, light interacts very strongly with and is strongly scattered by the pigment. The result is a broadband and highly diffuse reflecting material.

The scattering phenomenon is described by Mie Scattering Theory [2]. When the pigment particle size is optimized (at near the wavelength of light), the scattering efficiency is highest. This is due to the strong electromagnetic interaction between the scattering particle and the light that occurs when the particle size is similar to the wavelength of light.

SUMMARY

The phase II program has been successful in developing a substrate for light trapping and passivation properties. Although light trapping has been observed in the silicon layers on the new barrier-coated substrate, it has not been fully optimized. Conversion efficiencies exceeding 15% are expected as we continue our development efforts on the substrate and barrier layer. A 12.5% efficiency (60 μm thick) laboratory device has been demonstrated.

We will continue to focus on further developments for the basic fabrication technologies related to the formation of the monolithically integrated sub-module. This includes techniques for sub-element isolation, interconnection, and conductivity enhancement. Finally, manufacturing technologies will be adapted or developed for key fabrication processes.

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**Title: Nanostructure of Amorphous-Silicon-Based Solar Cell Materials by
Small-Angle X-ray Scattering**

Organization: Department of Physics, Colorado School of Mines, Golden, Colorado

Contributors: D.L. Williamson, principal investigator; N. Kang

Objectives

The general goals are to establish details of the nanostructure of a-Si:H and related alloys presently being incorporated into solar cells and to help determine whether particular nanostructural features are correlated with photovoltaic behavior. If certain features are found to be detrimental to solar cell efficiency and stability, then optimization efforts will be carried out with the film growers and device makers of the various NREL Amorphous Silicon Teams to improve existing deposition methods or consider alternate methods and materials.

Approach

The direct structural characterization method of small-angle x-ray scattering (SAXS) is being used to study nanostructural features ranging in size from the atomic up to approximately 30 nm. Features such as nanovoids, hydrogen-rich clusters, columnar-like growth, microcrystallites, surface roughness, and alloy composition fluctuations or segregation can all be detected with a high degree of sensitivity. For example, nanovoids of volume fraction 0.1 % are readily seen and their average size can be determined. Atomic-scale structure can be inferred from the x-ray diffuse scattering intensity. Anisotropy in the SAXS, as detected by a sensitivity of the SAXS to sample orientation relative to the x-ray beam, is direct evidence of oriented nanostructural features such as columnar-like growth.

The approach involves collaboration with the NREL Low-gap, Mid-gap, and High-gap Teams, particularly the film-making and device-making groups that supply relevant, systematic sets of samples to help address specific issues within the above objectives. We also collaborate with several groups around the world not supported directly by NREL but recognized as experts in the field. SAXS-suitable substrates are supplied by us to all collaborating groups. SAXS measurements made at a central facility allow accurate comparisons of the nanostructure of materials prepared by different deposition methods, conditions, and systems. Other in-house measurements complementing our SAXS studies include Raman spectroscopy, x-ray diffraction and flotation density. A high-quality annealing system is also available.

Results

The discussion will be separated according to materials appropriate to the low-gap, mid-gap, and high-gap components of a multijunction solar cell. The latter is the structure being developed to meet the long-range goal of 15% stabilized efficiency with the amorphous silicon thin-film technology.

Low-bandgap Material

PECVD a-Si_{1-x}Ge_x:H films deposited at Harvard on the cathode of an rf discharge possess opto-electronic properties that are greatly improved over any yet reported in the range of $x \geq 0.6$. The improvements are attributed in large part to the reduction in structural inhomogeneity as observed by SAXS, and partly to a reduction in midgap state density. The conditions of deposition that lead to these improvements are believed to be high electron temperature in the discharge plasma, which leads to favorable chemical radicals and high levels of ion bombardment [1,2].

It is possible to produce a-Si_{1-x}Ge_x:H films via the microwave plasma technique developed at United Solar Systems Corporation (USSC) [3] at a deposition rate of 4 nm/s with no detectable nanostructure and a void fraction below 0.01 vol.%. The formation of these structurally homogeneous materials is critically dependent on the application of a substrate bias during deposition. The material made under the bias on condition is much more homogeneous and yields the better solar cells [4].

Analysis of anomalous SAXS (ASAXS) data obtained at the German synchrotron facility (DESY) provides evidence of a non-uniform Ge distribution in one a-Si_{1-x}Ge_x:H film prepared at IACS [5]. The Ge composition fluctuations mimic the columnar-like microstructure previously reported for this material [6], suggesting that the Ge may be clustering along the column boundaries.

Mid-bandgap Materials

A film of hotwire a-Si:H, prepared with the same conditions presently being used to make solar cells in a team project involving NREL and USSC [7], has no detectable nanostructure and a void fraction below the detection limit of 0.01 vol.%. This film also has the highest flotation density (2.292 g/cm³) and a diffuse SAXS signal lower than any previous a-Si:H film, consistent with the lower H content (2-3 at.%) in this material.

An a-Si:H film deposited under conditions that yield single-junction cells with initial $V_{oc} = 1.04-1.05$ V and stabilized $V_{oc} = 1.01$ V at Energy Conversion Devices (ECD) shows no detectable nanostructure and a void density well below 0.1 vol.%. This is of interest since the low deposition temperature of 150°C leads to a high H content (estimated at ~18 at. % based on the measured flotation density, 2.166 g/cm³, and the diffuse SAXS signal). The use of high H₂ dilution seems to promote the homogeneous nanostructure.

Doping of a-Si:H with B via a 1% TMB-in-He source during PECVD deposition leads to a dramatic increase in 1 nm-sized nanostructure that increases systematically with the amount of doping. Assuming nanovoids, their volume fraction reaches 2.1 vol.%, a factor of about 50 larger than the undoped material [8].

High-bandgap Materials

Two sets of a-Si:H films prepared at the Tokyo Institute of Technology (TIT) by the chemical annealing technique [9] at low substrate temperatures (50-125°C) have high H contents and high optical bandgaps (1.91-2.05 eV). Some of the samples were partially microcrystalline but those that remained fully amorphous had significant inhomogeneity as detected by SAXS. Low flotation densities are consistent with high H contents and the presence of nanovoids, sometimes

at the 1 vol.% level. The opto-electronic behavior of this type of material suggests device-quality properties and enhanced stability [10] but its use in a device has not been tested to our knowledge.

Summary

We continue to accumulate evidence supporting the premise that a homogeneous nanostructure in a-Si:H-related materials yields the best devices. The most striking evidence has come from the collaboration with USSC on the microwave-deposited a-SiGe:H alloys. The use of a substrate bias to induce ion bombardment during high-rate deposition leads to a dramatic reduction in the nanovoids and to much better solar cell efficiencies. Similarly for the Harvard collaboration, conditions of enhanced ion-bombardment during PECVD growth of even higher Ge-content alloys ($x \geq 0.6$) led to films with reduced oriented nanostructure and very weak SAXS signals that are comparable to those from the best a-Si:H. The evidence of a non-uniform Ge distribution in a-SiGe:H alloys by ASAXS is intriguing and further work is underway to clarify this important issue.

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Title: Polycrystalline Thin Film Cadmium Telluride Solar Cells
Fabricated by Electrodeposition

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Objectives

The objective of this project is to develop improved processes for the fabrication of CdTe/CdS polycrystalline thin film solar cells. The technique we use for the formation of CdTe, electrodeposition, is a non-vacuum, low-cost technique that is attractive for economic, large-scale production.

Technical Approach

In FY 1996, our research and development efforts have focused on several steps that are most critical to the fabrication of high-efficiency CdTe solar cells. These include the optimization of CdTe and CdS electrodeposition processes, the effect of CdCl₂ treatment of CdS, the post-deposition annealing of CdTe, and back contact formation using Cu-doped ZnTe.

Results

Effect of CdCl₂ treatment of CdS films

We performed a systematic investigation on the effects of the CdCl₂ treatment of CdS on CdTe-CdS interdiffusion and on the properties of CdS films [1,2]. Performances of CdTe/CdS cells fabricated with both as-deposited and CdCl₂-treated CdS films indicated that J_{sc} is strongly affected by the CdCl₂ treatment of the CdS films. On average, J_{sc} is increased by 2.7 mA/cm² as a result of this treatment. V_{oc} is independent of the CdS processing. The enhanced short-circuit photocurrent results from the improved quantum efficiency in the spectral range close to the bandgap of CdS. The spectral response of cells fabricated with CdCl₂-treated CdS shows a sharp increase at the wavelength corresponding to the CdS bandgap (500 nm) and a very high quantum efficiency between 500 and 600 nm. The spectral response of cells fabricated with as-deposited CdS, on the other hand, shows a much more gradual increase at wavelengths longer than 500 nm. The quantum efficiency reaches high values only at wavelengths close to 600 nm.

The differences in spectral response originated from the change of optical transmission introduced by CdTe-CdS interdiffusion. Because of the finite solubility of CdS and CdTe within each other, interdiffusion between CdS and CdTe layers occurs during the final annealing of CdS/CdTe films. As a result, a CdTe-rich ternary phase (CdTe_{1-x}S_x) is formed in the CdTe layer. A CdS-rich ternary phase (CdS_{1-y}Te_y) may also be formed in the CdS layer. The degree of these interdiffusion processes is affected by the CdCl₂ treatment of CdS films and was quantitatively measured by monitoring the change of line shape of XRD patterns. For CdS/CdTe films prepared with CdCl₂-treated CdS, the CdS XRD peaks yielded a lattice spacing characteristic of pure CdS. For films prepared with as-

deposited CdS, on the other hand, the XRD pattern yielded an increased lattice spacing, indicating the formation of an alloyed phase. Therefore, while only a negligible portion of the CdS is converted to $\text{CdS}_{1-y}\text{Te}_y$ for the CdCl_2 -treated CdS, it is fully converted to the ternary phase when as-deposited CdS was used. The y value was estimated to be 4.4% in $\text{CdS}_{1-y}\text{Te}_y$. This large difference in the extent of Te diffusion into CdS is expected to originate from not only the differences in grain size, but also the differences in defect density in the two types of CdS films. As a result of the interdiffusion and formation of $\text{CdS}_{1-y}\text{Te}_y$, the optical transmission of CdS in the wavelength range of 500–600 nm deteriorates significantly if the CdS did not receive a CdCl_2 treatment prior to CdTe deposition.

We have also measured the photoluminescence of the CdTe/CdS films. For films prepared with as-deposited CdS, a broad peak at 1.74 eV was observed. This transition is characteristic of the $\text{CdS}_{1-y}\text{Te}_y$ ternary phase [3] and is attributed to a deep level associated with CdS structural defects introduced by Te diffusion in CdS. For films prepared with CdCl_2 -treated CdS, this peak was not observed. The photoluminescence results therefore confirm the results obtained from XRD, i.e., CdCl_2 -treated CdS remains pure CdS while non-treated CdS is fully converted to ternary phase during the final annealing step.

The diffusion of CdS into CdTe was also investigated. For CdTe/CdS films prepared with as-deposited and CdCl_2 -treated CdS, the sulfur content in the ternary phase was found identical, approximately 2.3% in both cases. The proportion of the ternary phase relative to the binary phase was slightly higher for films prepared with as-deposited CdS. The formation of the ternary $\text{CdTe}_{1-x}\text{S}_x$ phase implies significant consumption of the CdS layer. Based on the relative intensity of XRD peaks corresponding to the binary and ternary phases, we estimate a decrease of CdS film thickness of ~60 nm for a CdTe film thickness of 3.4 μm . This was confirmed by surface profilometry measurements performed after removing the CdTe layer mechanically. This high CdS consumption caused by CdTe–CdS interdiffusion plays a critical role in determining the smallest CdS thickness that can be employed in CdTe/CdS solar cells.

Back contact formation using Cu-doped ZnTe.

Thermally evaporated Cu-doped ZnTe has yielded very low contact resistance ($< 0.1 \text{ ohm.cm}^2$) on electrodeposited CdTe thin films and high fill factors (> 0.74) of the resulting cells [4]. Because of the well known high diffusivity of Cu in polycrystalline thin films, it is desirable to bring the Cu concentration in these materials to as low a level as possible while still maintaining the performance of the contact. Our previous studies investigated mostly ZnTe films doped with relatively high levels of Cu, between 4 and 10 at. %, with the best devices obtained at a Cu concentration of 6 at. % [4–6]. We have extended our research by studying ZnTe films doped with low concentrations of Cu and investigated systematically the structural, compositional, and electrical properties of the Cu-doped ZnTe films as a function of Cu doping and annealing temperatures.

The structure of the ZnTe films was studied with x-ray diffraction. For as-deposited films and films annealed at low temperatures, the crystalline phase of ZnTe showed a dependence on Cu doping level. Low Cu doped (< 3 at. %) films exhibited cubic (zincblende) phase with a preferred orientation of (111), whereas high Cu doped (6 at. % and 8 at. %) films showed hexagonal (wurtzite) phase. After annealing at a higher temperature (450°C), all films exhibited zincblende structure.

Electron probe microanalysis revealed that at low Cu concentrations (< 6 at. %), there is a deficiency

of cations (Zn, Cu); At Cu concentrations higher than 6 at. %, the cation concentration exceeds the anion concentration, suggesting that Cu in these films exists mostly in the Cu_2Te -like state. The cation deficiency at low Cu concentration suggests the existence of Zn vacancies which act as acceptors. The existence of Cu_2Te -like bonding, on the other hand, suggests that most of the Cu atoms are electrically inactive because all the valence electrons are fully coordinated.

Hall effect measurements performed on ZnTe films revealed several features: (1) The lowest resistivity was obtained at an annealing temperature of 350°C . At higher annealing temperatures, the resistivity increases; (2) Very high mobility ($20 \text{ cm}^2/\text{V}\cdot\text{s}$) was obtained at low (1 to 2 at. %) Cu doping and relatively low annealing temperatures (350°C). With increase in Cu concentration, the mobility decreases; (3) 2.0 at. % is the lowest Cu doping that can yield a p-type doping concentration of over 10^{18} cm^{-3} . At lower Cu concentrations (0.5 - 1.0 at.%), charge compensation leads to a very low doping concentration; (4) For films annealed at a low temperature (250°C), the highest doping efficiency was obtained with a Cu concentration of 2 at. %.

The activation energy of conductivity of ZnTe films was deduced from the temperature dependence of dark conductivity. The activation energy decreases with increasing Cu concentration and annealing temperature and was in the range between 0.2 and 0.5 eV. These values correspond well with the ionization energy reported for intrinsic defect levels in ZnTe (0.25 eV, and 0.5 eV) and are higher than the ionization energy of the Cu_{Zn} acceptor level (0.12, 0.15 eV) [7,8]. This indicates that intrinsic defects (e.g., Zn vacancies) are the dominant acceptors. This is consistent with the high degree of cation deficiency observed in low Cu-doped films. It is possible that the main effect of Cu was to create this cation deficiency rather than acting as acceptors directly.

CdS/CdTe solar cells were fabricated with ZnTe films containing low Cu concentrations. Good ohmic contacts were obtained on all films using Cu concentrations as low as 1.0 at. %. The ZnTe:Cu post-deposition annealing temperature was varied according to the Cu concentration used. For a Cu concentration of 2 at. %, the best cell performance was obtained at an annealing temperature of 270°C (Table 1). This is much higher than the optimal annealing temperature for ZnTe films doped with 6 at. % Cu (170°C). The much higher processing temperature used for the 2 at. % Cu doped films implies that the long-term stability of the resulting cells can be much higher.

TABLE 1. Effect of ZnTe post-deposition annealing temperature on cell performance. The Cu concentration was 2 at.%. CdTe films prepared by Solar Cells, Inc. were used.

Annealing Temp. ($^\circ\text{C}$)	η (%)	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	dV/dJ at V_{oc} ($\Omega\text{-cm}^2$)
200	1.8	532	9.4	0.36	20.1
270	13.3	796	23.9	0.70	4.5
350	7.1	678	20.7	0.50	18.8

Summary

The effect of CdCl_2 treatment of CdS films on the photovoltaic performance of polycrystalline CdTe/CdS solar cells was investigated. X-ray diffraction studies indicated a full conversion of CdS into $\text{CdS}_{1-y}\text{Te}_y$ for films prepared with as-deposited CdS and negligible formation of ternary phase for

films prepared with CdCl_2 -treated CdS. The difference in interdiffusion leads to differences in optical transmission of CdS films and the spectral response of CdTe/CdS solar cells. The short-circuit current density increased as a result of improved spectral response in the wavelength range of 500-600 nm for the CdCl_2 -treated CdS.

The effects of Cu doping concentration and post-deposition annealing temperature on the structural, compositional, and electrical properties of ZnTe were investigated. Low contact resistance and high fill factors were obtained using low-Cu-doped ZnTe as a contact layer in CdS/CdTe solar cells. The decreased Cu doping concentration is expected to improve the long-term stability of resulting CdTe solar cells.

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Title: Device Physics of Thin-Film Polycrystalline Cells and Modules

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Objectives

The objectives of this program are (1) the separation and quantification of individual losses in specific thin-film solar cells, (2) the detailed characterization of small modules, and (3) the presentation of a viable model for the forward-current loss mechanism.

CdTe Cell Analysis

Two cycles of a team project to investigate the effect of CdS thickness on CdTe cells were completed in 1996. In the first cycle [1], cells were fabricated at six collaborating laboratories with CdS thicknesses ranging from 500 to 3000 Å. Current fell with CdS thickness more-or-less as expected. It was about 4 mA/cm² less for the thickest compared to the thinnest. Voltage and fill-factor were reduced with the thinnest CdS, but showed no systematic changes above 1000 Å. Cycle two [2], involved seven fabrication laboratories and targeted thinner CdS (200 and 800 Å). Fig. 1 shows voltage and fill factor is a function of CdS absorption. 40% absorption corresponds roughly to 1000 Å. It is clear that the CdS thickness is generally reduced by CdTe deposition, presumably due to intermixing. In this cycle also, there was usually deterioration of voltage and fill factor for CdS layers less than 1000 Å, but there were exceptions even at the smallest thicknesses. In fact, recent cells from Golden Photon, which are not shown in Fig. 1, have a fill factor of 0.7 and a voltage over 800 mV with CdS so thin that there is no absorption within measurement error.

CI(G)S Cell Analysis

One project was to investigate two closely related effects observed in some CIS cells. These are (1) a significant voltage shift in dark curves before and after illumination, and (2) a distortion of the red-light current-voltage curve that largely disappears when blue photons are added [3]. Fig. 2 shows an example of dark and red-light curves before and after white-light illumination as well as the recovery of the red-light curve with time. The proposed explanation is that in some cases blue photons increase the carrier density of the CdS window sufficiently to move from a regime where the CdS/CIS band offset has an impact on the current-voltage curve to one where it does not. A second major project, where Jennifer Granata has been fabricating the cells at NREL, is the effect of sodium on junction quality [4]. Comparisons are made of CIGS cells on five different substrates with and without a barrier to block substrate sodium and with and without the deliberate introduction of sodium. Quite clearly the cells with neither added sodium nor sodium from the substrate showed weaker performance. Two other projects were measurement of transient CIS effects as part of a

collaborative team effort and the detailed comparison of high-efficiency CIGS cells fabricated at NREL. In the latter case, it was found that the best junction properties from the three primary deposition systems used at NREL were all quite similar.

Module Analysis

Ingrid Eisgruber completed a two-year development of polycrystalline thin-film module-analysis techniques [5,6]. This work included: (1) The relationship between nonuniformities in temperature or illumination and the output of a module; (2) The failure of the single-parameter series-resistance approximation and consequent need for a distributed resistance model, to analyze cells with the geometry typically found in thin-film modules; (3) A study of local-defect signatures, including the separation of shunting defects from those responsible for low photoresponse; (4) A multiple-chopping-frequency technique to separate variations in photoresponse and shunting among module cells when electrical access is limited to the end cells; and (5) The interpretation of laser-scan response when local intensity is one or more orders of magnitude above solar values.

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Blue Photon Absorption

Figure 1. CdTe cell voltage and fill factor as a function of CdS absorption. Cells from seven laboratories.

Figure 2. CIS dark and red-light curves before and after white-light illumination. Recovery shown at bottom.

Title: Development of High, Stable-Efficiency
Triple-Junction a-Si Alloy Solar Cells

Organization: Energy Conversion Devices Inc.
1675 West Maple Road, Troy, MI 48084

Contributors: X. Deng, Principal Investigator; M. Izu, S. J. Jones,
T. Liu and S. R. Ovshinsky

Objectives

The overall objective of this amorphous silicon research program is to develop high efficiency a-Si solar cells and to develop and improve processes for large area deposition of a-Si solar cells and modules. The knowledge obtained and technologies demonstrated in this program will be immediately incorporated into ECD's continuous roll-to-roll deposition process to further enhance its photovoltaic manufacturing technology.

Technology

In ECD's solar cell design, triple-junction a-Si alloy solar cells are deposited onto stainless steel substrates coated with Ag/ZnO back reflector. This type of cell enables us to use a continuous roll-to-roll deposition process to manufacture a-Si PV materials in high volume [1-5]. Using this design, ECD has previously achieved record high initial solar cell efficiency using the following features: 1) a triple-junction two-bandgap, spectrum splitting solar cell design; 2) a microcrystalline silicon p-layer; 3) a bandgap profiled a-SiGe alloy as the bottom cell i-layer; 4) a high performance Ag/ZnO back reflector; and 5) a high performance tunnel junction between component cells. The research team at United Solar have recently used the same design to prepare a 14.5% initial efficiency device, a new world record.

Approaches and Accomplishments

In this program, we are further advancing ECD's existing PV technology by performing the following tasks:

- Task 1: Optimization of large-area plasma deposition of a-Si films;
- Task 2: Optimization of large-area plasma deposition of a-SiGe films;
- Task 3: Research on $\mu\text{-Si p}^+$ deposition using VHF plasma; and
- Task 4: Optimization of a-Si solar cell back-reflector.

In the following, we summarize our research under various tasks of this program.

Improvement of deposition uniformity and quality over large-area for a-Si and a-SiGe

One of the key issues related to large area cathodes in a high volume PV manufacturing process is the deposition uniformity. We use ECD/United Solar's 5MW continuous roll-to-roll a-Si solar cell processor to study the deposition process related to large cathodes. To test the deposition uniformity, we deposit and evaluate solar cells whose a-SiGe intrinsic layers were made at different position of the deposition chamber in reference to the RF cathodes while the stainless steel web is under static condition. Figure 1(a) depicts one of the uniformity problems encountered when high deposition rates are used. This figure shows the performance of a-SiGe solar cell deposited near the gas inlet, the center, and near the gas outlet. The cells

for which data is shown in Figure 1(a) were made under unoptimized conditions and without the benefit of a Ag/ZnO back reflector. The I-V measurements for cell characterization were made using 530 nm cutoff filtered AM1.5 light. When cells were made from the exhaust side, the center and the gas inlet side of the cathode burn, it was found that on average for the bottom cell preparation the Ge content increased by 8-12% as one scanned from the exhaust to the inlet side of the cathode. As can be seen from the data in the figure, this increase in Ge content led to the expected decreases in V_{oc} and FF and an increase in J_{sc} when the properties were scanned across the cathode length. The increase in Ge content is confirmed with Energy Dispersive Spectroscopy measurement. Along with this increase in Ge concentration an increase in the i-layer thickness was also found as can be seen from the data in Figure 1(a). This uniformity problem leads to fluctuations in the Ge content across the i-layers of cells prepared with the web moving. These fluctuations in the Ge content can be observed in the SIMS data in the form of a near oscillatory profile of the Ge concentration. Such fluctuations in the Ge content should lead to variations in the bandgap and mobility edges across the i-layer which could hinder carrier collection.

We have extensively investigated this issue and found that the deposition rate and deposition temperature have strong effect on the thickness and Ge content uniformity. After optimizing the deposition process, we have significantly improved the deposition uniformity in terms of both the film thickness and Ge content, as shown in Figure 1(b).

Besides improving the deposition uniformity and quality of a-SiGe layer over large area, we have also optimized the deposition uniformity and quality of a-Si layer for the top cell intrinsic layer, under Task 1. Figure 2 shows an I-V curve for a top component cell deposited using large cathodes of the 5MW production machine after process optimization. The top cell, deposited on bare stainless steel without a back-reflector, shows a V_{oc} of 0.97 V and a FF of 73%, indicating high quality film deposition over the large area cathodes. Furthermore, we have deposited top cells with V_{oc} up to 1.00 V.

Figure 1. Device performance for a-SiGe solar cells with i-layer deposited near different positions of the cathodes: gas exhaust, center, and gas inlet. (a) before process optimization, showing non-uniform deposition; (b) after process optimization, showing uniform deposition.

Figure 2. I-V curve of an optimized top cell.

Figure 3(a). I-V curve of an a-Si solar cell with VHF p-layer.

Figure 3(b). I-V curve of an a-Si solar cell with RF p-layer.

Research on μ c-Si p^+ deposition using VHF plasma

Under Task 3, we have conducted comprehensive research to develop μ c-Si p^+ layer using Very High Frequency (70 MHz) deposition process with the objectives of 1) establishing a wider process window for the deposition of high quality p-materials, and 2) further enhancing the performance of a-Si solar cells by improving its p-layers.

Figure 4. RHEED pattern of a device with VHF p-layer at the top, showing high volume fraction of microcrystalline phase in the p-layer.

We deposited μ c-Si p-materials using a VHF plasma enhanced CVD process in a research scale multi-chamber load-locked solar cell deposition system. The substrate is SS/n-i in which the doped n-layer and the undoped a-Si intrinsic layer were deposited previously in ECD's roll-to-roll machines. A design of experiments (DOE) approach is used for the exploration and optimization of deposition parameters.

After process optimization, we have deposited VHF p-layer which provides higher solar cell performance than p-layer deposited using RF (13.56 MHz) plasma. Figure 3 (a) exhibits the I-V characteristics of a solar cell deposited in a small area R&D system using VHF plasma for the p-layer deposition, showing a V_{oc} of 0.93 V and a FF of 69%. This device performance is better than that of devices with p-layer deposited in the same system using RF plasma (V_{oc} of 0.95V and FF of 65%), as shown in Figure 3(b). Figure 4 is a RHEED pattern of a device with VHF p-layer on the top. The sharp line in the 220 and 311 rings and the dark background in between these rings indicate that the VHF p-layer is a microcrystalline materials with high degree of microcrystallinity.

By comparing the optimized deposition of VHF p-layer and RF p-layer, we found that the optimum condition for VHF p-layer requires a higher boron concentration in the inlet gas mixture compared with RF p-layer. This is due to the strong etching effect of VHF plasma which, on one hand, promotes microcrystalline formation and, on the other hand, etches the film from the i-layer. The etching of the i-layer by VHF plasma effectively put more Si species into the gas mixture therefore a higher ratio of BF_3

and SiH_4 is needed for the inlet gas to keep the same level of B/Si in the p-layer. Our observation that the device thickness reduces with longer VHF p-layer deposition supports this argument.

Optimization of a-Si solar cell back-reflector

We have performed extensive research to optimize the deposition process of the newly constructed 5MW back-reflector deposition machine. After process optimization, we have achieved highly textured and highly reflective Ag/ZnO back-reflector. Amorphous SiGe solar cell is deposited in R&D system onto these Ag/ZnO substrates to evaluate the back-reflector characteristics. Figure 5 is a QE curves for an a-SiGe single junction solar cell onto an optimized Ag/ZnO back-reflector deposited in the large area back-reflector machine. The QE curve shows excellent red response. The integrated short circuit current from the QE curve for AM1.5GL spectrum is 25.6 mA/cm^2 , indicating high performance of the back-reflector.

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Figure 5. Quantum efficiency curve of an a-SiGe device deposited on an optimized Ag/ZnO back-reflector produced in the 5MW roll-to-roll back-reflector machine.

Title: CIS Photovoltaic Technology

Organization: Energy Photovoltaics, Inc. (EPV)
Princeton, New Jersey

Contributors: Alan Delahoy, principal investigator; Jeff Britt, co-principal investigator; Zoltan Kiss, program manager; G. Butler, D. Chorobski, M. Doroba, J. Esler, F. Faras, J. Jaroszynski, G. McComiskey, A. Sizemore, F. Ziobro.

Objectives

The overall project goal is the demonstration of encapsulated large area Cu(In,Ga)Se_2 photovoltaic modules (with powers of about 35W) prepared using techniques and equipment that can be readily developed for cost-effective manufacturing. Achievement of this goal requires first and foremost a method and process for formation of device grade CIGS on large glass substrates with good adhesion and uniform characteristics of thickness, composition and electronic properties. A method is similarly required for formation of the relatively thick, top transparent conductor. Methods must be developed that are inherently scalable, and with due regard for safety, low materials cost, and uncomplicated process control.

Approach

Following demonstration of a 9.6% aperture area conversion efficiency for small laminated submodules, Energy Photovoltaics has moved aggressively to establish a complete pilot line for production of CIGS modules having an area of 4300 cm^2 (substrate size $96.5 \text{ cm} \times 44.5 \text{ cm}$). The line consists of a) a load-locked, 5 cathode, in-line sputtering system for metals and ZnO b) a load-locked pentium-controlled large area CIGS compound formation machine (Zeus), c) chemical bath deposition system for CdS, d) mechanical and other scribing stations, e) specialized diagnostic stations f) ultrasonic bonding for foil attachment g) vacuum laminator for EVA h) steady state and pulsed light I-V stations. The Zeus system contains a novel dual linear source for material delivery and can operate at substrate temperatures close to the softening point of glass while maintaining glass flatness. Smaller scale evaporation and selenization systems are used for CIGS recipe development and cross system comparisons.

Results

The primary task is absorber formation. Routes to absorber formation have included selenization of sputtered metal precursors and of Se-containing precursors in which the indium is deposited in the form of an indium selenide [1,2]. Taking advantage of the relatively high vapor pressure of Se and In_2Se_3 at moderate temperatures, these materials are supplied to large area plates by linear evaporative sources. Substrate translation is employed to achieve coating uniformity. It has been found that potentially troublesome issues such as adhesion, pinholes, stoichiometry and homogeneity are very sensitive to process type and processing conditions. Diligent experimentation has been required to conquer these pitfalls. With these areas under control we are confident that a renewed focus on intrinsic device efficiency will bring substantial rewards. Table 1 summarizes the PV parameters obtained for various devices and modules. Using a sequential type recipe (in which Cu is not supplied simultaneously with In) a device efficiency of 13.9% was achieved. Diagnostic cells formed on CIGS material prepared on 0.43 m^2 substrates in the Zeus system have exhibited efficiencies in excess of 10%. Currently, work is focused on mastering the module processing necessary to realize the potential performance of the Zeus material.

The replacement of the CdS window layer with a Cd-free material continues to be a high priority. Reasonable device results have been obtained with evaporated In_xS_y buffer layers, and improved short wavelength quantum efficiencies have been demonstrated [3]. Chemical treatment of the CIGS after its formation has also proved to be a useful technique [3].

With a view to improving film quality and throughput, CIGS depositions and chemical reactions during selenization have been studied by laser reflectance and differential thermometry [3]. Both techniques are sensitive to phase changes and allow identification of critical temperatures.

A further important task is optimization of the conducting ZnO applied to a CIGS module in order to maximize the module's efficiency. EPV currently employs pulsed bipolar sputtering of a $\text{ZnO}:\text{Al}_2\text{O}_3$ target in an Ar/O_2 atmosphere for coating 0.43 m^2 modules [4]. To a greater or lesser degree, all deposition variables affect the resulting ZnO:Al quality. Our approach to effective optimization has been a) to appropriately quantify the performance of different films, and b) to estimate performance of films prepared under new conditions to guide choice of future deposition parameters. A computer model that performs exact calculation of CIGS module efficiency for fixed CIGS parameters but with ZnO sheet resistance (R) and optical transmission (T) as input parameters is the tool that we have developed to quantify ZnO performance. Using this program we find the iso-efficiency contours for CIGS modules as a function of ZnO R and T to be as shown in Figure 1. The open and closed circles represent measured R , T pairs for ZnO films on glass prepared using the large area process under various conditions (including O_2 flow) and with various thicknesses. The figure allows immediate identification of the most suitable films. Also shown in this figure are two heavy solid lines representing modeled R , T contours for films sputtered with two different oxygen flows (but under otherwise identical conditions) with film thickness as a variable parameter. Along these contours, film thickness increases from $0.5 \text{ }\mu\text{m}$ to $3.0 \text{ }\mu\text{m}$. Curves such as these are used to select new deposition parameters. For example, for a given set of conditions, thickness should be chosen so that the heavy (R , T) contour is locally parallel to the iso-efficiency curves. In the presence of significant internal device series resistance, the iso-efficiency curves assume different slopes, as illustrated by the dotted lines in Figure 1. Under these conditions the ZnO should be thicker to limit excessive total resistance.

For certain sputtering configurations we have found that the sheet resistance of the ZnO:Al films can be reliably and permanently reduced by post-deposition annealing. Figure 2 shows the sheet resistance of a film measured in-situ upon ramping from room temperature to 160°C in vacuum at an average rate of $1.3^\circ\text{C}/\text{min}$. The final resistance was 0.56 times the starting value and remained essentially constant during cooling. Only small changes are observed in optical transmission after annealing. The five solid triangles in figure 1 represent (R , T) pairs for annealed ZnO films on glass. We have confirmed that a similar reduction in resistance is obtained for ZnO on CdS/CIGS.

During the course of experiments designed to uncover possible limiting factors in device conversion efficiency, a new method was developed to determine the internal resistance of thin film solar cells [5]. The method involves illumination of a small region of the cell with a laser beam sufficiently intense to make the internal resistance easily observable. For the CIS and CIGS cells examined, specific internal resistances ranging between 7×10^{-2} and $3 \times 10^{-4} \text{ }\Omega \text{ cm}^2$ were obtained. This technique was subsequently set up at NREL by Dr. T. J. McMahon and has also proved useful for understanding thin film CdTe cells.

The general layout of EPV's CIGS plates prior to lamination is shown in Figure 3. Such CIGS plates are currently being fabricated with powers of about 20W, representing a 5% aperture area efficiency. Table 1 shows measurements taken in sunlight. Considerably higher voltages should be obtainable upon realization

of more suitable Ga profiles. Intrinsic device fill factor also needs to be improved. Incremental improvement of our currently prepared ZnO can be anticipated, although substantially improved conductivity and transmission probably awaits implementation of reactive sputtering from a metallic target.

We are finding that the testing of CIGS modules can present some problems. The wide spectral response requires attention to light spectral content, the absence of light soaking with pulsed illumination can yield lower fill factors than those obtained under steady illumination, and I-V scan rates can also affect results.

Conclusions and Future Plans

Development of CIGS recipes that are appropriate for EPV's large area systems, and continuous improvement of the Zeus CIGS formation machine have resulted in CIGS plates that are flawless to the eye and that can be processed reliably into modules producing about 20 watts. Better control of the Ga profile, improved ZnO conductivity, and reduction of area loss will enable the 35 W goal to be met. This, we believe, will mark a significant milestone along the path to commercialization of thin film CIGS modules.

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Table 1: Summary of PV parameters for CIGS devices and modules

<i>device type</i>	<i>area & basis (cm²)</i>	<i>number of cells</i>	<i>V_{oc} (V)</i>	<i>I_{sc} (mA)</i>	<i>FF (%)</i>	<i>P_{MAX}</i>	<i>Eff. (%)</i>
R&D cell	0.422 total	1	0.633	13.3	69.6	5.87mW	13.9
R&D module	135.2 aperture	19	8.78	223	66.4	1.30W	9.6
Zeus diagnostic cell	0.159 active	1	0.466	5.39	64.7	1.63mW	10.2
Zeus plate	3939 aperture	83	33.8	1296	45.9	20.1W	5.1

Figure 1. Iso-efficiency contours for CIGS modules as a function of ZnO sheet resistance and weighted transmission, together with experimental and modeled data for ZnO.

Figure 2. Sheet resistance of ZnO measured in-situ during ramping to 160 °C.

Figure 3. Layout of monolithic CIGS plate prior to lamination.

Title: CdTe Module Testing and Study of Transients and Irreversible Effects in CdTe Thin Film Solar Cells

Organization: Florida Solar Energy Center, University of Central Florida, Cocoa, Florida 32922-5703

Contributors: Neelkanth G. Dhere, Principal Investigator, Lucy M. Orozco, Abhijeet Deshpande, and Kaustubh S. Gadre

Objectives

The overall objective of the study the transients and irreversible effects in CdTe polycrystalline-thin-film solar cells.

Technical Approach

CdTe module panels were installed after inspection and photography. Leads from the thermocouples, precision spectral pyranometer, RH series relative humidity transmitter, and barometric pressure sensor were connected to the data boxes on the roof. The data is transferred to the data acquisition equipment, and measurement and control system package. The Campbell data acquisition and control system is programmed to take one reading every 15 seconds. Data thus collected is averaged every 15 minutes and stored. The data is downloaded from the Campbell control system once every week. The stored data is transferred to MS Excel files for further analysis.

Inspection, Assembly, Mounting, and Data Acquisition

CdTe modules fabricated by Solar Cells Inc (SCI) were received in June 1996. Firstly the CdTe modules were carefully unpacked and inspected. Each module was photographed. All the modules were well-fabricated. There were no flaws visible to the naked eye. Following suggestions of colleagues from SCI, the modules were inspected with a magnifying lens to catalogue minute flaws. The worst flaws or patterns of flaws from each module were photographed by zooming in on them.

The twelve PV modules were assembled in three panels by placing them face down in sets of four on rubber mats. The support runners were placed in position and attached with bolts and washers. The assembled PV panels were lifted carefully with leather-gloved hands, flipped to bring the front side up, and were lifted carefully and placed on a fork lift. The panels were raised on to the roof of the low-bay laboratory of FSEC and placed on existing beams provided for mounting of solar arrays. Aluminum support structure was fabricated and mounted on the support beams. The modules were moved onto the support structure and lifted in position and bolted so as to be tilted at 24 degrees relative to the horizon. Figure 1 shows a photograph of the array.

Two sets of conduits were run from the PV array: one for power and another for data communication. There are eleven parameters to be monitored, three temperature measurements from the three solar panels, one ambient temperature (the ambient temperature being the ambient temperature below the solar panel), one thermocouple to measure the room temperature in the

Figure 1. SCI CdTe thin-film solar cell array

laboratory, voltage, current, sensor to measure the atmospheric pressure, and relative humidity sensor to measure the relative humidity and pyranometer. Arrangements have been made to monitor the wind speed. Shielded cables were used to transfer the data from the measuring instruments to the data box and from the data box to the data collection equipment.

The voltage and the current lines were collected in the power enclosure. The four modules in each panel are divided in two pairs both connected in series. The two pairs are connected in parallel. The three panels are connected in parallel. The 0-130 volt output of the solar array is connected from the power enclosure to a maximum power point tracker through a fused DC switch. Currently an 8 ohm one kilo-watt resistor connected across the maximum power point tracker serves as a load. The voltage leads were connected across a voltage divider circuit to step down the voltage from 130 V to 2.36 V to bring it within the measuring range of a channel in the Campbell data acquisition and control system. The current is measured by connecting a shunt resistance in series with the negative lead from the solar panel so as to collect a millivolt reading corresponding to the current. The voltage and the current measuring leads were transferred to the data box via a shielded cable.

The data box was used for transmitting the data to the Campbell data acquisition and control system via a 20 pair shielded data cable while the temperature readings were sent via a 8 pair thermocouple extension cable. The shields of both cables were properly connected to ground. The supply ground and the shield ground were protected by a fuse in the CR10 data acquisition system which will protect the sensors in case a large current flows through the ground. 12 V supply to operate the pressure sensor and the relative humidity measuring equipment was tapped from the CR10 data acquisition system. The 1.5 V to 5.6 V pressure output reading was reduced by half by collecting

its output across a voltage divider circuit. Similarly the 4-20 mA signal generated by the relative humidity sensor was converted to a millivolt signal. A copper constantan thermocouple was prepared to measure the reference temperature at the CR10X data acquisition system. The thermocouples and pressure, and relative humidity sensors along with the reference battery voltage were connected to the AM416 multiplexer. The voltage, current and the pyranometer signal wires were directly connected to the CR10X data acquisition system. The parameters directly connected to the data acquisition and control system were differentially measured while their respective shield wires were connected to the ground. The remaining shields were connected to analog ground.

An SC32A interface was used to connect the Campbell data acquisition and control system to a serially connected computer. A DC112 modem has also been installed, so that the data can be collected from any computer on the network. A program was written to collect the readings for the required parameters and download to the Campbell data acquisition system. It was programmed to collect readings at fifteen second intervals and an average reading being taken after every 15 minutes. Efforts were made to minimize the loss of signal during transmission by ensuring that there were minimum bends, twists and turns in the wires. Also wires were not routed near electrical cables. The power cables from the solar panel were routed independently through a metal conduit. Due to a minor error in the program the data for the current and the solar irradiation was not stored in the final storage area of the Campbell data acquisition system during the first few days. This error was rectified on Nov. 18, 1996. Hence data for current and irradiance is not available before this date. Readings are being collected and retrieved every week for tabulations and further study.

A DC fused switch was mounted along with the maximum power point tracker and a 1 KW wire wound resistor. Care was taken to mount the resistor at an isolated place and at a height where someone cannot inadvertently touch the resistor. Appropriate warnings have been displayed as a precaution. The resistor was clamped on a wooden stand and mounted with sufficient space around it to allow it to cool. Provision was made to avoid a reverse flow of current to the solar panel by connecting a diode across each of the panels. This has been done at the small data boxes where the leads from the solar panels were connected. The load wires were connected to a fused DC switch. The maximum power point tracker was connected after the switch. The load current was measured across the load resistor. Before beginning to collect the data the dark covers which were put on the panel were removed and the solar panel surface was cleaned. The current and voltage were constantly monitored to watch for any major variations or irregularities in the measured values. The load resistance was also observed to see if it was getting excessively hot.

A log is being maintained to record readings with an accurate multimeter and a clamp meter and is compared with the values measured by the sensors. Corresponding changes were made to correct the minor differences between the measured and the theoretical values. Initially an engineer collected the data from the different instruments and noted those as well as the readings measured by the Campbell data acquisition system. To reduce the errors, which may arise due to a change in the cloud condition, two engineers worked in tandem. Readings were taken simultaneously by both, one measuring the instrument voltage on the roof and the other observed and noted the values measured by the Campbell data acquisition system.

Module Performance from Nov. 20 to Dec. 31, 1996

Title: Polycrystalline $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ PV Solar Cells

Organization: Florida Solar Energy Center, University of Central Florida, Cocoa, Florida 32922-5703

Contributors: Neelkanth G. Dhere, Principal Investigator, Kevin W. Lynn, Mark E. Wollam, and Lucy M. Orozco

Objectives

The overall objective of the research project is to develop novel, low-cost scalable processes for the fabrication of stable and efficient copper-indium-gallium-diselenide, $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ and cadmium-telluride, CdTe polycrystalline-thin-film solar cells for economic, large-scale manufacture.

Technical Approach

PV Materials Laboratory of the Florida Solar Energy Center is carrying out studies with an aim to find a viable fabrication process to make CIGS solar cells that could be more easily transferred to a manufacturing process. The process uses two-stage selenization of magnetron sputtered metallic layers of Cu, In, and Ga in selenium vapor. Because sputtering of liquids can be problematic, CuGa alloy targets were fabricated. A two-stage selenization process was developed. The best results using a CuGa target with 22% Ga was an efficiency of 9.02% corresponding to the highest Ga_x content of $x = 0.18$. Since the optimum Ga_x content is known to be $x=0.28-0.32$, a second CuGa target with 66% Ga has now been added to achieve the higher gallium content. The goal was to obtain *double profiling* i.e. a high amount of Ga towards the back contact which decreases towards the p-n junction, and rises slightly again at the junction.

Gallium Content Enhancement in $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ Polycrystalline Thin Films

Several different deposition sequences have been chosen using the new CuGa [high 66% Ga] target. Figure 1 shows the deposition and selenization sequences. The thickness of individual layers have been provided in Table I. All selenizations were performed in the same manner, in a chamber under high vacuum (10^{-6} Torr). Following the preheating of selenium (99.999% pure) in a Knudsen-type Mo boat for 15 minutes, the selenium evaporation rate was raised to $25-50 \text{ \AA s}^{-1}$. The substrate temperature was then ramped up to 550°C in ~ 10 minutes. The samples remained at this temperature for approximately 30 minutes. The samples were then cooled to 300°C at a rate of about $12.5^\circ \text{C min}^{-1}$ while maintaining the selenium vapor incidence.

In the first experiment labeled New Series #1 (NS#1), the goal was to prepare a overall Cu-poor, $2.75 \mu\text{m}$ thick, thin film having the composition represented by $\text{Cu}_{0.92}\text{In}_{0.72}\text{Ga}_{0.28}\text{Se}_2$. In practice, the deposited layer thicknesses corresponded to the composition $\text{Cu}_{0.92}\text{In}_{0.72}\text{Ga}_{0.28+0.1}\text{Se}_2$. The additional $\text{Ga}_{0.1}$ was included to compensate for gallium that evaporated from the film during selenizations. The sequence of deposition of metallized layers and their thicknesses have been provided in Figure 1 and Table I. After each selenization, ohmic resistance of the films was

Selenization II
CuGa(high)
In
Selenization I
CuGa (low)
In
CuGa (low)
CuGa (high)
Mo
Glass

Figure 1. Sequence of depositions and selenizations of metallic layers

measured and the color of the films was noted. The film was uniform and dark grey after the first selenization. In this sample, the resistance measured after the first selenization was around 20 Ω . After the second selenization, the resistance of the films was around 6.5 k Ω . This time the color of the film was a noticeably lighter grey. Average composition of samples from new series NS#1 as analyzed by electron probe microanalyzer (EPMA) at an electron-beam energy of 20 keV is given in Table II. After analyzing a number of samples, it was determined that dark grey indicated a Cu-rich phase and the lighter shade represented a Cu-poor phase. The proportions Cu:In:Ga:Se near the surface as obtained by EPMA at an e-beam energy of 10 keV correspond to 23.03:26.53:3.20:47.24. In the bulk of the film the proportions Cu:In:Ga:Se correspond to 27.96:20.78:6.11:45.13. $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ thin films from series NS#1 had a Ga_x content of $x=0.244$ in the bulk of the film. The

Table I. Thicknesses of CuGa (high), In, and CuGa (low) layers in Angstroms

Series	Layer Thickness in Å						Totals		
	CuGa (high)	CuGa (low)	In	CuGa (low)	In	CuGa (high)	CuGa (low)	CuGa (high)	In
NS#1	815	4475	4625	1119	2490	204	5594	1019	7115
NS#2	1748	3832	3180	958	1713	437	4790	2185	4893
NS#3	1748	3832	3499	958	1184	437	4790	2185	5383
NS#4	1748	3066	3180	766	1713	437	3832	2185	4893
NS#5	874	3066	4893	766	0	1311	3832	2185	4893

best cell from this deposition sequence gave an efficiency of $\eta = 8.5\%$. This value is comparable to the earlier best efficiency of 9.02%.

From the first series NS#1, it was seen that Ga content was still too low. It was also decided to prepare a composite thin film with ~ 3000 Å thick CuGaSe_2 layer beneath a $2.7 \mu\text{m}$ thick $\text{Cu}_{0.92}\text{In}_{0.57}\text{Ga}_{0.43}\text{Se}_2$ layer. Hence in the second series NS#2 the layer thicknesses as shown in Figure 1 and Table I were chosen. These also included an additional amount of gallium equivalent $\text{Ga}_{0.1}$ to compensate for re-evaporation during selenization. From EPMA results, the proportions Cu:In:Ga:Se near the surface and the bulk of the film correspond to 27.85:19.79:6.40:45.96 and 27.99:17.45:8.90:45.65 (Table II). Thus in these samples, Ga_x content in the bulk of the film was significantly raised to $x = 0.36$. However, the copper content was excessive. The resistance values were low ($\sim 100\Omega$) after both the first and the second selenizations, indicating excessive proportion of copper content throughout the film.

Since copper content was too high, 10% more indium was added in the series NS#3 (Figure 1, Table I). These films had a Ga_x content of $x = 0.35$ and were more Cu-poor after the second selenization ($\sim 15 \text{ k}\Omega$). Unfortunately, the surface morphology was inhomogeneous. In the next series NS#4 (Figure 1, Table I), the composition was adjusted by reducing the total amount of $\text{CuGa}(22\%)$ by 20% while maintaining the amount of indium as in the series NS#2. This gave promising results. Resistivity values indicated a Cu-rich phase after the first selenization and a Cu-poor phase after the second. Moreover, surface morphology was uniform after both selenizations. Results of EPMA analysis (Table II) indicated Ga_x content near the surface to be $x \approx 0.26$ and $x \approx 0.33$ in the bulk. However, the films were not very adherent. One of the samples delaminated partially during the chemical bath deposition of cadmium sulfide hetero-junction partner layer.

In the series NS#5 (Figure 1, Table I), the entire amount of indium was included in the first metallized layers. Moreover, 40% $\text{CuGa}(\text{high})$ was transferred from the first metallized layers to the second. The idea was to prevent the formation of an undesirable InGa liquid phase during the second selenization. To obtain a Cu-rich phase after the first selenization, the amount of gallium in the first metallized layers was reduced to compensate for the additional indium. The results of composition analysis by EPMA for a representative sample are provided in Table II. Although Ga content follows the profile model, there may be two problems. Cu_y content did not fall between $0.86 \leq y \leq 0.96$ as it does in other high efficiency cells. Also resistivity values measured after the first selenization were high ($\sim 20 \text{ k}\Omega$). The increased bandgap from the higher gallium proportion was indicated in

Table II. EPMA Composition at 20 keV e-beam energy for films from new series NS#1-5

Series Number	Cu	In	Ga	Se
NS#1	27.96	20.78	6.12	45.13
NS#2	27.99	17.45	8.90	45.65
NS#4	25.31	18.62	8.25	47.82
NS#5	24.33	15.33	11.01	49.34

the spectral response of the solar cells. However, the conversion efficiency of solar cells formed from these films dropped to 4%. The efficiency reduction was mainly due to the lower fill factor arising from a very high series resistance. The higher gallium content thus seems to lead to a highly resistive gallium rich phase as well as poor crystallinity. The absence of a Cu-rich phase after the first selenization would impede the growth of large-grain and compact CIGS films with the benefit of fluxing action of Cu_{2-x}Se .

The most promising looking cells were from the series NS#4. By varying the sequence of depositions, it is expected to eliminate the highly resistive gallium rich phase. It should also improve the adhesion and crystallinity of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ thin films as well as the conversion efficiency of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ solar cells.

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Title: The Improvement of Near-Term CdTe Processing and Product Capabilities & Establishment of Next Generation CdTe Technology

Organization: Golden Photon, Inc., Golden, Colorado 80402

Contributors: John J. Kester, Scot Albright,

Objectives

Golden Photon, Inc. seeks to commercialize CdS/CdTe based photovoltaics through improvement of processing and manufacturing capability based on a solid understanding of the electronic properties of the device. Commercialization is directed at cost effective manufacturing that produces high efficiency modules approach meet the 20 year lifetime goal. At each stage of the development of manufacturing capability GPI will actively participate in safety, handling, and recycling programs for Cd containing material.

Approach

The optimization of efficiency and reliability of small cells and modules is guided by the quantification of device parameters, characterization of material properties, and the understanding of electronic phenomena on a molecular basis. With the goal of commercialization, these procedures for developing improved materials must be closely accompanied by the predictable control of manufacturing parameters. Once devices are completed, the results of accelerated testing of cells and modules must be correlated with long term outdoor exposure of modules under operating conditions. Our approach has included improvements in all areas of small cell and module production, characterization, and testing.

In addition to standard current-voltage testing, small cells and occasionally full size panels were characterized by a number of techniques depending on which part of the device was being probed. Quantum efficiency (QE) is measured using a tungsten filament lamp and monochromator. The QE has been measured at specific wavelengths or scanned. The relative quantum efficiency between 400 nm and the maximum near 620 nm gives a measure of the thickness of the CdS layer. The larger the response at 400 nm the thinner the CdS layer.

Within the past year GPI has upgraded its capabilities to measure capacitance and calculate carrier concentration. A LCR meter, voltmeter, and power source are computer controlled for measurement of capacitance as a function of voltage measured on cells. The acquisition program then calculates the carrier concentration as a function of depth in the device. This type of measurement was also used in capacitance/resistance measurements of sheet samples of CdTe. The frequency dependence allows separation of intragrain and grain-to-grain resistances.

Measurement of atomic composition of various films by mass spectroscopy is done on a routine basis to determine the effects of small amounts of dopants/contaminants on cell performance. The morphology of the CdTe layers is monitored by scanning electron microscopy. Changes in recrystallization procedures have a dramatic effect on the electronic and morphological

properties of the CdTe layer. Other projects have utilized the expertise of characterization facilities at NREL, including, time resolved photoluminescence, electron beam induced currents, energy dispersive x-ray spectroscopy, and x-ray photoelectron spectroscopy. On going work includes the techniques of Auger spectroscopy and infrared spectroscopy.

Numerous additional measurements for monitoring the manufacturing process were implemented in the past year. These measurements judge the quality of the product of each step in the process and allow correlation with final device parameters. With the NREL staff providing the baseline mechanism, GPI implemented a thickness monitoring technique for their CdS process. This just-off-line technique has allowed GPI to achieve statistical process control of this step in the manufacturing process.

GPI has upgraded its thermocycling capabilities to allow longer term cycling in different temperature and humidity environments. GPI has installed 24 hour light soak capabilities to allow accelerated testing of modules or small cells. GPI carries out initial test of process modifications by the use of small cells. By testing material from different areas of the same panel we not only have increased uniformity of results but also a larger statistical base and lower number of panels needed for testing. The small cells are encapsulated using a process similar to our panel encapsulation and placed on GPI's outdoor array.

Results

Improvements in process measurement and control have led to modules with higher efficiency and better long term stability[1]. Figure 1 shows an example of this improvement for a module from a recent batch. The normalized output for this 2' x 2' module is 29.3 watts. The total area efficiency of this panel was 7.8%, the efficiency based on the aperture area was 8.7%, and the active area efficiency was 10.4%. This data was taken after 10 weeks of exposure on GPI's outdoor array. This module demonstrated excellent stability by showing only 1.7% degradation after two weeks with no further change in output power after that period. This module showed similar stability behavior to others prepared in the same manner from this batch. The primary cause for the improvement in module efficiency was a change in the recrystallization process's time/temperature profile.

The long term stability has been demonstrated on modules on GPI's outdoor array. An example is shown in Figure 2 which has shown stable output for almost one year. This module was recently tested at NREL and had a $P_{\max} = 23$ watts. The rate of degradation of this module was less than 0.1 watt/year or 0.4%/year.

As well as raising the overall efficiency of module output, the uniformity of efficiency across the panel was improved over the past year. When small cells are made from different areas across the panel and the average efficiency is greater than 10% we often see a standard deviation of less than 0.5% efficiency or approximately 5 % standard error. The lowest standard error that has been achieved on panels that have been crosscut (64 cells with 0.8 cm² area) is 3%. For manufacturing reproducibility it is important to demonstrate quality product over many panels.

As an example during the past year, 90% of a 41 module batch were within 1 watt of the 24.5 watt average.

The understanding of atomic and molecular properties has continued with projects which examine the electronic effects of processing changes. Specific projects have included dopants, passivation, back contact issues, impurity levels in individual layers of the device, and CdTe morphology. The most significant progress has been made in the area of understanding of effects that CdTe morphology has on the final device parameters.

The effect of dopants was investigated in terms of the type, the concentration of dopant, and the method of introduction into the material. While there was some variation among the dopants used the largest effect on devices was seen in the concentration dependence of the dopant. High concentrations of dopants were clearly detrimental to the cell, particularly in voltage. The effect on the voltage was correlated with the change in carrier concentration as a function of depth as derived from data of capacitance as a function of voltage. Additional improvements in the uniformity of cell parameters were obtained when the method of incorporation of the dopants was changed to allow consistent dispersion of the dopant within the device.

Substantial changes in the electronic properties of devices were obtained with changes in morphology of the CdTe layer. Significant changes in morphology were produced by changes in the time and temperature profiles of the recrystallization process for CdTe. Through the optimization of the recrystallization process improvements were made in efficiency and long term stability of the device. The increase in efficiency was correlated with a decrease in series resistance of the device and an improvement in the uniformity of collection efficiency of the absorber layer.

The principle contributions to series resistance of the device come from the sheet resistance of the transparent conductive oxide layer, the back contact, and the conduction through the CdTe layer outside of the junction region. To address the last of these issues the sheet resistance of the CdTe layer was measured as a function of the various processing steps. Specially prepared CdTe layers were produced for measuring sheet resistance. The processing conditions were adjusted to have the morphology of the material match that of the CdTe near the back contact. Modeling of the intragrain resistance and grain to grain resistance and capacitance of the Cd layer allowed the separation of contributions by frequency dependent measurements. The primary conclusion was that the grain-to-grain resistance was the largest contribution to the resistance of this layer. In addition, it was determined that the improved morphology due to recrystallization produced lower sheet resistance with greater stability to exposure on an outdoor array.

Besides a change in series resistance the improvement in recrystallization also produced greater uniformity in collection efficiency as determined by electron beam induced current (EBIC) and photoluminescence studies. The photoluminescence intensity was greater from material which had the improved recrystallization indicating an overall better collection efficiency. The EBIC signal from the a cross section of the device indicates the collection efficiency either as a function of depth from the junction or a function of position parallel to the interface indicating uniformity. The EBIC signal from the improved recrystallization process was more uniform

than the old recrystallization. A digitization of the EBIC traces taken 1 micron from the junction region show three times the standard deviation in photocurrent collection for the old recrystallization process compared with the new process.

Conclusions

Significant improvements have been made in the efficiency and long term stability of modules from GPI's manufacturing process. These improvements have come about because of a greater depth of understanding of the electronic and morphological properties of our devices. The goal for the coming year will be greater reproducibility and uniformity within panels and batches of panels so that GPI can resume low cost production and sale of modules.

References

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Figure 1. Current versus voltage scan of a Golden Photon, Inc. module measured by NREL after ten weeks on an outdoor array.

Figure 2. Output power versus time for a 2' x 2' module on GPI's outdoor array

Title: Optimization of Transparent and Reflecting Electrodes for Amorphous Silicon Solar Cells

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Summary of Current Project Objectives

Transparent conducting materials are essential components of many kinds of solar cells, in which they serve as front-surface electrodes. Most designs for highly reflective back contacts also call for a transparent conducting layer. The compositions of these transparent conducting layers are usually based on oxides of tin, indium and/or zinc, and are referred to as transparent conducting oxides (TCO). In addition to having low electrical resistance and low optical absorption, the structure of a front-surface TCO must minimize reflection losses. The TCO must also resist degradation during cell fabrication and use. Finally, the method for making the TCO must be inexpensive and safe.

Our objectives are to improve the performance of TCO materials and the methods for their production. We aim to reduce their electrical resistance, optical absorption and reflection losses, and to lower the deposition temperature to avoid thermal degradation of other cell components. For the production method, the prime consideration is to deposit the TCO layers at a high rate with relatively simple apparatus. The method chosen is chemical vapor deposition (CVD) at atmospheric pressure, since it has been demonstrated in the glass-coating industry to be the most cost-effective method for making large areas of TCO coatings.

Work was carried out during the past year on the following three tasks:

Task 1. Optimize the ratio of the electrical conductivity to the visible absorption for fluorine-doped zinc oxide (ZnO:F) films made by a more robust APCVD process from less hazardous precursors. The goal will be to deposit ZnO:F films over an area of 10 cm by 10 cm with a sheet resistance of less than 12 ohms per square, thickness uniformity $\pm 5\%$, visible haze of about 12 to 18%, and optical absorption of less than 4% at 550 nm.

ZnO:F films meeting all these goals in Task 1 were finally achieved during the past year. Amorphous silicon solar cells prepared on this material showed increased currents, confirming its high transparency, but the contact resistance needs to be reduced.

Task 2. Prepare transparent conductors having the structure glass/textured ZnO:F/smooth TiO_2 :Nb/Si (superstrate design). Use these structures as substrates for the deposition of amorphous silicon cells having microcrystalline p-layers (in collaboration with Penn State University). The optical absorption of the ZnO:F/ TiO_2 :Nb shall not exceed 4% at 550 nm.

Initial samples were made of the Task 2 structure glass/textured ZnO:F/smooth TiO_2 , demonstrating the chemical and physical compatibility of the layers, and the processes used to deposit them.

Task 3. Work with manufacturers to put into practice the large-scale production of fluorine-doped zinc oxide (ZnO:F) transparent conductors.

Initial inquiries were made of several companies, and one was found to be interested in scaling up the process into commercial production.

Task 1. Optimize the ratio of the electrical conductivity to the visible absorption for fluorine-doped zinc oxide (ZnO:F) films made by a more robust APCVD process from less hazardous precursors. The goal will be to deposit ZnO:F films over an area of 10 cm by 10 cm with a sheet resistance of less than 12 ohms per square, thickness uniformity $\pm 5\%$, visible haze of about 12 to 18%, and optical absorption of less than 4% at 550 nm.

We looked for a new CVD process which would have the following advantages:

- 1) a safer, non-pyrophoric zinc precursor.
- 2) a liquid zinc precursor from which the vapor reactant mixture may be made conveniently and in a well-controlled manner.
- 3) chemistry which permits premixing of all the reagent vapors, in order to facilitate uniform, reproducible deposition over large areas.
- 4) less sensitivity to disturbance by trace amounts of contaminants such as oxygen and water vapor.

We succeeded in finding a CVD process which achieves these objectives. It uses a vapor mixture of the N,N,N',N'-tetraethylethylenediamine chelate of diethylzinc, ethanol, hexafluoropropene and optionally, an inert carrier gas such as nitrogen. This vapor mixture is brought into contact with a substrate heated to a temperature in the range of about 400 to 500 °C. Under these conditions, a transparent, electrically conductive, infrared reflective film of fluorine-doped zinc oxide is deposited on the substrate. The N,N,N',N'-tetraethylethylene-diamine chelate of diethylzinc is a non-pyrophoric liquid, in contrast to the hazardous, pyrophoric liquid diethylzinc. This reactant may be vaporized by passing a carrier gas through the heated liquid in a bubbler, or by spraying the liquid into a flow of heated carrier gas.

The N,N,N',N'-tetraethylethylenediamine chelate of diethylzinc may be prepared by slowly adding diethylzinc to dry N,N,N',N'-tetraethylethylenediamine while stirring under an inert nitrogen atmosphere and cooling to remove the heat of reaction. The product is a non-pyrophoric liquid that can be distilled at 92 °C under a pressure of 20 millibars. It does react slowly with air, so it should be handled under an inert atmosphere of nitrogen.

Adding a small amount of fluorine (typically less than about one atomic per cent) to zinc oxide dramatically increases its electrical conductivity. In the practice of this CVD process, a suitably reactive fluorine-containing vapor is added to the zinc chelate vapor and the alcohol vapor, to deposit fluorine-doped zinc oxide on a heated substrate. Hexafluoropropene is a convenient source of fluorine.

The liquid N,N,N',N'-tetraethylethylenediamine chelate of diethylzinc was vaporized by injecting it at a rate of 0.1 milliliters/min from a syringe pump into a flow of 8 liters per minute of dry nitrogen preheated to a temperature of 200 °C. Dry ethanol was placed in a bubbler and heated to 70 °C. Dry nitrogen flowed through the bubbler at a rate of 1.0 liter/minute, and the vapor mixture exiting from the bubbler was diluted by an additional flow of 1.6 liters/minute of dry nitrogen. Hexafluoropropene gas flowed from a pressurized supply tank at a rate of 0.2 liters/minute into the ethanol/nitrogen gas mixture.

These two vapor mixtures were combined at a tee joint, from which they flowed through a line heated to 200 °C into the entrance to a CVD chamber measuring 10 cm wide by 0.6 cm high by 14 cm long (in the direction of the gas flow). A 10 cm by 10 cm glass substrate rested on a plate forming the bottom of the CVD chamber. The glass rested in a machined depression equal in depth to the thickness of the glass. In this way the gas flow was not disturbed from its uniform, laminar progress as the glass and its supporting plate move through the coating chamber.

The glass plate was preheated to a temperature of about 450 °C, while the top plate of the CVD chamber was held at about 300 °C. The bottom plate supporting the glass substrate was then moved at a uniform rate of 1/3 inch per minute through the CVD chamber.

On the surface of the glass plate there was deposited a transparent coating of fluorine-doped zinc oxide with a maximum thickness of about 800 nanometers. The sheet resistance was as low as 12 ohms per square, and the absorption of visible light was less than 2%.

Samples of the new ZnO:F were sent to the University of Delaware and to Solarex for evaluation of their use in amorphous silicon solar cells. Optical measurements at Solarex confirmed the high visible transmission of these films, 84 to 87%. Sheet resistances were as low as 12 ohms per square, the target value. Haze values ranged up to 12%, just at the lower end of the desired range of 12 to 18%. The thicknesses of the films were considered to be quite uniform over their 10 cm by 10 cm areas, with thicknesses around 800 nm. Future samples will be made slightly thicker in order to decrease the sheet resistance and increase the haze values. Detailed measurements are listed in the following table:

Sample #	Sheet r (W/Sq)	Transmission (%)	Haze (%)	Thickness (nm)
1	13-21	86-87	1.9-2.3	n/a
2	13-44	85-87	3.8-7.2	n/a
3	12-19	84-85	7.8-9.5	800
4	12-18	84-86	7.1-10.7	750
5	12-23	84-85	8.9-11.8	800

Results are given in the following table for superstrate tandem cells made at Solarex in two separate runs on two of these samples:

TCO Type	Voc V	FF %	Jsc mA/cm ²	Effic. %	J1 mA	J2 mA
Harvard ZnO#3	1.45	67.3	10.22	9.97	9.72	10.3
Solarex ZnO	1.45	70.2	9.62	9.79	9.12	10.55
SnO ₂	1.47	70.5	9.82	10.18	9.32	9.74

Harvard ZnO#4	1.42	65.7	9.85	9.19	9.35	10.29
Solarex ZnO	1.43	69.4	9.87	9.80	9.37	10.15
SnO ₂	1.44	71.4	9.53	9.80	9.03	10.05

Similar results were obtained for Delaware's single-junction cell:

TCO Type	Voc V	FF %	Jsc mA/cm ²	Effic. %	Roc Wcm ²
Harvard ZnO	0.856	60.5	15.3	7.9	12.5
Solarex SnO ₂	0.875	67.0	14.5	8.5	7.0

Quantum efficiency measurements show that the current is increased at all wavelengths, with the smallest increases in the red end of the spectrum. It is expected that when samples with higher haze levels are prepared, even higher currents will be found for the red wavelengths.

The voltages of the cells prepared on ZnO are about 20 mV lower than those prepared on SnO₂. The fill factors are also significantly lower, by an average of 5%. These deleterious factors negate

the advantage of the higher currents found for the ZnO. Both of these deleterious effects relate to an electrical contact between the silicon and ZnO that is less satisfactory than that with SnO₂.

In order to overcome this problem with the electrical contact between the amorphous silicon and the ZnO:F, a thin layer of SnO₂ will be deposited over the ZnO:F. This structure, thin SnO₂/thick ZnO:F/glass should provide a transparent electrode with the best features of the two materials. The thick ZnO:F should provide high transparency, and the thin SnO₂:F should provide good low-resistance contact to the amorphous silicon.

Task 2. Prepare transparent conductors having the structure glass/textured ZnO:F/smooth TiO₂:Nb/Si (superstrate design). Use these structures as substrates for the deposition of amorphous silicon cells having microcrystalline p-layers (in collaboration with Penn State University). The optical absorption of the ZnO:F/ TiO₂:Nb shall not exceed 4% at 550 nm.

There are several potential advantages to inserting a transparent, conductive layer of titanium dioxide between the top zinc oxide and the silicon layers of a superstrate solar cell:

- 1) The titanium dioxide is stable enough so that microcrystalline p-silicon could be deposited directly on it. Cells with this structure are expected to have increased voltage and current.
- 2) The titanium dioxide layer would reduce the reflection of light, because it has a refractive index (about 2.3) which is intermediate between that of zinc oxide (1.9) and amorphous silicon (about 3).
- 3) This effect should provide increased current.
- 3) One source of instability in amorphous silicon solar cells is the possible reduction of the transparent metal oxide by the silicon. Such a reduction is possible for tin oxide and zinc oxide, but not for titanium oxide, which should thus provide increased stability.

Previous work under this subcontract showed that niobium doping of titanium dioxide is not necessary to make it conductive enough to form a barrier layer between amorphous silicon and another transparent conductor. Exposure of pure titanium dioxide to a hydrogen-containing plasma causes a slight chemical reduction and a large increase in its electrical conductivity. This slight chemical reduction occurs during the plasma-assisted deposition of amorphous silicon onto a TiO₂ layer. A similar slight chemical reduction takes place when TiO₂ films are treated with nascent hydrogen generated by mixing zinc dust and hydrochloric acid solution on the surface of the film.

Thick reduced TiO₂ films (about one micron) show a slight gray color in transmission, indicating that a slight increase in absorption accompanies the reduction. In the thinner films (less than 0.1 micron) envisioned as barriers, this absorption should be negligible.

Now that work under Task 1 of this subcontract has led to an effective process for deposition of uniform ZnO:F films, work will begin on preparing bilayers with the structure TiO₂/ZnO:F/glass.

Task 3. Work with manufacturers to put into practice the large-scale production of fluorine-doped zinc oxide (ZnO:F) transparent conductors.

Contact was made with manufacturers of belt furnaces designed for atmospheric pressure chemical vapor deposition. One of them has agreed to cooperate in setting up the new process for deposition of ZnO:F discussed under Task 1 of this report. In it, glass plates up to 16 inches wide can be coated.

1. NREL Subcontract XAN-4-11318-05, Bolko von Roedern, technical monitor.

Title: **Application of CIS to High Efficiency PV Module Fabrication**

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Objectives

The objectives of this R & D partnership program are the development and demonstration of a low-cost, non-vacuum deposition technique for the growth of CIS and related alloy layers and the use of these layers for the fabrication of high efficiency solar cells and modules.

Approach

CIS and related compound absorbers have been used in thin film solar cell structures with conversion efficiencies of above 15%. A review of the literature shows that high efficiency CIS cells have so far been fabricated on layers grown by the vacuum co-evaporation technique or by various versions of the two-stage selenization method employing evaporated or sputter deposited precursor films. Evaporation techniques are difficult to scale up because of film uniformity and material utilization considerations. Sputtering techniques are better suited for large area deposition, however, they require expensive vacuum equipment and sputtering targets. Therefore, a low cost, non-vacuum technique with a capability to process large area substrates would be very attractive for the growth of CIS layers for photovoltaic applications. In this R & D partnership program ISET has developed and demonstrated such a technique.

Soda-lime glass substrates were used in this work. Mo contact layers were deposited on the soda-lime glass substrates by D.C. magnetron sputtering. CIS films were grown on the Mo surface by a low-cost, large-area, non-vacuum technique. Solar cell fabrication steps included deposition of a thin CdS layer by the commonly used chemical bath deposition approach. A ZnO layer was then deposited on the CdS surface using a MOCVD method. Solar cells of 0.09-1.00 cm² area were defined on the substrates using photolithographic techniques. Both films and devices were characterized to understand the nature of the material grown by the non-vacuum approach. In addition to solar cell fabrication, work was also done on sub-module processing. The module integration approach was the same as the technique used on vacuum based devices. The Mo scribing was done by laser. The two scribes following CIS deposition were done mechanically.

Results and Discussion

The solar cells fabricated on CIS layers obtained by ISET's non-vacuum technique initially yielded efficiencies in the 8-10% range, clearly demonstrating the potential of this low cost process. These cells had respectable V_{oc} (>0.45 V) and FF (>0.65) values. The J_{sc} values, however, were rather low. The results from an in-depth analysis of a typical device is shown in

Table 1 under the column labeled "10.2% cell". A review of the device parameters and the photocurrent loss mechanisms indicated that the early devices fabricated on films grown by the non-vacuum process were very much comparable with the CIS cells fabricated at ISET on evaporated and selenized absorber layers. The only notable difference, however, was the rather large unidentified photocurrent loss of about 7 mA/cm², which brought down the quantum efficiency curve uniformly across the whole spectrum of the measured response. SEM, EBIC and EDS studies were then initiated to understand this phenomenon.

Parameters	10.2% cell		12.4% cell	
	Light	Dark	Light	Dark
Shunt r ($\Omega\text{-cm}^2$)	700	1100	1300	3400
Series R ($\Omega\text{-cm}^2$)	0.2	0.2	0.3	0.5
Diode Factor, A	1.9	2.0	1.6	1.55
p ($\times 10^{16} \text{ cm}^{-3}$)	2.7		1	
J _{sc} Losses (mA/cm ²)				
reflection	3		4	
window loss	2		2	
deep penetration	3.5		3.3	
unidentified	7		1	

Table 1. Device parameters, carrier densities and photocurrent loss mechanism analysis results for the two cells fabricated on non-vacuum CIS layers.

Figure 1 shows a surface EBIC image taken from the 10.2% efficient device. Clearly, there was a high density of "low-response" regions in this cell, which appear as dark spots in the EBIC image. The dark regions constitute about 20% of the total device area shown in Fig. 1 and this can explain the origin of the unidentified, wavelength independent current loss of 7 mA/cm² observed in the data of Table 1.

Most of the small-size low-response areas in Fig. 1 are round in shape with diameters ranging from 5 μm to 30 μm . A closer look revealed that the large low-response areas were created by convergence of two or more small-size ones, and that there was almost always a large dome-like surface feature close to the center of each low-response area. A high magnification SEM of a 100 μm size low-response area is shown in Fig. 2. The large surface features labeled as C and D are clearly seen in this micrograph. EDS analysis made at the locations indicated on this figure showed that the active device region (A) contained both Zn and CIS, whereas, the spots within the low response region (B,C,D) contained only CIS. The chemical composition of the CIS material at points B,C and D were all the same. Therefore, it was concluded that the low response areas were caused by physical detachment of the CdS/ZnO window layer around the region where the dome-like surface features were present, and that the large surface features at C and D did not result from a compositional non-uniformity, such as excess Cu, in the CIS films obtained by the non-vacuum method. Cross sectional SEM was then used to investigate the nature of the domes.

Cross-sectional SEM studies showed that the dome-like features resulted from the presence of near-spherical voids within the CIS layer. It was further observed that a 3 μm size void could

Fig. 1. EBIC surface image of the 10.2% cell.

Fig. 2. SEM of a low-response region showing the large surface features (C and D). EDS data was taken from locations A,B,C and D. The scale bar corresponds to 10 μm .

effect an area of approximately 10 μm diameter in size, and that some of the domes lacked the ZnO layer on top of them. Having found the origin of the photogenerated current loss and the rough surface structure of the CIS layer giving rise to that loss mechanism, efforts were concentrated on the improvement of the morphology of CIS films grown by the non-vacuum technique. The stoichiometric uniformity and electronic quality of these films would clearly be adequate for the fabrication of higher efficiency devices once their morphology was improved. The cross sectional SEM of Fig. 3 shows the morphology and grain structure of the new generation of films prepared by ISET's non-vacuum technique. Although there are still small voids present near the CIS/Mo interface, the surfaces of these layers are smoother than those of the early films discussed before. The grain structure observed in Fig. 3 is also improved. Well formed columnar grains of $>1 \mu\text{m}$ size can be seen in this micrograph.

Results of an in-depth analysis of a 12.4% efficient cell (13.3% active area) fabricated on the film of Fig. 3 are tabulated in Table 1, under the column labeled "12.4% cell". This improved device had lower diode factor values and the unidentified current loss mechanism disappeared, as

Fig.3. Cross sectional SEM taken from the improved device demonstrating lower void density and better film morphology. The scale bar corresponds to $1.0 \mu\text{m}$.

expected. When the quantum efficiency data for the 10.2 % cell and 12.4% device were compared, it could be seen that the improved device had better long-wavelength response which is reflected in the smaller loss due to deep penetrating photons as indicated in Table 1.

In addition to discrete cell fabrication, work was also carried out to fabricate integrated sub-modules on CIS layers grown by the non-vacuum technique. A 25 cm^2 area sub-module containing seven cells yielded about 8.2% efficiency. The open circuit voltage per cell in this device was 0.438 V. The current density at the cell level was calculated to be 34.29 mA/cm^2 by taking into account 95% area utilization in the module structure. Fill factor was limited by the sheet resistance of the ZnO layer employed as well as the ZnO/Mo contact resistance.

Conclusions

We fabricated over 10% efficient solar cells on CIS layers grown by a non- vacuum deposition technique. Improvement of the morphology and density of the CIS films resulted in devices with over 12% efficiency. ISET's non-vacuum technique is low cost and it can effectively be applied to large area film deposition. A 25 cm^2 sub-module with over 8% conversion efficiency was fabricated in this work. Development is now in progress to establish a facility to produce up to 1 ft^2 size modules by the non-vacuum approach. Efforts are also under way to introduce Ga and S into the absorber layers for bandgap engineering and fabrication of higher efficiency cells.

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Title: **Comprehensive Research on Amorphous Silicon and Alloy Materials and Devices**

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Objectives

The primary objective of this program is to develop more stable and higher quality a-Si:H materials and devices by using alternative deposition techniques. The principal new technique used has been remote, reactive, plasma beam deposition, using a reactive plasma generated by an ECR discharge.

Introduction

The properties of a-Si:H and alloys depend critically upon the microstructure of the material. Amorphous Si is not homogeneous, but rather has voids of different sizes and orientations. Also, the bonding of H with Si is complex; it is not simply a random Si-H bond. Both bonding and voids are manifestation of a complex local microstructure in the material. In particular, simple structural arguments would predict that the internal surfaces of voids are likely to have not only Si-H, but also SiH₂ type bonds, because some of the Si atoms on the internal surface of the voids may form a more relaxed structure during growth by bonding with two H atoms and two Si atoms, rather than with three Si and one H. Ample evidence for both clustered H bonding, and for voids, exists in the literature.

These microstructural variations in bonding and structure directly lead to light-induced instability of a-Si:H, because the weaker bonds can break in response to recombination energy of electrons and holes. The microstructural deformities, in turn, depend critically upon the growth chemistry of the material. Therefore, altering growth chemistry is a direct route to altering microstructure, and therefore, the properties and stability of the material.

Experimental Approach

To understand the importance of growth chemistry on microstructure, consider how the material grows from a plasma. See Fig. 1. The initial Si surface can be considered to be dangling bonds, into which appropriate Si radicals can be inserted to grow the material. The most likely radicals generated by the plasma process are SiH₂ and SiH₃. The insertion of SiH₂ leaves behind a surface which is active, with a dangling bond, ready to receive another radical. But the insertion of SiH₃ into a vacant site makes the site inactive, because of the bonded H. Thus, having more than one radical present in comparable density leads to active and inactive sites for further insertion. That is a prescription for non-uniformity on a microscopic scale.

To reduce these inhomogeneities, we use a high H dilution plasma process. H has three roles in growth. First, it acts to enhance radical selectivity, increasing the production of SiH_3 compared to SiH_2 . Second, it serves to homogenize the sites, since an excess of H bonds to the site, and then, the next H atom removes the bonded H. Third, it does etching-during-growth, penetrating into the subsurface region, leading to etching away of the weakest bonds during growth. The reactor we use, a remote ECR reactor, produces a high flux of atomic H ($10^{12}/\text{cm}^3$) at a very controllable energy which reacts with silane or germane to produce the necessary material. We have described the materials results in a previous report.

Device Fabrication

Previously, we had shown that we could make very good devices in the superstrate geometry (devices on tin oxide substrates). However, the intrinsic problems with diffusion of B at high temperatures led us to an alternate geometry, the substrate geometry, where the devices are deposited on a stainless steel substrate. The device geometry consists of ss/n/i/p, with a semi-transparent Cr contact on the p layer which allows about 20% of the light to be transmitted. The device results are shown in Fig. 2, and the excellent fill factor is an indication of the quality of the device.

Device Stability

We had previously shown that the stability of the superstrate devices appeared to be better than comparable glow-discharge devices. During this period, we have investigated the stability of substrate devices, produced using glow discharge, ECR with H-dilution (H-ECR), and ECR with He-dilution (He-ECR) processes. In Fig. 3, we show the relative degradation in the fill factor of the three a-Si:H devices as a function of degradation time. From the figure, it is apparent that the H-ECR process produces the most stable device of the three. The He-ECR device had *less* total bonded H content (4%) than the H-ECR device (7-8%). Yet, the H-ECR device was much more stable. This fact illustrates the point that it is the chemistry during growth, and not the H-content per se, which is important in determining stability.

Conclusions

In summary, we have systematically investigated the effects of plasma chemistry on the properties of a-Si:H materials and devices. We find that the stability of both materials and devices depend critically upon growth chemistry, and that, by controlling the growth chemistry by using a remote ECR process, we can control the stability of both materials and devices.

Non homogeneous growth

Figure 1. Steps in the growth of a-Si:H, showing how insertion of different radicals in the absence of H dilution leads to non-homogeneous growth

Fig. 2 I(V) curve for a substrate cell, showing high fill factor

Fig. 3 Relative degradation in fill factors of three cells, prepared using different techniques, all with similar initial fill factors and i layer thicknesses. The H-ECR cell degrades much less even though it has more H than He-ECR cell.

Title: Atomic Scale Characterization of Hydrogenated Amorphous Silicon Films and Devices

Organization: National Institute of Standards and Technology (NIST)
Boulder, Colorado

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Objective

The overall objective is to assist the development of a cost-effective hydrogenated amorphous silicon (a-Si:H) photovoltaic (PV) technology. This is done by improving understanding of the film growth mechanisms that limit the efficiency of current PV devices, and devising ways to overcome these limitations.

Technical Approach

Two types of measurements are being pursued to attain this overall objective. The first results from our recent discovery that small silicon particulates, formed in the discharge, are continuously incorporated into the growing film. This effort is directed toward measuring these particles in the discharge, and finding methods to diminish their growth and incorporation into the PV film. The second measurement is designed to establish the electrical characteristics of cross sectioned PV cells, as a function of illumination and light induced degradation, to establish where losses and degradation are occurring.

Particulate incorporation into a-Si:H films

In recent years many measurements in silane or silane/argon discharges have shown that silicon particulates form in the plasma and are suspended there due to acquiring a negative charge. This charge, combined with strong discharge-sheath electric fields, normally prevents the particles from reaching the substrate during film growth. However, we have discovered that very small particles (2-15 nm diameter) are continuously deposited into the film during growth, in sufficient quantity to be a potential explanation for the deleterious electrical properties that limit PV efficiency [1]. This occurs for plasma parameters that are typical of those used at most facilities for optimized film production. The growth of these particles in the discharge also appears to limit usable film-growth rates, hence cell production costs.

We believe that the cause of this particle incorporation is that, as suspended silicon particles grow in size but have not yet exceeded ~10 nm radius, some become temporarily neutralized and diffuse into the plasma sheath. There a fraction of the particles become positively charged and are driven by the sheath field into the substrate. It is very likely that voids and carrier traps occur within the a-Si:H film at the particle-film boundaries, with deleterious consequences on PV efficiency. We are carrying out studies to see if it is possible to mitigate this particle incorporation.

The easiest way to detect particulate growth and behavior in the discharge is by light scattering, so we are using this method to investigate how the particle sizes and behavior depends on discharge and deposition parameters, and on possible particle-elimination methods. Light scattering detects particles larger than those that we find incorporated into the film, but it provides a detailed and immediate diagnostic of the particles suspended in the plasma. When complemented with scanning tunneling microscope (STM) studies of particles that have deposited into the film, it provides an excellent basis for developing an understanding of particulate behavior and mitigation techniques.

The speed and character of particle accumulation in silane rf discharges depends on the electrode and substrate-holder geometries, as well as gas mixture, pressure, flow rate and discharge power. Unfortunately, almost all previously reported particulate studies have not utilized geometries and conditions appropriate for growing a-Si:H PV devices, so we find it necessary to evaluate all of these factors. We normally use conditions and geometries that mimic device manufacturing as well as is possible in a small scale system. For pure silane, the gas flow rate is ~ 1.5 sccm/cm², the discharge power is varied to yield 0.5-2 Å/s film growth rate, and (300 °K) pressures are 0.1-0.5 Torr. Fig. 1 gives one example of the discharge geometry, where, except for the rf electrode, all surfaces exposed to the plasma are grounded. We have also studied deposition geometries with an insulator in place of the grounded plate behind the rf electrode, and with the rf electrode the same size as the opposite, grounded electrode.

We have developed a powerful new method of light scattering to measure particle sizes and densities within the discharge. As shown diagrammatically in Fig. 2, this method employs a frequency-doubled YAG laser beam (532 nm) focused into a thin sheet within the plasma. The light scattered by particles is imaged onto a CCD camera, and each pixel detects scattering from a separate, $\sim 10^{-8}$ cm³ discharge volume. Since particle densities are less than 10^8 /cm³, the scattering from individual particles is thereby separated and the intensity in each pixel yields the size of the particle responsible for the scattering.

Data from the arrangement in Fig.2 are combined with video imaging of scattering from the entire discharge region, without resolving individual particles. The particle scattering varies with time from discharge initiation. The first place that particles accumulate is at the downstream edge of the discharge, approximately midway between the electrodes. Over a time of 1-100 seconds this cloud of particles grows to yield a steady-state scattering signal at the downstream end. At the higher pressures this is accompanied by additional particles accumulating upstream between the electrodes; the cloud of particles appears to grow in the upstream direction, in some cases filling the entire discharge. This same phenomena occurs with silane dilution in H₂, at somewhat higher total pressures and gas flows. This strongly suggests that lower pressures are preferable, as long as they are not so low that the discharge voltage and the accompanying film ion bombardment is greatly increased. We also find that adding a small irregularity to the surface of the normally smooth substrate electrode enhances particle accumulation. This implies that smoother surfaces and rounded electrode and substrate-holder edges are desirable.

The cause of this form of particle accumulation is that a strong electric field stops the negatively charged particles near the discharge "sheath", which occurs a few mm from the electrodes and at the discharge edges. The gas flow drags particles downstream, so they accumulate primarily against the sheath at that end of the discharge. There they grow in size until large enough (> 500 nm) to be dragged through the sheath toward the pump. These particles do not directly harm the PV film, but the upstream growth of the particle cloud is more deleterious, as well as a more subtle effect. Particles accumulated at the downstream edge replace a large fraction of the free electrons in this region, thereby modifying the local discharge. As more (negatively charged) particles attempt to enter this region they can be stopped by a resulting electric force, thereby accumulating further upstream. As pressure is increased with constant mass flow (sccm), the drag force on the particles is unchanged but flow velocity decreases, allowing particles to grow larger while being transported through the discharge. Thus at lower pressure small particles (~ 1 nm) arrive at the edge of the particle cloud, and in this high particle-density region they are readily neutralized and absorbed onto the larger particles. But at higher pressures larger particles reach the particle cloud, and these are more likely to remain negatively charged. Thus, they are stopped by the electric field rather than agglomerating, and they accumulate further upstream. Thus as pressure increases the particle cloud extends further upstream, filling our discharge at 0.5 Torr. As the discharge length increases to produce large PV panels larger particles will reach the particle cloud, and this problem will increase in severity.

Cross sectioned PV cells

Efficiency and stability of a-Si:H PV cells depend on many factors, and efficient cell design requires models that incorporate these as correctly as possible. This experiment is directed toward obtaining a better understanding of the distributed contributions to cell photocurrent, photo voltage and light induced degradation in the cells of NREL PV Team manufacturers.

We cleave glass-substrate cells in our vacuum chamber, and use a STM to measure the electrical properties versus depth through the cleaved cell surface. The STM probe tunnels into different regions of the exposed surface of the operating cell, with and without illumination. This experiment has been constructed and tested, and procedures are being refined. It requires very exacting probe and sample positioning under computer and STM-feedback control, in order to find the cleaved surface of the cell without "crashing" the probe on the insulating glass substrate. This has been achieved, and we have also developed the STM hardware and software needed to carry out STM i-V spectroscopy across the cell surface. A in-vacuum, STM-current amplifier with 1 fA current sensitivity is operational, as required to achieve the measurements on the high-resistivity intrinsic layer. We are currently working on a problem associated with the tip approach; the probe tip tends to accumulate a nonmetallic layer of atoms during the approach. This may be due to loose surface atoms resulting from cleaving, or to the approach across the cleaved corner. We will try modifications of the approach algorithm, voltage pulsing to clean atoms from the probe, and gentle hydrogen bombardment of the cleaved surface to overcome this problem.

Conclusions

Obtaining high quality a-Si:H PV cells by rf discharge deposition from silane requires very low deposition rates, typically $\sim 1 \text{ \AA/s}$, and this is the primary limit on the throughput of a production line. Efforts to overcome this limitation include higher frequency discharges and tandem cells with thinner intrinsic layers, and these have been partially successful. However, the reason for this limitation has not been apparent, so it has been difficult to devise major improvements. The data reviewed above has shown that increasing the deposition rate much above this characteristic value can cause particle accumulation throughout the plasma, implying that this is limiting the acceptable power deposition and resulting film growth rates. We are currently studying particle removal techniques, which if successful should lead to improved deposition rates and perhaps film electronic quality as well.

1) D.N.Tanenbaum, A.L.Laracuate, and A.Gallagher, Appl.Phys.Lett. 68,1705 (1996)

Fig. 1. Cross section of one arrangement of the discharge electrodes, which are ~ 5 cm wide.

Fig. 2. Diagrammatic representation of the light-scattering setup used to measure scattering from individual particles.

Title: Wide Bandgap Solar Cell With High Stabilized Performance

Organization: The Pennsylvania State University, University Park, PA16802

Contributors: R.W. Collins, C.R. Wronski, Principal Investigators; Lihong Jiao, Yeeheng Lee, Hongyue Liu, Zhou Lu, Sangbo Kim, Joohyun Koh, Selena Semoushikina

Objectives:

The objectives of this research are to: (i) develop intrinsic materials for improved wide-bandgap solar cells through an improved understanding of the growth process; (ii) establish linkages among material and solar cell parameters for wide-bandgap amorphous silicon and silicon-carbon alloys; (iii) optimize wide bandgap amorphous silicon-carbon alloys, high hydrogen-content amorphous silicon, and/or microcrystalline p-layers; (iv) develop TCO/p-layer and p/i-interface formation procedures for optimum solar cell performance; and (v) optimize stabilized performance of cells deposited with real time control of i-layer grading. The broader objective of the research is to assist the U.S. a-Si PV industry in achieving 15% stable efficiency multi-junction a-Si modules for large scale utility use.

Approach:

The research in this program specifically applies to the activities of the NREL Wide Band Gap Team addresses the following issues: (i) Novel Intrinsic Materials Optimization; (ii) Improved Understanding of Stability in Materials and Solar Cells; (iii) Device Modeling; (iv) Solar Cells Optimized for the p- and i-Layers; (v) Novel p-Type Layer Optimization; (vi) Solar Cell Interfaces.

The approach taken is to establish a systematic approach for improving the performance and stability of the wide bandgap solar cell by taking into account two critical issues. The first is that in the preparation of a-Si:H-based solar cells, the properties of very thin layers may differ from those of thick layers prepared under the same conditions and in addition the layers of a structure may interact during deposition. We apply real time measurements using real time spectroscopic ellipsometry (RTSE) to continuously characterize the nucleation, film growth and microstructure during the deposition of the various layers of the p-i-n and n-i-p solar cell structures. The second issue is that of reliably correlating the properties of these materials to the performance and stability of the solar cells. This is carried out with detailed characterization and analysis on both thin film materials as well as a wide range of characteristics in various solar cell structures fabricated from those materials.

Results:

All of the above areas were addressed and the results obtained led to significant advances in the understanding of the issues and systematic improvements in materials as well as performance and stability of various solar cells. Examples of results from the different areas addressed are presented together with an illustration of the striking, unique capabilities of RTSE.

Conventional PECVD materials were optimized being guided by the in situ studies and measured parameters for thin films. Wide bandgap absorber a-SiC:H materials have been obtained with defect densities, in the annealed state, comparable to those in lower bandgap a-Si:H, but because of their much larger light induced degradation, these materials are considered unsuitable for practical applications. However, wide bandgap intrinsic a-Si:H materials, with mobility gaps larger than 1.85 eV, and their solar cells have been fabricated using 10:1 hydrogen dilution which exhibit better

stability than the commonly used undiluted, lower bandgap, a-Si:H materials and solar cells. Part of the differences in the materials have been attributed to charged defects.

For the first time direct quantitative correlations between the degradation of solar cells and their intrinsic films have been established with materials prepared with H_2 dilution[1]. Both diluted cells and films deposited at different temperatures are found to reach a steady state of degradation under AM1 illumination within 100 hours. This distinct difference in kinetics from the undiluted materials and cells, and the ability to reach steady state degradation in < 100 hours, are being utilized as a new probe for further improving our understanding of the mechanisms limiting cell stability.

The relative contributions of the bulk and p/i interface regions to the degradation of solar cells were quantified using diluted and undiluted i-layer cells together with custom cells having distinct diluted and undiluted layers in the bulk and p/i interface regions. It is found that the degradation kinetics in these cells is primarily controlled by the light induced changes in the bulk rather than at the p/i interface, even though in the annealed state the p/i interface plays a key role in determining V_{oc} .

Significant progress has been made in establishing a methodology which for the first time leads to meaningful modeling of a-Si:H solar cell structures. This was achieved after establishing reliable material parameters for the densities and types of gap states from self-consistent analysis of detailed measurements on the corresponding thin film materials. Various characteristics of Schottky barrier and p-i-n solar cell structures have been self-consistently fitted in both the annealed and degraded states by including both charged and neutral defects which consist of three Gaussian distributions, rather than the two Gaussians commonly used in AMPS modeling. The device modeling has advanced to a stage where meaningful sensitivity studies could be carried out on the custom cell structures.

Optimization of solar cells for p- and i-layer performance was carried out by varying the deposition conditions for the i-layers using different p-layers and p/i interface regions, as well as with atomic hydrogen treatment. We have found that the open circuit voltage of cells increases as the bandgap of the i-layer is widened, with the increases being more pronounced in cells prepared with hydrogen diluted i-layers. With no buffer layers, V_{oc} as high as 0.96 V has been obtained and it was shown that atomic hydrogen p/i interface treatments result in small but significant improvements in the open-circuit voltage. By using the V_{oc} versus light intensity characteristics, combined with the simulations using AMPS, a picture is emerging as to what the relative contributions to V_{oc} are from the p/i interface region, the bulk i-layer, and the built-in potential, V_{bi} .

Accurate thickness control at the level of 1-2 monolayers has been achieved for amorphous and microcrystalline solar cell components using real time optical measurements[2]. A capability of characterizing and better controlling the bandgap profiles in compositionally graded structures has also been developed and is being employed to further increase V_{oc} . Novel widegap amorphous and microcrystalline p-layers have been developed and incorporated into p-i-n and n-i-p solar cell structures. High quality a-SiC:H p-layers, doped with TMB, have been obtained with an optical gap of 2.0 eV. The mixed phase (microcrystalline plus amorphous) materials, prepared using hydrogen diluted mixtures of SiH_4 , CH_4 , and TMB, are found to have poor crystallinity and transport properties which are dominated by the amorphous component. Using RTSE, microcrystalline Si p- and n-layers in the actual n-i-p and p-i-n device structures have been characterized and compared with their thick counterparts which are normally used for property evaluation.

High V_{oc} 's have been obtained with microcrystalline Si p-layer growth on the i-layer in n-i-p cells after hydrogen plasma treatment of the i-layer which enhances the nucleation density of the microcrystallites. Direct correlation has been noted between nucleation and V_{oc} , depending on the interface treatment and V_{oc} as high as 0.94 V has been obtained. Very wide optical absorption onsets have been detected in these layers, at 2.2-2.4 eV, which are attributed to small nanocrystals whose optical properties appear to be affected by quantum confinement.

Procedures were developed to characterize and control interface layers during their fabrication and protocols established for controlling the various layers. Monolayer-level contamination right at the p/i interface of p-i-n cells, due to the gas exchange process, were detected and quantified using RTSE. An atomic H filament step has been developed for atomic H permeation into the interface regions for passivation of defects, which leads to higher and more stable V_{oc} for cells. Optical gaps within 100 Å of the p/i interface in p-i-n cells have been profiled and provide realistic inputs, based on actual experimental observations, for modeling of the effects of interfaces on cell performance.

Reliable parameters of carbon composition and bandgap grading at the p/i interface for modeling the buffer layers of different thicknesses were obtained using RTSE. Using least-squares regression analysis we were able to characterize the time evolution of: (i) the carbon content in the top 10 to 20 Å of the bulk layer; (ii) the bulk layer instantaneous deposition rate; and (iii) the surface roughness layer thickness on top of the bulk layer during buffer layer growth. The derived depth profiles, carbon content and bandgaps are very useful not only for solar cell modeling but also for bandgap engineering of better devices. RTSE has been used as a real time probe to monitor the formation of the amorphous/microcrystalline junctions of n-i-p solar cells. Illustrative results are presented here on the i-layer surface modification occurring with 133 second hydrogen plasma exposure prior to microcrystalline p-layer deposition using $\text{SiH}_4:\text{CH}_4:\text{H}_2:\text{B}(\text{CH}_3)_3:\text{He}$ of ratio 0.6:0.4:200:0.2:10. The microcrystalline p-layers prepared under these conditions are determined to be mixed-phase p-type $\mu\text{c-Si:H/a-Si}_{1-x}\text{C}_x\text{:H}$ composite materials from an ex situ analysis of optical data.

Results of the structural analysis during the 133 s hydrogen plasma exposure of the i-layer are summarized in Fig. 1. Parts (a) and (b) show that during exposure, (a) the top ~300 Å of the i-layer is modified such that ~0.14 volume fraction of additional Si-H bonds develops from Si-Si bonds (corresponding to an increase in the bonded H-content by 3.5 ± 1 at.%), and (b) the initial 28 Å thick surface roughness on the i-layer increases by 23 Å to 51 Å. A study correlating atomic force microscopy (AFM) and RTSE has shown that the 23 Å of roughness induced by the hydrogen plasma is in the form of atomic-scale, surface-connected nanovoids. In contrast, the initial 28 Å is in the form of surface modulations with an in-plane scale of 300-400 Å. Figure 2 shows the optical gap determination for the i-layer before and after hydrogen plasma exposure. The high energy ϵ_2 data are most reliable since the low energy data (<2.5 eV) penetrate into the unmodified region (deeper than ~300 Å). Figure 2 shows that the gap increases by 0.06 eV due to the increase in H-content.

Figure 3 shows the results of simplified RTSE modeling of the nucleation of the mixed-phase $\mu\text{c-Si:H/a-Si}_{1-x}\text{C}_x\text{:H}$ p-layer on H_2 plasma-modified and unmodified i-layer surfaces. In this modeling, the p-layer thickness and void volume fraction are free parameters. Figure 3 shows that H_2 -plasma exposure leads to a nuclei contact thickness two-fold lower than that obtained without the exposure. This corresponds to a four-fold increase in the nucleation density of the p-layer, presumably due to the 23 Å atomic scale roughness (see Fig. 1). The increase in nucleation density accounts for the increase in V_{oc} from ~0.4 to 0.85 V, observed upon incorporation of the H_2 plasma process step, since the p-layer coverage of the i-layer after 200 Å is expected to be enhanced at the higher nucleation

density. Further improvements directed by RTSE are expected to result from optimization of the H-treatment and doping gas mixture.

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FIG. 1. RTSE analysis results for H_2 plasma exposure of the a-Si:H i-layer of an n-i-p solar cell including: (a) modification of the top 300 Å of the i-layer by incorporated H, expressed in terms of $f_{\text{Si-H}}$, the volume fraction of Si-H bonds that are formed from Si-Si bonds in the near-surface of the i-layer; (b) evolution of the surface roughness thickness, $d_{\text{s,sub}}$, on the i-layer.

FIG. 2 Determination of the optical gaps that characterize the near-surface of the i-layer before (circles) and after (triangles) exposure to a H_2 plasma used to enhance the nucleation density of the overlying p-layer. The data tend to converge at low energies since the light penetrates into the unmodified region for the H_2 plasma-modified surface.

FIG. 3 Void volume fraction plotted as a function of film thickness obtained in a one-layer analysis of RTSE data collected during deposition of the p-layers of two Cr/n-i-p solar cells. In both cases the p-layer is a mixed-phase $\mu\text{-Si:H/a-Si}_{1-x}\text{C}_x\text{:H}$ prepared using a flow ratio of $\text{SiH}_4\text{:CH}_4\text{:B(CH}_3)_3\text{:He:H}_2 = 0.6\text{:}0.4\text{:}0.2\text{:}10\text{:}200$. For the closed circles, the only difference is that a H_2 -plasma treatment of the i-layer was performed prior to p-layer growth.

Title: Development and Application of a
Computer Model for CdTe and CuInSe₂
Based Solar Cells

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Contributors: J. L. Gray, principal investigator

Objective

The purpose of this research program is to develop an accurate numerical model for CuInSe₂ (CIS) and CdTe based solar. The model, ADEPT (A Device Emulation Program and Tool), is used to analyze and aid in the design of CIS and CdTe based solar cells and is being released to the photovoltaic community. An additional objective is to use the model to analyze existing devices and to predict performance.

Approach

ADEPT has been demonstrated to be a useful tool for interpreting the performance of existing solar cells. The accuracy of ADEPT in predicting cell performance depends on several factors. In well understood material systems, such as crystalline, the predictive ability of detailed device simulation codes is quite good. In thin film devices, such as CIS and CdTe based solar cells, the predictive ability of these codes is not as good. Basic characterization of these materials is still an active area of research and is complicated by variations in the material parameters resulting from fabrication methods and even different facilities. In a graded band gap structure these difficulties are multiplied.

ADEPT generates a numerical solution to a set of three coupled partial differential equations commonly referred to as the semiconductor equations. These are Poisson's equation and the hole and electron continuity equations. Coupled with auxiliary equations for the displacement field and carrier currents, these are solved for the electrostatic potential and the hole and electron concentrations on a domain defined by the device structure subject to appropriate boundary conditions and the device operating conditions.

Availability

ADEPT has a Home Page on the World Wide Web (WWW) at the following URL:

<http://dynamo.ecn.purdue.edu/~grayj/ADEPT/adept.htm>

In addition, ADEPT may also be run directly through the WWW, without the necessity of downloading and installing the program, via the Semiconductor Simulation Hub. The Hub is a set

of network-based laboratories that provide tool kits of programs for various scientific fields. Students, researchers, and engineers can access software, run the tools, view results, and download data via a specialized WWW-server that interfaces to standard WWW browsers. The Hub is currently being used for on- and off-campus education, to support research activities, and as a test bed for network-based, on-demand high-performance computing. The URL for the Semiconductor Simulation Hub is:

<http://csehub.www.ecn.purdue.edu:8000/SimHub/>

Recent Results

The capability of the research version of ADEPT has been extended to include steady-state small signal analysis [1]. This extension will allow the simulation of capacitance-voltage characteristics. Some results are shown below [1]. Figure 1 shows a simulated C-V for a CdS/CIS thin film solar cell. A useful feature of detailed numerical device simulation is that all the internal parameters are accessible. Examination of these parameters can provide insight into the operation of the device. In Figure 2, a plot of the imaginary part of the small-signal charge density shows which regions of the device are contributing to the capacitance for the C-V in Figure 1.

Figure 1. Simulated capacitance-voltage characteristic.

Figure 2. Small signal charge density showing edges of depletion region.

Reference

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Title: Thin-Film Photovoltaic Partnership Program CIS-Based Thin Film PV Technology

Organization: Siemens Solar Industries
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Introduction

The primary objective of this contract (#ZAF-5-14142-03) is to establish reliable high-throughput, high-yield thin film deposition processes in order to make CIS a viable option for the next generation of photovoltaics. The primary goals are to demonstrate performance as well as commercial viability via the milestones of a champion prototype 13% efficient large area module and sets of modules in 1-kW arrays composed of steadily increasing efficiency, reaching 1 kW of 12% efficient large-area modules by the end of the third year. This paper reports on progress toward these objectives and goals through approximately the first year of this contract; September 1995 through December 1996.

Industrial Perspective

Multinary Cu(In,Ga)(Se,S)_2 absorbers (CIS-based absorbers) are promising candidates for reducing the cost of photovoltaics well below the cost of crystalline silicon. CIS champion efficiencies have continually improved culminating in 17+% efficient solar cells fabricated at NREL (1). Small area, fully integrated modules exceeding 13% in efficiency have been demonstrated by four groups (2). Long-term outdoor stability has been demonstrated at NREL by 1 ft. X 1ft. and 1 ft. X 4 ft. SSI modules which have been in field testing for as long as seven years (2,3). The availability of natural resources and the effect of manufacturing and deployment upon the environment both appear to be acceptable (2,3). Cost projections indicate about \$1.00/Wp based on projection of present processing to large area and high volumes and based on the measured efficiency of small-area mini-modules (2,3).

However, challenges remain to scale the process to larger area, and to pass accelerated environmental testing. The SSI 10x10 baseline process needs to be reproduced on larger areas. The origin of thermal transient behavior needs to be identified and eliminated if possible. A package design needs to be developed which can enable the completed modules to pass standard environmental qualification testing.

From an industrial perspective, the full process sequence anticipated for use in the final product must be mastered and rigorously demonstrated. To this end, SSI has abandoned development based on individual cells in favor of the "mini-module": twelve cells monolithically interconnected on a 10 cm X 10 cm substrate (4). Fabrication of these mini-modules exercises all aspects of large area module production. The application of statistical process control (SPC) techniques to this well defined mini-module baseline process rigorously demonstrates process yield and reproducibility.

Demonstrated Performance

A reproducible low variation baseline has been demonstrated for over two thousand mini-modules (Figure 1). Efficiency versus time is plotted with separations between groups of data indicating deliberate

Figure 1. Control chart showing efficiency of more than two thousand mini-modules.

changes in the baseline process. Non-baseline experimental data is not included and identified “special causes” have been removed.

After lamination and outdoor exposure, modules typically have even higher efficiencies. Laminated mini-module efficiencies after outdoor exposure average 12.4% and multiple laminated mini-modules over 13.5% efficient have been demonstrated.

Long-term outdoor stability has been demonstrated at NREL where 1 ft. X 1ft. and 1 ft. X 4 ft. modules have been field tested for as long as seven years (1). NREL also monitors an SSI provided 1-kW array of CIS modules (5). The modules are kept under load and measured every half-hour. This in-service data corrected to standard conditions has demonstrated both module and array stability with no seasonal variation.

Process Scale-up

For each step in the process, the impact of the larger part size has been tested in the baseline process. For example, by cutting 30 cm X 30 cm circuits into nine 10 cm X 10 cm circuits the performance uniformity of the larger parts has been measured in the baseline process. Such experiments have indicated that larger area parts should yield the same level of performance as small parts. However, large-area circuit performance has not yet achieved the same level as the baseline. Baseline circuit plate efficiencies are about 11.5% whereas 30 cm X 30 cm performance is about at 8%. Identical performance is achieved for 10 cm X 10 cm and 30 cm X 30 cm circuits plates when fabricated in the large reactor. These results indicate that reactor differences are responsible for performance differences; the part size itself is not the cause of performance differences.

Absorbers obtained from the baseline process and from the large reactor have been characterized using bandgap measurements, SIMS, ICP, sheet resistance, contact resistance, etc. Observed differences between absorbers from the two reactors have been related to the design of the large reactor. For example, SIMS analysis, Figure 2, reveals that the profile of sulfur concentration is a significant difference between absorbers from the two reactors (6). To date, hardware and process implementation changes in the large reactor defined to mitigate these differences have been only partially successful. The results of these studies imply that changes in the materials of construction and/or the physical design of the large reactor are required to transfer the baseline process to larger areas.

Figure 2. Comparison of SIMS sulfur profiles for absorbers from different reactors.

Accelerated Environmental Testing

Although stable for in-service conditions, circuits encapsulated in a standard glass/EVA/circuit laminate have failed thermal and humidity-freeze cycling accelerated environmental tests. These standard environmental qualification tests involve exposure to 85°C and such exposure can cause a decrease in efficiency (7). Efficiency typically recovers with light exposure (4, 8). The effects of light exposure before, during and after accelerated environmental testing have been explored in testing at NREL (9, 10, 11). Thermal and humidity-freeze cycling degraded performance by between 10 and 30 points with less degradation for light exposure during the environmental tests. However, independent of light exposure during thermal cycling, performance recovered to within five points of initial performance for most laminates after subsequent outdoor exposure.

Modules have also failed the 1000-hour damp heat test where, in addition to a thermally induced degradation which recovers with light exposure, moisture penetration into the package can cause irreversible loss of performance (7, 8). Improved package designs have been pursued along with efforts to identify the origin of moisture sensitivity in the circuits by separating and examining the effects of the two major environmental stress factors: heat and humidity. For example, interconnect test structures, which are essentially mini-module circuits but with double interconnects configured to allow independent measurement of ZnO to Mo contact resistance and ZnO sheet resistance, were exposed to damp heat (10, 11). Both contact resistance and sheet resistance increase and these increases correlate with water penetration into the laminate observed as fogging of the EVA.

Exploration of edge seal options to prevent water vapor ingress has been performed using laminated 30 cm X 30 cm ZnO coated plates with electrical contacts for ZnO sheet resistance measurement (10, 11). Sheet resistance increases with damp heat exposure, again correlating with EVA fogging. With subsequent outdoor exposure, the ZnO sheet resistance returned to pre damp-heat exposure values, though recovery was not accompanied by a visual decrease in EVA fogging. Edge seal options that significantly inhibit water vapor ingress and the resultant increase in sheet resistance have been demonstrated. Observations indicate that improving the adhesion between the edge seals and the laminates will further improve resistance to water vapor ingress.

Summary

SSI has repeatedly executed a baseline 10 cm X 10 cm mini-module process rigorously demonstrating process reproducibility and yield for CIS-based devices. Laminated mini-module efficiencies after outdoor

exposure have averaged 12.4%, with champion mini-modules over 13.5%. Excellent long-term outdoor stability has been demonstrated at NREL.

Process scale-up is systematically proceeding from the foundation of this reproducible low variation baseline process; however, large-area circuit performance has not yet achieved the same level as the baseline process. This performance difference has been characterized and related to design differences between baseline and larger area absorber formation reactors. For all other process steps, the impact of the larger part size has been tested in the baseline process. This approach has demonstrated that performance is not directly related to part size; larger-area circuits should achieve the same level of performance as baseline circuits.

Although stable for in-service conditions, SSI CIS-based devices have failed standard accelerated environmental tests. SSI has separated and examined the effects of the two major stress factors during accelerated environmental tests: heat and humidity. Degradation induced by high temperatures during accelerated environmental testing has recovered for normal in-service illumination and temperature conditions, while humidity induced degradation has exhibited reversible and nonreversible components. Laminate edge seal options that significantly inhibit water vapor ingress have been demonstrated and improved adhesion between the edge seals and the laminates is expected to further improve resistance to water vapor ingress.

Acknowledgments

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Title: High-Throughput Manufacturing of Thin-Film CdTe Photovoltaic Modules

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Abstract

Solar Cells, Inc. ("SCI") has manufactured and installed over 50kW of thin-film CdTe modules with an average total area efficiency of greater than 6.75%. These installations have demonstrated reliable performance at or above system ratings. In addition, modules routinely pass extensive stress testing. A champion 60cm x 120cm module has been measured at 61.0 watts or over 9.0% aperture area efficiency. SCI has initiated the scaling of its pilot line process to a multimegawatt level. This paper summarizes the status of these development activities including equipment specification, support programs, and product validation.

Introduction

Cadmium telluride (CdTe) has become recognized as one of the leading materials for low-cost, thin-film photovoltaic (PV) modules. In 1991 SCI began a PV module manufacturing development program to demonstrate the technology's many advantages such as deposition rate, device stability, device performance, and process flexibility. Due to the success of these efforts, SCI began a manufacturing initiative in late 1993 in conjunction with support from The Department of Energy's PVMaT program. Current program activities include equipment specification, support programs development, and product validation.

Equipment Specification

The processes used to manufacture thin-film cadmium telluride modules are listed in Table 1. These processes have been demonstrated routinely on a 100 kW pilot production line. SCI has completed the specifications of all the major components of a 20MW manufacturing line. SCI has specifically concentrated on the advancement of a high-throughput semiconductor deposition system ("HTDS") and two industrial laser scribing machines. These steps present the most relevant issues related to scaling the pilot line to an industrial multimegawatt process such as cycle time, process control, and material utilization. These systems will be integrated with approximately 40 other pieces of equipment to produce modules at an annual nominal capacity of 20MW.

Table 1. Processes for Manufacturing Thin-Film CdTe Modules

TCO Inspection/Preparation	Scribe 3
Scribe 1	Busbar Application
Semiconductor Deposition	Encapsulation
Film Thickness Check	Potting
Post Deposition Treatment	Safety Checks
Scribe 2	Pmax Test
Metal Deposition	Final Inspection

As reported earlier, the HTDS (Fig. 1) incorporates many advantages over SCI's prototype deposition system including increased throughput and continuous operation (1). The production system has been built for continuous feed of 60cm x 120cm TCO-coated substrates at a throughput of one substrate/minute. The pressure control and conveyor systems were upgraded from the original construction to increase throughput and system reliability. Preliminary tests of these systems, along with the heating systems, resulted in a continuous 24-hour run in which over 1,400 60cm x 120cm substrates were processed with a 100% yield. The deposition components have also been upgraded to include design features which greatly enhance material utilization and deposition rate.

Figure 1. Photograph of high-throughput semiconductor deposition system

The scribing systems are completely automated to scribe the 60cm x 120cm substrates. The systems have four lasing beams that can scribe in either direction over the substrate so that various products (i.e. 17V and 65V) can be produced with low changeover time. The control features for these systems also allow for enhanced tracking of the process performance on a real-time basis. Due to developments on SCI's prototype laser system and the industrial laser systems, scribing cycle times have been reduced by over 90%.

Support Programs

An important part of the development effort is to establish programs which effectively handle safety, health, and environmental issues that accompany the production, deployment, and disposal of these modules. SCI has engaged outside agencies and consultants to conduct safety and health audits of the manufacturing facilities and to formulate appropriate programs and corrective actions. These programs include basic training programs as well as specific operational plans such as industrial hygiene and biological monitoring. Test results have confirmed that these programs are very successful in mitigating and eliminating plant risks.

Environmental efforts have focused on waste minimization and material reclamation and recycling (2). These process have been demonstrated at prototype levels. This work, begun under SCI's PVMaT

subcontract, is now being commercialized with the support of a two-year, \$925,000 Small Business Innovative Research subcontract. The objective of the work is to fully develop and commercialize a full-scale reclamation and recycling process primarily targeted at CdTe modules but flexible enough to be utilized in other recycling efforts such as florescent light tubes and video monitors.

Product Validation

The baseline SCI product is a 60cm x 120cm high-voltage ($65V_{max}$) module targeted at grid-connected applications. SCI projects that this product, along with a patented support structure, will reduce the cost of photovoltaic installations to below \$3.00 per watt by the year 2000. This product has been installed at several sites (see Table 2).

Table 2. SCI Thin-Film CdTe Module Installations

Location	Size	Installation Date
Edwards AFB, CA	25.0 kW	April 1996
Toledo Edison, Ohio	14.0 kW	October 1995
PVUSA, Davis, CA	10.8 kW	September 1995
NREL, Golden, CO	1.0 kW	June 1995
STDI, Las Cruces, NM	0.5 kW	February 1995
Tunisia	1.0 kW	January 1995
Toledo, Ohio	1.2 kW	August 1994

The installation at Edwards AFB incorporates 624 modules and has been measured at over 27.0kW at the DC junction box in mid-summer (Fig. 2). SCI supplied not only the modules but its proprietary panelization and support structure developed in part under its PVMaT subcontract. The project also confirmed that these designs result in greater than a 40% reduction in costs of encapsulation, potting, connections, and panelization when compared to its pre-PVMaT design. The majority of this reduction is the result of incorporating frameless panelization and replacing the junction box with a pigtail.

Figure 2. Photograph of 25.0 kW array at Edwards AFB, California.

The Toledo Edison array consists of over 200 modules. The array is grid-connected and has been in operation for over twelve months. The array will be expanded to 100kW by the end of 1998.

SCI also installed an array of 264 modules at the PVUSA demonstration site in Davis, California. This array has been measured at 12.0kW at the DC junction box and has operated well since its installation in September 1995.

Acknowledgments

The author is pleased to acknowledge the efforts of the SCI development team. The extraordinary capability and dedication of this team was essential in achieving the results described in this paper. The work reported here was supported in part by NREL under subcontract No. ZAI-4-11294-02.

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Title: **Amorphous Silicon Research**

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Objectives

The major Phase II objectives are to: (i) improve throughput by 20% over baseline and decrease silicon alloy feedstock by 20% without loss in stabilized module performance, and (ii) demonstrate amorphous silicon (a-Si:H) alloy tandem-junction modules with an average aperture area (at least 900 cm²) stabilized conversion efficiency of at least 9% for a run of at least 18 modules at greater than 75% yield.

Approach

Solarex has been developing the process to make multijunction a-Si:H solar cells and modules for the last several years. Recent efforts have focused on improving the throughput and increasing the material feedstock utilization while assuring good stabilized conversion efficiencies in large-area modules [1,2]. The progress that has been made at Solarex has advanced the amorphous silicon based multijunction technology to a maturity level where large-area commercial modules are technically and economically viable. Consequently, Solarex is building a manufacturing plant in James City County, Virginia, to produce multijunction large-area modules with a capacity of 10 MW/year. The construction of the plant is nearing completion, and commercial production is slated to start in January 1997.

Results

The basic tandem junction device structure employed is: glass/TCO/p-i-n/p-i-n/ZnO/Al where the front junction employs an intrinsic a-Si:H absorber layer with a bandgap of ~1.78 eV and the back junction employs an a-SiGe:H alloy with a bandgap ranging from 1.45 eV to 1.55 eV. The front contact is ~600 nm of textured tin oxide, a transparent conductive oxide (TCO) deposited by atmospheric pressure chemical vapor deposition (APCVD). The amorphous silicon based layers are deposited by plasma-enhanced chemical vapor deposition (PECVD). The first layer consists of ~10 nm of p-type a-SiC:H alloy deposited on to the TCO coated glass. The front intrinsic a-Si:H layer is deposited from a mixture of silane and hydrogen. The intrinsic layer is followed by ~10 nm of phosphorus doped microcrystalline silicon. The second a-SiC:H p-layer forms the tunnel junction and part of the second junction which is followed by a bandgap graded a-SiGe:H alloy layer deposited from a mixture of silane, germane and hydrogen. This intrinsic layer is followed by ~20 nm of an amorphous silicon n-layer which completes the p-i-n/p-i-n structure. The rear contact comprises of ~100 nm of ZnO deposited by low-pressure chemical vapor deposition (LPCVD) followed by ~300 nm of aluminum deposited by magnetron

sputtering [3]. This device structure resulted in an average initial efficiency of $\sim 9.6\%$ with a standard deviation of $\pm 0.39\%$ on 1 ft^2 modules.

The "baseline 1" Si process initially developed for the Solarex 4 ft^2 pilot line had a relatively low bandgap ($\sim 1.45 \text{ eV}$), relatively thick a-SiGe:H i-layer in the back junction which generated a current density of about 10 mA/cm^2 . The average initial efficiency of this process (at 100% yield) was $\sim 9.5\%$ and at 70% yield was 9.7% . The average light-induced degradation of a large number of modules after 600 hours of continuous illumination under one-sun has been established to be $\sim 17\%$ which was confirmed by an independent measurement at NREL. Thus, the process led to modules with average stabilized efficiencies over 8% . Figure 1 shows the distribution of initial efficiencies of a batch of 40 modules produced with the "baseline 1" process. On the average, the conversion efficiency measured at NREL is about 6% higher than that measured at Solarex.

FIGURE 1. Initial conversion efficiency of baseline 1 process modules (4 ft^2).

While the "baseline 1" process was a good starting foundation to gain manufacturing experience we have been seeking improvements in the manufacturing throughput and material costs. In 1995 we concentrated on reducing the deposition time by developing a tandem device with thinner i-layers. This decreased the deposition time by $\sim 18\%$ over that of the "baseline 1" process without a significant penalty in the stabilized efficiency. We optimized the tandem device by employing thinner i-layers and increasing the bandgap of the back junction by reducing the germanium content [3]. This "baseline 2" process has resulted in a reduction in the current generated by the tandem structure but has increased the fill-factor and the open-circuit voltage. Moreover, the stability of thin tandems have improved - the light-induced degradation has been reduced from $\sim 17\%$ to 14% - 15% . The average stabilized efficiency (at 70% yield) is 7.8% which is close to that obtained with the "baseline 1" process, but with a significantly improved cost-effectiveness.

We have studied the influence of two types of tin oxide coated glass: (1) textured tin oxide deposited on low-iron glass at Solarex and (2) commercially available textured tin oxide deposited on sodalime glass. We have optimized the deposition of the first p-layer in such a way that essentially the same open-circuit voltage (V_{oc}) and fill factor (FF) are obtained on both types of TCO for tandem junction modules. Figure 2 shows the photovoltaic parameters of two batches (36 modules each), one batch deposited on Solarex TCO on low-iron glass and the other deposited on commercial TCO on sodalime glass using the "baseline 2" process. The V_{oc} and the FF are essentially the same while the loss in J_{sc} and consequently the loss in initial efficiency is entirely due to the optical properties of the glass (low-iron versus sodalime) and the optical properties of the tin oxide coatings (Solarex versus commercial).

FIGURE 2. Amorphous silicon process baseline 2 on Solarex coated tin oxide on low iron glass and commercial tin oxide coated sodalime glass.

In the "baseline 2" process the deposition of the entire intrinsic layer is carried out using silane heavily diluted in hydrogen. We have developed a 2-step process in which the high hydrogen dilution is limited to a narrow region near the p/i interface which preserves the advantage in device stability obtained with a high H-dilution throughout the i-layer but significantly decreases the total deposition time. This has allowed us to reduce the deposition time from the "baseline 2" process by ~ 12% without any penalty in the stabilized efficiency. This process has been successfully scaled-up to 4 ft² tandem modules.

While we have developed a baseline capability for the SnO₂ front contact deposition, we are also developing the next generation front contact, i.e. zinc oxide (ZnO). It has long been recognized that ZnO is potentially a superior TCO material to SnO₂ as a front contact. It is inherently more

transparent than SnO_2 resulting in as much as a 10% increase in J_{sc} for a-Si:H based multijunction solar cells. Depositing ZnO using an LPCVD process with diethylzinc, H_2O and a dopant such as B_2H_6 at low substrate temperatures adds additional advantages over APCVD SnO_2 in controllability and ease of manufacturing. However, difficulties do exist in incorporating ZnO into modules: (1) there is a contact barrier at the ZnO/a-SiC:H p-layer interface which causes a lower FF and V_{oc} if the same p-layer is used, (2) it is difficult to scribe ZnO cleanly and reliably by laser, (3) higher module shunt currents occur with ZnO which is probably due to surface debris generated from the LPCVD deposition process. To address these issues, we have optimized the ZnO and the p-layer deposition conditions to maximize the gain in J_{sc} to 6-10% and to minimize the losses in V_{oc} and FF due to a contact barrier to <2%. We have also optimized the ZnO laser scribing process so that very clean scribe edges have been obtained and the shunt current due to the ZnO scribe is largely eliminated.

We have obtained an improvement of $\sim 8\%$ in short circuit current for 1 ft^2 modules by developing a ZnO/Ag/X composite rear contact as compared to the ZnO/Al rear contact. The yield for this composite rear contact was also found to be as good as that for the standard ZnO/Al rear contact.

As part of our exploratory research to understand and minimize the light-induced degradation, we have made a surprising discovery - the light-induced degradation in a-Si:H solar cells can be reversed by the application of a strong reverse bias while the cells are exposed to intense illumination. The rate of this reversal of the degradation is strongly dependent on the strength of the electric field, the temperature and the light intensity [4].

Summary

Solarex has focused on developing tandem junction modules that can be manufactured with high yields, good material utilization and high throughputs. As a result of an extensive research and development program, a robust manufacturing process has been developed that produces large-area tandem junction modules with stabilized conversion efficiencies of about 8%. In the beginning of 1997, Solarex will start producing 8 ft^2 tandem modules in James City County, Virginia for use in both remote and grid-tied applications.

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Title: Research On Polycrystalline Thin Film Submodules Based on CuInSe₂ Materials

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Objectives

In FY 1996, Solarex entered a three year cost sharing contract with NREL. The primary objective of this contract was to develop all the pertinent process steps necessary for the fabrication of a 413 cm² CIGS module. Major consideration was placed on making all process steps low cost and easily transferable to a manufacturing situation. Research also continued on 58 cm² substrates for both submodule and devices fabrication in areas that complement large area module fabrication.

Major Accomplishments in FY 1996 include:

- 15.2 % solar conversion efficiency from a 20 minute CIGS deposition process
- deposited uniform CIGS films on 522 cm² substrates
- developed a reactive ZnO sputtering process

Background

Cu(In,Ga)Se₂ (CIGS) based materials have demonstrated potential for producing high efficiency solar cells and submodules [1,2]. Necessary to making high quality modules are improvements in the quality of the absorber and contact layers and in the interconnect structure. In FY 1995, Solarex demonstrated proof of concept with the fabrication of a 13 % (active area) conversion efficiency on a 40 cm² submodule [1]. This achievement was enabled by the development of absorber and window layers capable of producing 15.5 % (total area) device efficiency [1]. Commercialization of CIGS as a solar material requires stringent control on the uniformity and reproducibility of absorber and contact layers, while maintaining low direct costs and fast process times. All of these issues are currently being addressed as part of our research program.

Technical Approach

Task 1: Window Layers, Contacts and Substrates

The window layer consists of a cadmium sulfide (CdS) buffer layer deposited by chemical bath deposition and a zinc oxide (ZnO) bilayer RF sputtered from a ceramic target. Both processes have demonstrated optical and electrical uniformity over 522 cm². For higher module efficiencies, a doped ZnO layer with higher conductivity and better optical transmission is needed.

In an effort to improve ZnO quality, while reducing material costs and deposition time, a reactive sputtering process was investigated. The reactive process has yielded films with resistivities as low as 3.4 ohms/ square and excellent optical transmission in the visible spectrum. Figure 1 compares the current loss behavior of the reactive process with that of the RF sputtered ZnO normally used. The reactive films have current losses comparable to or better than ZnO films sputtered from a ceramic target. Optical losses in the infrared region are still a significant problem with both

processes, but avoidable through the use of a wide band gap absorber layer [3]. A module using a top contact with a sheet resistivity of 3.4 ohms/square would have excellent current collection permitting the use of wider segments and fewer interconnects. The reactive process is also much faster and less expensive to operate than the RF sputtered process.

Work on the interface behavior of CdS and ZnO films continues. Although the electrical and optical properties of the individual films are well defined on glass substrates, their interaction with each other and with CIGS is not fully understood. Recent evidence has shown that a significant variation in the electrical and optical properties occurs depending on the thickness of the CdS buffer layer and on the method in which the ZnO is deposited [3]. Typically, the ZnO sheet resistivity is greater when it is sputtered onto a CdS or CIGS film when compared to that of the glass witness piece. Understanding the chemical and physical events leading to this behavior is crucial in achieving the maximum conversion efficiency available in modules.

Task 2: CIS Absorber Layers

Addressing the issue of process speed, a modified CIGS deposition process has been evaluated. Using this process, the CIGS deposition time has been successfully reduced to less than 30 minutes while maintaining the quality of the CIGS absorber. Figure 2 shows the J-V characteristics of a 15.2% efficient device made using a 20 minute CIGS deposition 'recipe'. Device efficiencies remained high, 13 % to 14 %, even as deposition times were further reduced down to 10 minutes. The development of a high speed process has direct impact on throughput and ultimate manufacturing costs.

Essential to high efficiency module fabrication is the large area deposition of stoichiometric and uniform CIGS material onto a heated substrate. Recently, CIGS has been successfully deposited on substrates up to 522 cm². Both scribed and unscribed molybdenum/glass substrates were used. The films are visually uniform, specular and adherent. The compositional uniformity of one film is shown in Figure 3. Earlier work at Solarex has shown that high efficiency devices and submodules can be attained over a wide range of Cu/(In + Ga) ratios using the same deposition process [5]. Previously, smaller submodules and devices have been fabricated using the same process in a matrix over the same 522 cm² area which exhibit efficiencies ranging from 11.5 % to 13.3 % [4]. A photograph of CIGS deposited onto a scribed, 522 cm² molybdenum substrate is shown in Figure 4.

Conclusions

In 1996, significant gains were made in reducing the process time needed to grow high quality CIGS absorber layers. This, in conjunction with, the successful scale up of all deposition process to large area (522 cm²) places Solarex well on the way to the development of a commercially viable CIGS manufacturing process. With further optimization, reactive sputtering of ZnO may provide an inexpensive and fast alternative to RF sputtered ZnO. Research efforts were also directed towards a better understanding of the interactions between the absorber and contact layers.

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Figure 1: Typical behavior of J_{sc} loss due to optical absorption in the ZnO window layer versus its sheet resistivity for the reactive and RF sputtered processes.

Figure 2: J-V characteristics of a 15.2% device where the absorber layer was deposited in 20 minutes.

Figure 3: A contour plot showing the compositional variation in terms of the atomic percentage ratio of Cu/(In +Ga) over a 522 cm² area.

Figure 4: A photograph of CIGS absorber layer deposited on a 522 cm² scribed Mo/glass substrate.

Title: **Research on Wide Bandgap, Amorphous Silicon Based Solar Cells.**

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Contributors: Eric A. Schiff, principal investigator; Lin Jiang, Indra Nurdjaja, Prasanna Rao.

In 1996 our research has focused on wide bandgap materials, in conjunction with our participation in the wide bandgap team of the Amorphous Silicon Research Project. We are working primarily on the following topics:

- Electroabsorption studies of a-Si based solar cells to probe their built-in potential. We seek a tool to permit us to directly assess V_{bi} as it varies with differing n^+ and p^+ layers. The built-in potential is one of the key parameters which determines the open circuit voltage obtainable in a solar cell. Our research progressed sufficiently that we proposed that *interface dipoles* are limiting built-in potentials and open-circuit voltages for some a-Si:H solar cells.
- Electron and hole mobility measurements in a-Si based materials. Work in the last year has included a study of correlations between hole time-of-flight measurements and two other important measurements: steady-state photocarrier gratings, and photocapacitance. We are also continuing our program of time-of-flight measurements on new, amorphous silicon related devices, include triode-deposited amorphous silicon, hot-wire deposited amorphous silicon, modern silicon-germanium alloys, and microcrystalline silicon.

In this year's report we shall describe the built-in potential research. Our research contract was acknowledged in the following publications in 1996, which may be consulted for information on our other research topics.

"Electroabsorption measurements and built-in potentials in amorphous silicon *pin* solar cells," L. Jiang, Q. Wang, E. A. Schiff, S. Guha, J. Yang, and X. Deng, *Appl. Phys. Lett.* **69**, 3063--3065 (1996).

"Non-Gaussian transport measurements and the Einstein relation in amorphous silicon," Q. Gu, E. A. Schiff, S. Grebner, F. Wang, and R. Schwarz, *Phys. Rev. Lett.* **76**, 3196—3199 (1996).

"Fundamental transport mechanisms and high field mobility measurements in amorphous silicon," Q. Gu, E. A. Schiff, J.-B. Chevrier, and B. Eguer, *J. Non-Cryst. Solids* **198—200**, 194—197 (1996).

"Field collapse due to bandtail charge in amorphous silicon solar cells," Q. Wang, R. S. Crandall, and E. A. Schiff, in *Conference Record of the 21st Photovoltaic Specialists Conference* (IEEE, 1996), 1113-1116.

"Two-layer model for electroabsorption and built-in potential measurements on a-Si:H based solar cells," L. Jiang and E. A. Schiff, in *Amorphous Silicon Technology—1996*, edited by M. Hack, *et al* (Materials Research Society, Pittsburgh, 1996), *in press*.

Electroabsorption and Built-in Potentials

Our electroabsorption measurements involve measuring the modulation of the optical transmittance across a *pin* solar cell as a function of an external, reverse bias voltage. Without a great deal of thought, it is clear that the measurements should also reflect any internal, built-in potential V_{bi} across the cell. Graphs of the modulated transmittance through the cell as a function of external voltage are offset by a voltage V_0 which, ideally, can be identified with V_{bi} .

In practice, this simple program is complicated significantly when the external and built-in potentials are dropped across two (or more) optically distinct layers. The signature of this effect is that the offset potential V_0 depends upon the measuring wavelength. We have developed a procedure which handles this complexity by combining the wavelength-dependence measurements and auxiliary, voltage-dependent capacitance measurements. The details of the technique are now published [1], and we shall not describe them here.

In this report we shall instead concentrate on the results we obtain with the technique. We first discuss Fig. 1, which is essentially a textbook figure illustrating the potential profiles in a solar cell with distinct *p* and *i* layers; for simplicity we assume that the *n* layer and the *i* layer are identical except for differing Fermi level positions. The built-in potential for this cell is the sum of the band-bending voltages V_p and V_i illustrated in the figure:

$$V_{bi} = V_p + V_i$$

For a homojunction solar cell (ie. an a-Si:H *p*-layer for the present example) the built-in potential can be computed from knowledge of the bandgap and the Fermi level positions E_p and E_n (relative to the bandedges) in the *p* and *n* layers, respectively. Thus for a-Si:H one would anticipate $V_{bi} = (E_g - E_p - E_n)/e \approx 1.3$ V or so (using 1.8 eV for the intrinsic bandgap, and 0.4 eV and 0.1 eV for the transport activations energies of *p* and *n* a-Si:H, respectively). The calculation is only illustrative; the assumption that the electronic structures of *p*-type and intrinsic a-Si:H are identical can certainly be challenged.

The intentional use of a distinct *p*-layer materials such as microcrystalline Si or a-SiC:H requires a correction to the formula above which accounts for the different bandgap of the *p*-layer. The first correction is the band offset between the valence bands in the two materials ΔE_v . This is illustrated in Fig. 1 with the solid curves, and inspection of the figure yields:

$$eV_{bi} = E_g - E_p - E_n - \Delta E_v$$

For a microcrystalline *p* layer adjacent to an intrinsic a-Si:H layer ΔE_v has been estimated recently to be about 0.26 Volts [2]. The anticipated loss in V_{bi} due to the band offset is more than compensated for by the reduced transport activation energy in *p*-type microcrystalline Si (essentially 0). One estimates $V_{bi} \approx 1.44$ V.

In Table I we present our estimates of V_{bi} for six *pin* solar cells with nominally identical microcrystalline *p* layers and amorphous *n* layers. The solar cells were prepared at United Solar Systems Corp. and at Energy Conversion Devices, Inc.. Two types of intrinsic layers are involved: "conventional" a-Si:H (denoted LH), and a-Si:H prepared with "high hydrogen dilution" of the

silane gas (HH). The latter material has a somewhat larger bandgap, and yields larger open-circuit voltages.

We draw attention to the following features of these results. First, none of the built-in potentials measured with electroabsorption approach the expected value of 1.4 V. Second, the built-in potentials vary significantly for differing intrinsic layers, and in particular are about 0.2 V larger for the HH samples. This effect is not anticipated in the simple model for the built-in potential described above – even after corrections (not given here) for the differences in intrinsic and n -layer materials for HH cells.

Both of these features can be readily accommodated using the hypothesis of *interface dipoles* between the p and i layers. In Fig. 1 the dashed curves show the band-bending including the effects of both the band-offset ΔE_V and also the interface dipole Δ , which reduces V_{bi} :

$$eV_{bi} = E_g - E_p - E_n - \Delta E_V - \Delta$$

Interface dipoles are well known in crystalline heterostructures, and have been exhaustively studied for Schottky barriers, where they are often invoked to explain very weak dependence of the built-in potential upon the work function of the metal used to prepare Schottky diodes. To our knowledge, they have not been seriously suggested heretofore for a-Si:H solar cells, although they were examined in photoemission studies of the a-SiC:H/a-Si:H interface [3].

In conclusion, we offer the following suggestions regarding built-in potentials in a-Si:H based solar cells.

- Interface dipoles reduce the built-in potential in a-Si:H solar cells, apparently by as much as 0.4 V or more. A built-in potential of 1.4 V, which is the estimate without inclusion of interface dipoles, is not likely to seriously limit open-circuit voltages in a-Si:H based solar cells, which are generally 1.0 V or less. However, built-in potentials of 1.0 V are a significant concern, since they are comparable to the measured V_{oc} values.
- Interface dipoles are apparently readily modified. They are not simply the result of the atomic differences in the base materials (cf. Fang and Ley [3]), but also reflect the defects at the interface. This second proposal is consistent with the surprisingly large improvement in V_{bi} for high-hydrogen dilution intrinsic layers and for the frequent observation that the p/i interface can be crucial to obtaining high values for V_{oc} . It may also explain the apparent contradiction between estimates for the band offsets in two independent experiments on the c-Si/a-Si:H interface [4,5].

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Fig. 1: Profiles of the conduction and valence bandedges E_C and E_V in *pin* solar cells with differing *p* and *i* layer materials; the figure illustrates band offsets ΔE_C and ΔE_V and the interface dipole Δ .

Table I: Open circuit voltages and built-in potentials for six solar a-Si:H based *pin* solar cells (microcrystalline Si *p*-layers)

Sample Codes and Notes	Thickness (μm)	V_{oc} (V)	V_{bi} (V)	J_{sc} (mA/cm ²)	FF
HH (treated) USSC/8386#22	0.25	1.039	1.22	8.96	.761
HH (untreated) USSC/8387#22	0.25	1.033	1.17	9.35	.744
LH (treated) USSC/8389#23	0.25	0.957	1.03	10.86	.746
LH (untreated) USSC/8390#22	0.25	0.950	1.02	11.43	.734
HH ECD/LL825	0.5	1.02	1.25		
LH USSC/RF3240	0.5	0.94	0.98		

Title: Thin Film Amorphous Silicon Alloy Research

Organization: United Solar Systems Corp.
Troy, Michigan 48084

Contributors: S. Guha, principal investigator; E. Akkashian, A. Banerjee, E. Chen, T. Glatfelter, M. Haag, G. Hammond, M. Hopson, N. Jackett, H. Laarman, M. Lycette, J. Noch, T. Palmer, S. Sugiyama, D. Wolf, J. Yang, and K. Younan.

Objective

The principal objective of this R&D program is to expand, enhance and accelerate knowledge and capabilities for the development of high-performance, two-terminal multijunction hydrogenated amorphous silicon (a-Si:H) alloy cells and modules. The near-term goal of the program is to achieve 12% stable module efficiency by 1998 using the multijunction approach.

Approach

The major effort of this program is to develop high efficiency component cells and incorporate them in the triple-junction structure to obtain the highest stable efficiency. Efforts were directed toward improving the back reflector, component cells and the tunnel junctions between them. Scale-up issues for module fabrication were investigated and a new laser-processed design for module fabrication was developed.

Status/Accomplishments

- Replacing hydrogen with deuterium in the intrinsic layer is found to improve cell stability against light exposure. The deuterated alloys are believed to have a different structure from that of the hydrogenated alloy.
- The *template* effect was investigated by making cells on thin and thick *n*-type layers. The results do not show any difference in cell performance.
- The incorporation of a microcrystalline *n* layer in a multijunction cell is seen to improve cell performance.
- State-of-the-art component cells show the following initial active-area performance. Top cell on stainless steel: $V_{oc} = 1.054$ V, $J_{sc} = 6.2$ mA/cm², FF = 0.76 and $P_{max} = 5.0$ mW/cm². This is the highest V_{oc} of a high quality a-Si alloy single-junction cell reported in the literature. Middle cell on back reflector: $V_{oc} = 0.79$ V, $J_{sc} = 21.24$ mA/cm², FF = 0.646 and $P_{max} = 10.84$ mW/cm². This is the highest efficiency reported for a-SiGe alloy solar cell. Bottom cell on a back reflector and measured under AM 1.5 illumination with a cut-on filter of wavelength greater than 630 nm: $V_{oc} = 0.631$ V, $J_{sc} = 12.2$ mA/cm², FF = 0.671 and $P_{max} = 5.2$ mW/cm². This is also the highest power output from the bottom cell reported in the literature.
- Triple-junction cells have been fabricated, demonstrating the world's highest initial active-area efficiency of 14.6% (Fig. 1) and stable active-area efficiency of 12.8%. This a major improvement over the previous highest stable efficiency of 11.1% reported last year. The initial active-area efficiency of the cells was confirmed by National Renewable Energy Laboratory (Table 1).

- The improvement in the stable cell efficiency over the last several years is shown in Fig. 2. It is interesting to point out that we started work on improving the stable efficiency (rather than the initial efficiency) in 1992, and within a period of one year, made quick improvement in double-junction efficiency from 10.1% to 11.2%. For almost a period of two years (from January 1994 to January 1996), we were stuck at 11.1% efficiency for triple-junction cells even though we knew, based on theoretical considerations, that these cells should give higher efficiency than the double-junction ones. During this time, we made improvements in the component cells, and when they were properly incorporated in the triple-cell structure, we made an improvement in efficiency from 11.1% to 12.8% in a period of eighteen months.
- Scale-up issues have been addressed by depositing cells over one-square foot area, and average active-area stable efficiency of 11.1% has been achieved over this area.
- The laser-drilling approach has been used to obtain stable total-area efficiency of 9.8% using a triple-junction structure of 12.5 cm² area.

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TABLE 1. Comparison of Initial Triple-cell Efficiency (area of ~0.25 cm²) as Measured at NREL and United Solar.

Sample	V _{oc} (V)	I _{sc} (mA)	FF (%)	J _{sc} (total area) (mA/cm ²)	η (total area) (%)	J _{sc} (active area) (mA/cm ²)	η (active area) (%)	Measurement Laboratory
L8605 #42	2.357	2.104	74.39	7.721	13.5	8.28	14.5	NREL
L8605 #42	2.357		72.3			8.57	14.6	United Solar
L8605 #34	2.335	2.116	73.29	7.721	13.2	8.22	14.1	NREL
L8605 #34	2.349		72.1			8.57	14.5	United Solar
L8606 #21	2.336	1.973	76.09	7.403	13.2	7.93	14.1	NREL
L8606 #21	2.344		74.5			8.23	14.4	United Solar
L8606 #34	2.340	1.955	75.23	7.265	12.8	7.77	13.7	NREL
L8606 #34	2.334		74.8			8.23	14.4	United Solar

Figure 1. J-V characteristic of a triple-junction cell showing a 14.6% initial efficiency.

Figure 2. Progress of stable multijunction cell efficiency at United Solar.

Title: Photocharge Transport and Recombination Measurements
in Amorphous Silicon Films and Solar Cells
by Photoconductive Frequency Mixing

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Program Outline

This research program is concerned with the characterization of the photoconductive properties of a-Si:H, a-SiC:H and a-SiGe:H films from "round robin" sources by the photomixing technique so as to separately determine drift mobility and photomixing lifetime. By the measurements of temperature and electric field dependence of the drift mobility and the degradation studies which are performed on selected films by *in situ* light soaking, the effects of deposition conditions on the transport properties were investigated. These studies contribute to determine the optimization of these materials and devices and our understanding of the Staebler-Wronski instability. The photomixing technique consists of heterodyning two monochromatic laser beams when a dc bias is applied which results in photocurrent composed of a dc and microwave photomixing current; these two photocurrents allow a determination of the drift mobility (μ_d) and photomixing lifetime (τ) of the dominant photo generated carriers [1]. In addition, the technique was extended to measuring the photoresponse of solar cell devices.

Accomplishments

I. Effect of the Hydrogen Content on Transport Properties for a-Si:H Films

The transport properties of intrinsic hydrogenated amorphous silicon samples with the hydrogen content ranging from over 12% to less 1%, which were produced by the hot-wire technique at NREL, were systematically studied by the photomixing techniques. In the present report the effect of deposition condition, especially the hydrogen content or substrate temperature, on the transport properties for a-Si:H films was analyzed.

Figures 1-3 show the photoconductivity σ_{dc} , μ_d and τ at room temperature in the annealed state as a function of substrate temperature at the electric field of 6000Vcm^{-1} . Both σ_{dc} and μ_d decrease monotonically with the increasing of the substrate temperatures or decreasing of hydrogen content. These results indicate that with increasing deposition temperature (T_s), the density of defects, both charged and neutral defects, must increase to account for the decrease of the photoconductivity and the drift mobility. Only one exception is the sample produced at a substrate temperature 360°C and 2-3% H content, which shows a slight increase in the drift mobility. The increase or decrease of charged defects with increasing T_s is also evidenced by the decrease or increase of the drift mobility, as the charged defects can enhance the scattering of electrons, especially if they form long-range potential fluctuations. In other words, a change in the deposition temperature not only affects the

density of midgap defects, but also, very importantly, affects the charge state profile of these midgap defects. The non-monotonic variation of the photomixing lifetime versus substrate temperature in Figure 3 indicates that the photomixing lifetime is sensitive to other factors in the production process than the hydrogen content.

A lowering of the drift mobility μ_d may be due to a relative increase in the width of conduction band tails. By measuring the dc and the ac photoconductivities at a single photomixing frequency as a function of temperature, the spread of the band tail ϵ can be determined by curve fitting according to an expression for the drift mobility μ_d derived in reference [2]. Figure 4 shows the derived parameter ϵ as a function of the substrate temperature. The width of the conduction band tail ϵ increases with increasing substrate temperature until 360° C while it decreases for higher substrate temperatures.

The light induced degradation was measured on these samples in order to see whether T_s influences the Staebler-Wronski effect. Light induced degradation studies were performed to determine σ_{dc} , τ and μ_d as a function of illumination time. The light soaking was performed *in situ* employing a He-Ne laser with an intensity of 4 suns over a period of 5 hours. Continuous degradations of σ_{dc} , μ_d and τ were found during light soaking which obey different stretched exponential laws. Figure 5 shows the light induced photoconductivity decay, represented by $(\sigma_{dc})_{LS}/(\sigma_{dc})_{AN}$ as a function of T_s ; $(\sigma_{dc})_{LS}$ and $(\sigma_{dc})_{AN}$ are dc photoconductivities in the light-soaked and in the annealed state respectively. The light induced photoconductivity decay increases with the decreasing of T_s , except around $T_s = 360^\circ$ C. This indicates that the hot-wire samples with the hydrogen content about 2-3% show an increased stability compared to the samples of adjacent compositions. This is consistent with a previous report that the metastable defect densities for the HW samples with hydrogen concentration of about 2-3% show a decrease in the Staebler-Wronski metastability upon the light soaking [3].

The light-induced defects as well as the native defects, which serve as recombination and trapping centers, can be charged and can form certain potential barriers or fluctuations. The electric field dependence of the drift mobility and the photomixing lifetime of these samples were measured in the annealed state (annealed at 150° C for 1 hour then cooled down to room temperature in air) and in the light-soaked state (after light soaking for 5 hours at 4 suns). It was found that the drift mobility increases with increasing electric field, the photomixing lifetime decreases with increasing electric field, while the photoconductivity is essentially independent of the electric field in the range from 1,000 Vcm⁻¹ to 10,000 Vcm⁻¹ covered in our experiments. The range of the potential fluctuations could be determined through a curve fitting procedure according to a model of charge transport through potential barriers which we have presented earlier [4]. Figure 6 shows the range of the long-range potential fluctuations of the samples in the annealed state as a function of T_s . As discussed previously [4] the longer ranges seem to be correlated with a lower concentration of charged defects as scattering centers.

II. Photomixing Measurement on Solar Cell Devices

Photomixing measurements were performed on Schottky structures on PECVD and hot-wire films produced by NREL (Crandall, Mahan, Nelson). From these measurements it was possible to determine the product of the absorption coefficient and the width of the depletion layer, the product of the absorption coefficient and the diffusion length as well as the transit time of carriers through the

depletion layer. Measurements on p-i-n structures have been initiated; these structures were obtained from United Solar. Measurements on device structures will continue as samples become available from various team members.

III. Improvement of the Experimental Setup

We changed and re-arranged some equipment in our photomixing experimental system. We changed the He-Ne laser to increase its output intensity and stability. This higher laser intensity should enable us to research the screening effects due to an increased amount of free carriers. The mixing frequency and the effective modulation index were determined for the new laser. A stepped neutral density filter was installed for use in intensity dependence measurements in order to obtain information about the depth of the potential fluctuations and the screening effects.

Conclusions

The photomixing technique on a-Si:H thin films has revealed that the transport parameters can systematically studied as a function of sample preparation conditions. A detailed study of hot-wire prepared samples was completed and the results are being submitted for publication [5].

The electric field dependence of the mobility has enable us to determine the range of the potential fluctuations. As measurements of the screening effect on long-range potential fluctuations due to a variation of the illumination intensity combined with electric field dependence measurements are continued, we will be able to determine the depth of these potentials. First results of intensity measurements will appear in the proceedings of the 14th NREL/SNL Photovoltaics Program Review Meeting [6].

We have also demonstrated, that the photomixing technique can also be extended to solar cell device structures and can determine a number of junction parameters pertinent to device performance. First measurements on p-i-n structures (United Solar) were performed and will be continued as new samples become available from various team members.

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Fig. 1: Photoconductivity vs. substrate temperature.

Fig. 2: Drift mobility vs. substrate temperature.

Fig. 3: Lifetime vs. substrate temperature.

Fig. 4: Width of conduction band tail vs. substrate temperature.

Fig. 5: Photoconductivity decay ratio vs. substrate temperature.

Fig. 6: Range of LRPF vs. substrate temperature.

Title: Processing and Modeling Issues for Thin Film Solar Cells

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Objectives and Technical Highlights

The objectives of IEC's four year subcontract with NREL are to advance the state-of-the-art in thin film PV modules by improving thin film deposition, device fabrication, material and device characterization, and related manufacturing technology of solar cells based on CdTe, Cu(InGa)Se and a-Si. Accomplishments during the fourth phase include: fabricating CIGS cells having efficiencies of 15% with Ga content up to 50% and bandgaps up to 1.3 eV; identifying poor photocurrent collection as limiting CIGS cells with higher Ga content; determining interdiffusion coefficients of Ga and In with CIS/CGS diffusion couples and were found to be comparable; use of CdTe_{1-x}S_x absorber layers and vapor CdCl₂ processing to control diffusion of S into CdTe; obtaining state-of-the-art V_{oc} (> 850 mV) on CdTe devices with films made by physical vapor deposition and treated with CdCl₂ vapor; improving efficiency of a-Si devices from ~9 to ~10% with improved rear contact and n-layer processing.

Results

High V_{oc} Cu(InGa)Se₂-based Solar Cells

Fabrication and detailed device analysis of cells with Cu(InGa)Se₂ absorber layers deposited by elemental evaporation which contain $x \equiv [\text{Ga}]/([\text{In}]+[\text{Ga}])$ from 0.27 to 0.81 and bandgap (E_g) from 1.16 to 1.54 eV and detailed device analysis was completed. The Cu(InGa)Se₂ films were deposited with no gradients in the Ga and In to allow effects of increasing Ga to be characterized without differences due to gradients in the electrical or optical properties. There were no changes in structure or morphology of the films as the Ga content increased. Solar cells with the configuration glass/Mo/Cu(InGa)Se₂/CdS/ZnO/MgF₂ have ~15% efficiency for $x < 0.5$ or $E_g < 1.3$ eV [1]. V_{oc} increases over the entire bandgap range up to 820 mV with $E_g = 1.54$ eV but the efficiency falls off for $E_g > 1.3$ eV. Still, with $x = 0.72$ and $E_g = 1.47$ eV a device had V_{oc} = 0.804 V, J_{sc} = 20.7 mA/cm², FF = 69.0 %, and $\eta = 11.5$ %. Analysis of current-voltage measurements showed that the diode behavior under illumination for $E_g > 1.3$ eV could not be described by a simple diode equation which assumes a constant current collection [2]. Quantum efficiency measurements as a function of voltage confirmed that this is primarily attributable to a voltage dependent current collection which results in a decrease of FF and J_{sc}. Finally, Cu(InGa)Se₂ films with a Ga gradient were shown to improve FF in the high bandgap cells, apparently by improving the current collection.

Characterization of Mo/Cu(InGa)Se₂ Contacts

The Mo/CuInSe₂ contact properties and structural effects of the Mo layer on the subsequent Cu(InGa)Se₂ growth were characterized. A novel device configuration was developed to allow the current-voltage characteristics of the back contact to be separated from the rest of the operating solar cell [3]. This was used to show that the Mo/CuInSe₂ contact is ohmic with negligible contribution to the series resistance of the device, even when the complete device shows blocking or non-ohmic contact behavior in addition to the primary diode. A correlation was demonstrated between the relative orientation of the Mo and Cu(InGa)Se₂ films, as measured by XRD [4]. Mo films deposited in separate dc sputtering systems using different processes were found to result in

different degrees of relative (110) orientation. Cu(InGa)Se₂ films with $E_g = 1.2$ eV were deposited by elemental evaporation in a single run on the different Mo films. The Mo film with the stronger (110) orientation resulted in a Cu(InGa)Se₂ film with nearly random orientation, similar to a powder diffraction pattern. However, the Mo with weaker (110) orientation resulted in Cu(InGa)Se₂ films which were (112) oriented with the normalized (112) peak intensity 2 orders of magnitude greater than for the powder sample. Completed solar cells on these Cu(InGa)Se₂ films had nearly identical device efficiency (14.4 and 14.5%, respectively), demonstrating that the Cu(InGa)Se₂ orientation is not directly correlated to device behavior but does depend on the Mo structure.

Interdiffusion of In and Ga in Cu(InGa)Se₂

Selenization of Cu/Ga/In precursor layers in flowing H₂Se results in a two phase film with CuGaSe₂ near the Mo contact and CuInSe₂ at the top of the film [5]. Devices fabricated from these films behave like CuInSe₂ devices with no significant increase in V_{oc} regardless of the Ga content in the starting precursor stack. However, a high temperature, 600°C, in-situ anneal in an inert atmosphere converts the films to single phase Cu(InGa)Se₂ and gives an increased V_{oc} in devices consistent with the Ga content of the precursor. The interdiffusion of Ga and In in this system was quantified by fabricating CuGaSe₂/CuInSe₂ diffusion couples and annealing them at temperatures up to 650°C for 30 min in Ar [6]. Auger depth profiles before and after annealing were measured and the interdiffusion coefficients of In and Ga were determined from them using Fick's second law of diffusion for the case of two semi-infinite layers. This gave $D(In) = 1.5 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ and $D(Ga) = 4.0 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$. The profiles of the total of In+Ga as well as Cu and Se remained constant after the anneal. The similar interdiffusion coefficients of In and Ga indicate that the gradient in the as-selenized films is not caused by different diffusion rates of In and Ga in the ternary or quaternary phases.

Utilizing Thin CdS Window Layers in CdS/CdTe devices

To address control issues related to cell fabrication with thin CdS (< 150 nm thick) [7], two approaches for controlling CdS loss during processing were developed: 1) use of CdTe_{1-x}S_x absorber layers to reduce the driving force for interdiffusion [8], and 2) use of CdCl₂ vapor processing [9] in which the temperature-time profile of the CdTe/CdS structure and the CdCl₂ source material are independently controlled. Table 1 shows that cells made with CdTe_{1-x}S_x absorber layers having x near the solubility limit of S in CdTe at ~420°C [10] exhibit relatively constant V_{oc} with decreasing CdS thickness. The CdTe cells on the same CdS films exhibit the V_{oc} falloff reported previously.

Annealing the CdTe/CdS structure at temperatures near 550°C in argon prior to exposure to CdCl₂ vapor enhances performance, primarily the V_{oc} . For example, a cell fabricated with the anneal had: $V_{oc} = 853$ mV, $J_{sc} = 21.0 \text{ mA/cm}^2$, FF = 67%, and 12% efficiency. The control cell, without the anneal, had similar J_{sc} and FF but $V_{oc} = 806$ mV. SEM and XRD analyses show that the treatment partially recrystallizes the CdTe film. This step may anneal out defects that are otherwise not affected by the CdCl₂ treatment at lower temperatures.

Quantification of CdTe-CdS Interdiffusion

X-ray diffraction profiles of high-angle peaks in CdTe films allow determination of S content after CdCl₂ processing. We have shown that the S composition in processed films does not exceed the solubility limit of 5.8% determined for S in CdTe_{1-x}S_x [10]. Modeling techniques developed for diffusion of metal couples have been used to generate XRD peak profiles to compare with the measured profiles. For PVD cells, delayed delivery of CdCl₂ species to the heated CdTe/CdS structure results in profiles that can be explained by a simple grain-boundary and bulk diffusion model. Heating the CdTe/CdS structure and CdCl₂ in unison (as in surface treatments) results in profiles attributable to chemical mixing near the interface with enhanced loss of the CdS layer. As

part of its role in the NREL teaming activities, IEC is applying these analysis techniques to devices made by the members of the NREL CdTe window layer team. Coupling this analysis with J-V and QE measurements, the effects of processing variations on CdS loss and device performance can thus be established for a variety of cell fabrication methods.

CdTe Device Stability

CdTe/CdS solar cells have been known to exhibit reversible and irreversible degradation after being subjected to temperature, voltage and illumination conditions similar to those expected in field conditions. Some devices respond by displaying high series resistance and/or evidence of a reverse diode—both characteristics which could be attributed to the back contact. Analysis of the IEC light J-V curves indicated that there were at least two mechanisms responsible. Reversible effects included increases in series resistance and decreases in J_0 of the reverse diode upon application of reverse bias (with opposite changes upon forward bias); permanent effects included an additional increase in series resistance and a reduction in collected photocurrent [11]. At this point it is not clear whether all CdTe devices display these effects or have the same sensitivity to these stresses.

Textured SnO₂ and ZnO substrates for a-Si devices

The structural, optical, and electronic properties of 7 types of textured TCO were characterized and identical devices were fabricated on all 7 TCO materials [12]. ZnO gave 0.6 mA/cm² higher current generation than SnO₂, but poorer FF and V_{oc} in all cases. Bulk TCO film properties were insufficient to predict performance in solar cells. Novel transparent devices with structure of glass/TCO/n-i-p/ITO were characterized to determine the relative importance of scattering and reflectivity [13]. A detachable external back reflector (BR), either smooth or textured Ag, was optically coupled to the glass. It was found that substrate texture is significantly more important than BR reflectivity in increasing red response. Devices on smooth TCO substrates with textured BR have higher specular reflection losses, hence lower J_{sc} , than devices on textured substrates with smooth BRs. The QE at 700 nm for a device on a textured substrate with a smooth Ag BR was 3 times higher than for a device on a smooth substrate with a textured BR (0.32 vs. 0.11).

Improved n-layer and back contact processing leading to ~10% a-Si devices

The compatibility of ITO/Ag, ZnO/Ag and Ti/Ag back contacts with a-Si or μ c-Si n-layers was evaluated [14]. The TCO contacts were sputtered ITO or ZnO. Table 2 shows that the efficiency is improved with the μ c-Si n-layer for all contacts. Both V_{oc} and J_{sc} are improved with the μ c-Si n-layer due to its higher conductivity and transparency, respectively. Both ITO and ZnO give comparable FF on μ c-Si n-layers (68-69%) but ZnO gives higher J_{sc} due to an increased red response. The FF for devices with a-Si n-layers and TCO/Ag back contacts is 10-20% lower than for μ c-Si n-layers due to curvature around V_{oc} suggesting formation of a rectifying TCO/a-Si contact [14]. Table 2 shows that the n-layer and back contact must be optimized together to achieve maximum benefit, increasing efficiency from 8.2 to 9.8%

NREL Research Team and Other Collaborations

IEC is strongly involved in the NREL research team effort, having a leadership role in the a-Si Multijunction Device Design Team and the CIGS New Junction teams, and as active members of the CdTe team. During this phase, we have had significant collaborations with the following organizations: AstroPower, Colorado School of Mines, Colorado State University, Corning Glass, Energy Conversion Devices, Harvard University, International Solar Electric Technology, Lockheed Martin, Materials Research Group, National Renewable Energy Lab, Penn State University, Princeton University, Purdue University, Siemens Solar, Solar Cells, Inc., Solarex Thin Film, University of Florida, University of Illinois, University of South Florida, and Villanova University.

Education and Training

An important part of IEC's mission is to provide training in PV technology for engineers and scientists. During this fourth phase, three students who received education and training at IEC were hired by two U.S. PV companies. Four University of Delaware students and one Stanford University student received graduate degrees based on their PV-related research at IEC. Three professionals completed their post-doctoral studies. We also trained a Fulbright Scholar, Dr. Issakha Youm from Senegal, who helped to develop new CdS and CdTe processing methods reported above.

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Table 1. Open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF), and change in CdS thickness (Δd) for CdTe/CdS and CdTe_{1-x}S_x/CdS devices.

Cell Type	Initial d(CdS) (nm)	Final d(CdS) (nm)	Δd (nm)	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)
CdTe/CdS	105	25	80	572	24.2	56
CdTe/CdS	135	65	70	684	23.2	60
CdTe/CdS	170	115	55	775	20.5	67
CdTe _{0.95} S _{0.05} /CdS	105	75	30	769	22.6	60
CdTe _{0.95} S _{0.05} /CdS	135	85	50	782	21.6	62
CdTe _{0.95} S _{0.05} /CdS	170	130	40	769	20.3	56

Table 2. Performance of glass/SnO₂/p-i-n/TCO/Ag devices with a-Si or μ c-Si n-layers.

back contact	TCO process	n-layer	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	Eff. (%)
Ti/Ag	none	a-Si	0.863	13.5	70.2	8.2
Ti/Ag	none	μ c-Si	0.875	14.0	69.8	8.5
ITO/Ag	w/ O ₂	a-Si	0.853	13.8	60.0	7.0
ITO/Ag	w/ O ₂	μ c-Si	0.865	14.9	69.1	8.9
ZnO/Ag	w/ O ₂	a-Si	0.864	14.9	52.0	6.7
ZnO/Ag	w/ O ₂	μ c-Si	0.888	16.2	68.0	9.8
ZnO/Ag	w/o O ₂	a-Si	0.872	15.0	62.6	8.2
ZnO/Ag	w/o O ₂	μ c-Si	0.887	16.2	68.6	9.8

Title: Processing of CuInSe₂-Based Solar Cells: Characterization of Deposition Processes in Terms of Chemical Reaction Analysis

Organization: Chemical Engineering, Electrical Engineering, and Materials Science and Engineering Departments, University of Florida, Gainesville, FL 32611

Contributors: Tim Anderson, principal investigator; Paul Holloway, Kevin Jones and Sheng Li, co-principal investigators; C.H. Chang, M. Hilali, C. Huang, L. Rieth, N. Shepherd and B. Stanbery, graduate research assistants

Objectives

This research effort was initiated in May 1995 to develop a novel high-rate processing technique for device quality thin films of CIS-based materials. Important objectives of the program are the development of a plasma-assisted CIS deposition process and subsequent rapid thermal processing of optimized precursor film structures. Fundamental studies on junction formation in CIS, the effects of contaminants such as sodium on the kinetics of the growth and recrystallization processes, and phase equilibria in the Cu-In-Se system are key components of the research program.

Approach

A multidisciplinary team is investigating a processing sequence that involves the initial growth of a highly ordered structural template at relatively low rate, followed by the rapid deposition of the bulk of the absorber film's mixed-phase precursor using a plasma-assisted deposition technique. This structure is then rapid thermally processed to recrystallize the film from the seed layer. The high rate deposition utilizes an Electron Cyclotron Resonance (ECR) plasma selenium source to reduce the deposition temperature, ensure efficient incorporation of selenium in the film, and provide a driving force at the surface to overcome kinetic limitations of thermal growth at high deposition rate. Through our participation in the Thin Film Partnership Program, we also are exploring an alternative dry process (MOCVD) to deposit buffer layers. We are studying a potentially lower-cost, manufacturable process for conductive, transparent ZnO "window" layer deposition based on DC sputtering from metallic zinc targets using boron or silicon doping. The team is using a variety of characterization techniques, including the development of a new nondestructive and contactless method for measuring electronic defect state lifetimes in CIS films (Dual-Beam Optical Modulation: DBOM).

A second thread of research is the growth of single crystal CIS films to provide insight on growth mechanisms. High crystalline quality films are being grown at low temperature on single crystal substrates by migration enhanced epitaxy (MEE). These investigations will increase our understanding of the role of vacancy defect phases at junctions and the effect of "contaminants" such as sodium on the growth kinetics of CuInSe₂. The thermochemistry and phase equilibria in the Cu-In-Se system are being rigorously assessed using the CALPHAD approach and critical missing data are being measured.

Results

During FY 1996 considerable progress was made in establishing the necessary device processing infrastructure. The migration enhanced epitaxial deposition system was transferred from Boeing and further developed, the RTP system was constructed and tested, CdS growth by both CBD and MOCVD was demonstrated, and sputter depositions of Mo and ZnO were performed. This progress has positioned the team to begin optimization of the device manufacturing process and investigation of single crystal CIS structures. Concurrent with equipment construction, progress was achieved in two areas not dependent on the CIS processing capability: development of the DBOM technique to measure electronic defect state lifetimes and understanding the thermochemistry and phase equilibria in the Cu-In-Se system.

Measurement of Excess Carrier Lifetime by DBOM

We have undertaken to adapt a non-contact, nondestructive characterization technique previously developed for the measurement of photogenerated excess carrier lifetimes in silicon-on-insulator wafers to the characterization of photovoltaic absorber films and junction structures. This Dual-Beam Optical

Modulation (DBOM) technique has been used to provide measurements of the effects of processing conducted in several laboratories as part of the Junction Team's activities under the auspices of the Thin Film Partnership Program.

The contactless DBOM technique is based on the modulation of the transmitted intensity of an infrared (IR) probe beam ($h\nu < E_g$) by a visible pump beam ($h\nu > E_g$) which causes IR absorption in the CIS film. The fractional change in the transmitted intensity of the IR probe beam is directly proportional to the effective lifetime of the absorbing states in the CIS film. To the extent that this absorption is due to free photogenerated carriers, the DBOM technique can be used to determine the excess carrier lifetimes in CIS films. The DBOM technique allows areal mapping of the absorbing state lifetimes across the CIS film with a spatial resolution using the current apparatus of about 2 mm. It is also possible to perform depth profiling of the absorbing state lifetimes in the film by changing the wavelength (and hence the absorption depth in the film) of the pump beam.

The DBOM technique has been successfully employed [1] in this way to measure changes in the effective lifetime of the absorbing states in CIGS films resulting from deposition of CdS by various techniques including Chemical Bath Deposition (CBD), sputtering, and Metal-Organic Chemical Vapor Deposition (MOCVD). The calculated changes in effective lifetime of the absorbing states in the CIGS films were quite dramatic. It has become clear, however, that the analytical model used to convert measured fractional changes in absorption of the IR probe beam into an effective lifetime must be modified before it can be applied to quantitatively assess effects in the high field depletion region of an *n-p* junction structure such as this. Reformulation of the analytical model is underway and a complementary effort to numerically model the measurement has been initiated in collaboration with Purdue University.

Thermochemistry and Phase Equilibrium of the Cu-In-Se System

A critical assessment of the Cu-In-Se thermochemical and phase diagram data using standard CALPHAD procedures is being performed [2]. The outcome of this research will be a full description of the ternary phase diagram that will be useful for optimizing the deposition and annealing processes, suggesting alternative precursor film compositions, and understanding the junction formation process. Experimental work has also been performed to measure critical missing data.

A reassessment of the unary Se system was performed and new values for the thermodynamic properties of $\text{Se}_5(\text{g})$ and $\text{Se}_6(\text{g})$ were suggested. Application of the resulting thermodynamic properties to the Se evaporation process predicts that the dimer is the dominant species above ~1000 K, while Se_5 is the dominant species in the temperature range 600 to 1000 K. Given possible differences in sticking coefficients and reaction kinetics, a change in growth mechanism is expected as the source temperature is varied through this transition.

The In-Se system was next examined. A preliminary assessment indicated an inconsistency between the experimental liquidus data for In-rich solutions and the assessed phase diagram. The lack of experimental data on the behavior of the liquid solution or incorrect expressions for the Gibbs energy of formation of the compounds is believed to be responsible for this inconsistency. Thus a set of galvanic cells was constructed to measure Gibbs energy changes.

The activity of In was determined in the composition range $0.10 < x_{\text{Se}} < 0.65$ and the temperature range 800 to 975 K. The experimental In-Se phase diagram shows a liquid-liquid miscibility gap extending from $0.05 \leq x_{\text{Se}} \leq 0.30$ at the monotectic temperature 793 K. The measured indium activity data showed a constant value for $x_{\text{Se}} = 0.10, 0.15, 0.20$ and 0.25 , consistent with a miscibility gap. The measurement at $x_{\text{Se}} = 0.30$, however, produced a lower indium activity value and suggests a narrower extent of the miscibility gap than previously reported. The data showed that positive deviations from ideal solution behavior are present for In-rich compositions ($x_{\text{In}} \geq 0.7$), but negative deviations are evident at higher Se contents. Furthermore, differential thermal analysis of several synthesized alloys confirmed the previously reported transition temperatures. Expressions for the Gibbs energy of formation of InSe, In_6Se_7 and In_2Se_3 were derived from the EMF data. These data, along with literature data, were assessed and the evaluated In-Se phase diagram is shown in Figure 1.

An assessment of the Cu-Se system was next performed that included the four intermediate solid phases (Cu_2Se , Cu_3Se_2 , CuSe , CuSe_2) as line compounds. Excellent agreement between the assessed and experimental phase diagram was found, as shown in Figure 2. Four line compounds were included with only Cu_2Se melting in a congruent fashion (1393.5 K). The vapor species in equilibrium with the condensed phases in the Cu-Se system are Cu(g) , $\text{Se}_n(\text{g})$, CuSe(g) , and $\text{Cu}_2\text{Se(g)}$, with $\text{Se}_2(\text{g})$ the most prominent species. The assessed Se_2 partial pressure in equilibrium with the liquidus, Cu_2Se , CuSe , and CuSe_2 was calculated and good agreement was apparent between the calculated T-p curve and the experimental data.

With the binary phase diagrams assessed, a preliminary evaluation of the $\text{Cu}_2\text{Se-In}_2\text{Se}_3$ pseudobinary system was performed. To verify this diagram a series of alloys was synthesized from Cu_2Se and In_2Se_3 powders by long term annealing at various temperatures. X-ray diffraction analysis of quenched samples revealed agreement with the evaluated phase diagram, with the exception that the sphalerite phase exhibited a wider homogeneity range. EMF measurements allowed the Gibbs energy of formation of the Cu-rich chalcopyrite and sphalerite phases to be determined.

Device Processing

With the full ternary phase diagram beginning to emerge from the assessment effort described above, the reaction pathways for conventional processes are being understood, as well as suggesting alternative pathways. Predictions of phase diagrams along other tie-lines indicate the existence of a very low temperature eutectic valley for those tie-lines which cross the $[\text{Cu}]/[\text{In}] = 1$ meridian on the Se-rich side of the 112 phase. An improved manufacturing process is characterized by high throughput, reproducibility and low processing temperature. These criteria are met by a process that rapidly deposits precursor structures containing binary compounds (reproducibility), followed by low temperature (RTP) liquid phase assisted synthesis of the 112 phase. Candidate precursor structures have been identified that use compositions along this eutectic valley to create a low temperature, liquid phase assisted recrystallization process. These structures are now in the process of being fabricated and tested.

As a preliminary study, films of Cu and Se (~ 100 nm) codeposited at $\sim 200^\circ\text{C}$ on soda-lime glass substrates coated with Mo (~ 8 μm) were characterized. WDS analysis indicated a film composition of $43.2 (\pm 1.2)$ at % Cu, and high resolution XRD showed scattering peaks characteristic of the hexagonal layered compound CuSe . In addition unidentifiable XRD peaks were observed which disappeared upon subsequent RTP. Since the proposed reaction schemes involve excess Se, this result is promising.

Growth of CuInSe_2 on single crystal SrF_2 was also demonstrated using migration enhanced epitaxy. WDS analysis gave a Cu/In ratio of 0.92, and XRD demonstrated that the films were polycrystalline CuInSe_2 . Further optimization is now being pursued to improve substrate preparation procedures and identify regimes 2-D growth of single crystal films.

Summary

A vertically integrated CIS PV device fabrication facility has been established that includes Plasma Migration Enhanced Epitaxial (PMEE) deposition of CIS, RTP, DC sputtering of ZnO, CBD or MOCVD of CdS, and RF sputtering of Mo [3]. This processing capability is being used to pursue two lines of research. One path is to develop an alternative reaction pathway that would lead to improved manufacturability of CIS PV cells. The second path is to use single crystal substrates and PMEE to better understand deposition mechanisms (e.g., Na surfactant effects).

Improvements in the manufacturability are being researched in a number of aspects of the process. First a novel precursor composition and structure is being sought that will provide a low temperature melt to promote large grain growth. The full ternary Cu-In-Se phase diagram is being constructed, and this work has suggested novel precursor compositions and structures that should give a low temperature eutectic melt. Work on both RTP and DC sputtering of ZnO is being conducted to decrease processing time. A non-destructive contactless optical probe has been developed to probe the effective carrier lifetime and offers the potential for use in process control.

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Figure 1. Assessed T-x Phase Diagram for the In-Se System

Figure 2. Assessed T-x Phase Diagram for the Cu-Se System

Title: Experimental Study of Photodegradation in a-Si:H Solar Cells*

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Contributors: Daxing Han, principal investigator; L. E. McNeil, co-principal investigators; C.N. Yeh, research associate

Objective and Outline of the approaches

Our objective is to understand recombination and metastability in amorphous silicon alloys, especially in p-i-n device structures. Our research project is primarily aimed at determining the position and precursor states involved in the SWE, and to gain a better understanding of the relationship between material characteristics and solar cell performance.

During the contract year of 1996, we continued our experiments on electroluminescence (EL) before and after light soaking. We have completed the technique for electronic profile, $E(x)$, measurements by the null-current method. We are continuing vigorous collaborative efforts : with Liyou Yang at Solarex and with Qi Wang at NREL on photodegradation studies of H-diluted and non-diluted solar cells by EL spectroscopy; with Yue Wu in our department and H. Mahan and R. Crandall at NREL we studied the microstructure of high stability hot-wire samples by NMR; with Baojie Yan and G. J. Adriaenssens at K.U.Leuven, Belgium we have studied DOS in p-i-n solar cells by both post-transit photocurrent and EL spectroscopy.

Six papers have been published or are to be published and two abstracts have been submitted as a result of this year's research.

The Most Interesting Results

1. The effect of H dilution near the p/i interface region of a-Si:H p-i-n solar cells studied by EL

Several laboratories report [1,2] that the a-Si:H solar cells with H-dilution have better performance after light-soaking than those without H-dilution. More interestingly, Wang et al. [2] at NREL found that a few hundred Å i-layer near the p/i interface with H-dilution gives almost the same results as that of the whole 0.4-0.5 µm i-layer growth with H-dilution. The mechanism involved in H-dilution remains unclear.

Our previous work found [3] that EL spectroscopy is a sensitive tool to study the recombination process and defect energy profile in a-Si:H p-i-n solar cells. a-Si:H p-i-n solar cells with H-diluted (p-i_H-n), partially H-diluted (p-i_H-i-n), and non-diluted i-layers (p-i-n) were made at NREL on transparent conducting oxide (TCO) substrates using rf glow discharge method.[2] The p-i_H-i-n cell has a 200-300 Å H-diluted layer near the p/i interface with the remaining i-layer non-diluted. EL spectroscopy was used to study the role of H dilution. [4,5]

Figs. 1a, b, and c show the EL spectra at 290, 200, and 150 K, respectively. The EL spectrum at room temperature gives information about radiative recombination via defects. One can see in Fig. 1a that both the intensity and the lineshape of the defect-band from the p-i_H-n and p-i_H-i-n cells are similar, but different from the p-i-n cell. The defect EL peak energy is ~0.85 eV for the p-i_H-n and p-i_H-i-n cells but ~0.9 eV for the p-i-n cell. Besides, in the p-i-n cell, a much weaker EL intensity indicates a stronger non-radiative recombination via the defects. Fig. 1b shows the EL spectra at 200 K where both the defect-band and main-band luminescence can be seen. One

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Fig. 1 EL spectra for p-i_H-n (O), p-i_H-i-n (Δ), and p-i-n (◇) cells at (a) 290 K, 0.8 V, (b) 200 K, 2V, and (c) 150 K, 4 V.

and the energy profile of the deep states (DBs), $N_d(h\nu)$, can be obtained from $I(t)$. Figs. 2a and b show the results from a pair of p-i_H-n and p-i-n cells made at Solarex. Comparing the results in Figs. 2a and b, we conclude first, a single-peak band of ~ 0.9 eV in the p-i_H-n cell and a dual-peak band of ~ 0.9 and 0.75 eV in the p-i-n cell; second, the energy distribution shows a mirror-

notices first that the main- and the defect-band emissions show separated peaks for the p-i_H-n and p-i_H-i-n structures. Secondly, the main-band peaked at 1.2 eV for the p-i_H-n cell while it peaked about 1.1-1.15 eV in the p-i_H-i-n cell. Finally, a broad peak around 1.0 eV is observed as shown in the diamonds for the non-H-diluted p-i-n cells. This is a result of the overlap of the ~ 0.9 eV defect-band and ~ 1.1 eV main-band in the p-i-n cell. The tail-to-tail recombination dominates at low temperature as shown in Fig. 1c. A narrow main-band (full width at half height 0.24 - 0.27 eV) peaked at 1.2 eV for the p-i_H-n, and 1.1 eV for the p-i_H-i-n cell, with a 0.85 eV shoulder of the defect-band is observed. However, a broad 0.38 eV band peaked at ~ 1.1 eV is observed in the p-i-n cell. Again, this is a result of the overlap of the ~ 0.9 eV defect- and ~ 1.2 eV main-band in the p-i-n cell. The main-band peak energy in the p-i_H-n cell locates higher than that in the p-i_H-i-n, and p-i-n cells. The narrowest band tail is found in the whole i-layer H-diluted p-i_H-n cell. (This is also indicated in the temperature dependences of forward current and EL efficiency).

Therefore, we conclude that the H-dilution processing modifies the properties of both the deep states (see Fig. 1a) and tail states (see Figs 1b and 1c).[4,5] The similarity of light-soaking behavior from both the p-i_H-n and p-i_H-i-n cells implies that the defect states which mainly originated from the i-layer near the p/i interface region may play an essential role for the V_{oc} in this group of cells.

2. DOS in p-i-n solar cells analyzed from both post-transit photocurrents and EL spectra

To clarify the correlation of the EL defect band to the deep state energy profile, post-transit photocurrent experiments[6] were carried out in several groups of cells in which the lineshapes of the $EL_d(h\nu)$ were different. The transient photocurrent in the post-TOF time regime, $I(t)$, is electron-emission limited,

symmetric feature in $EL_d(h\nu)$ and $N_d(h\nu)$. This can be understood as the transition path corresponding to EL_d is the transition between the valence band tail and the DBs, but the $N_d(h\nu)$ profiles are due to the electron thermal emission from the DBs to the conduction band edge. The above comparison study proves that not only the difference of the defect EL spectrum lineshape between p-i_H-n and p-i-n cells but also the room temperature EL spectrum can be used to study the defect energy profile in solar cell structures.

Fig. 2 left: EL spectra at 300 K, applied voltage 0.8 V; right: DOS energy profile measured by the post-TOF technique from 0.5 μm p-i_H-n and p-i-n cells.

3. A New H Distribution in Hot-Wire a-Si:H Studied by Nuclear Magnetic Resonance (NMR)

The new hot-wire (HW) material exhibits less photodegradation than a-Si:H grown by the traditional glow-discharge (GD) technique.[7] Unique features of the most stable HW a-Si:H are the very low H content of 2-3 at. % compared to 8-10 at. % in device quality GD a-Si:H and the low DB density. It is not clear what microstructure could permit such efficient termination of DBs and strain reduction in HW a-Si:H. Understanding the microstructure of HW a-Si:H could provide valuable insight into the ideal micro-structure of an a-Si:H network with very low defect density and high structural stability.

The H distributions were characterized by ^1H NMR spectrum and multiple quantum NMR.[8,9] The microscopic structure of the clustered hydrogen complexes in the HW is significantly different from that of the device quality GD a-Si:H. This is evidenced by the broad 50 kHz linewidth of the broad component in the HW sample versus less than 35 kHz in GD a-Si:H. The hydrogen clusters associated with the broad line in the HW sample have a typical size of at least 14 H atoms compared to about 6 in device quality GD a-Si:H. The dispersed H atoms, which give rise to the narrow component of the ^1H spectrum in the HW sample, account for less than 0.3 at.%; this is about a factor of 10 smaller than in device quality GD a-Si:H. Therefore, an ideal a-Si:H network with low DB and high stability may not necessarily be homogeneous. We show a Cartoon of the H distribution in HW and GD a-Si:H samples in Fig. 3a and b.

Fig. 3 Hydrogen distribution of

(a) GD a-Si:H, 8-10 at.% H
 isolated H 2-3 at.%
 clustered(6 H) 6-7 at.%

(b) HW a-Si:H, 2-3 at.% H
 isolated H 0.2 at.%
 clustered(>14 H) 2 at.%

4. Internal-electric-field Profile

Since the charge collection process in a-Si:H based solar cells depends upon field-assisted drift in the internal-electric-field, experimental knowledge of internal-electric-field profiles could be crucial to clarifying the mechanism involved in metastability. We studied the internal electric field profile by using a transient-null-current method. Our preliminary results show that the more stable V_{oc} in p-i-H-i-n cells can be attributed to a lower defect density near the p-i interface that results in an increase of the field strength from 2.6 Vcm^{-1} to $3.2 \times 10^4 \text{ Vcm}^{-1}$. The stronger field strength result from hydrogen-dilution is attributed to the lower density of defects near the p-i interface, which act as non-radiative recombination centers.

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Title: Microscopic Origins of Metastable Effects in a-Si:H and Deep Defect Characterization in a-Si,Ge:H Alloys

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The primary research goals of this program are to elucidate the basic mechanisms by which a-Si:H degrades with light exposure, and to study the defect structure in low bandgap a-Si,Ge:H alloys. During the past year we have carried out the following studies: (1) An evaluation of light induced degradation in a-Si,Ge:H glow discharge samples produced at United Solar Systems Corporation; (2) The completion of our evaluation of the electronic properties of a-Si,Ge:H/a-Si:H heterojunctions samples; and (3) A study of light-induced degradation in glow discharge a-Si:H comparing hydrogen and helium diluted silane with pure silane produced samples.

Approach and Results

Our research related to degradation in the low band-gap a-Si,Ge:H alloys examined seven films deposited by the rf glow discharge method at United Solar Systems Corporation (courtesy of J. Yang and S. Guha). Five of the samples had Ge fraction in the range 30 to 35at.% (most suitable for cells), while the remaining two samples had Ge fractions near 20at.% and 50at.%, respectively. For each sample we carried out sub-band-gap phot capacitance and transient photocurrent spectroscopy to examine the optical transitions associated with deep defects, and also drive-level capacitance profiling measurements to deduce the thermal transitions associated with the defects. Samples were examined in a dark annealed state, as well as a light soaked state produced by exposure from 70 to 100 hours to a focussed tungsten halogen light source. Appropriate long pass filters were employed to achieve uniform carrier generation rates over the 1 to 2 μm thickness of each sample. Measured light intensities at the sample surface ranged from 4 to 6 W/cm^2 . The samples were immersed in methanol during light exposure to maintain a surface temperature below 65°C.

Drive-level capacitance profiling yields a direct quantitative estimate of deep defects in a band of thermally excited transitions we will refer to as TH1. The density of these defects generally increases by a factor of 2 to 2.5 after light soaking as displayed in Fig. 1(a). The sub-band-gap phot capacitance and photocurrent spectra reveal two defect sub-bands: one representing transitions from a defect electron into the conduction band (to be denoted as OP1), and the other from the valence band into an empty defect level (denoted as OP2). The details of the analysis of these spectra to deduce the properties of these defect bands have been described previously. From auxiliary measurements we know that there must exist significant contributions from at least two distinct defect sub-bands in the a-Si,Ge:H alloys. A reasonable working hypothesis is that the OP2 transition is due to valence band electrons excited into D^+ states, while the TH1 and OP1 bands correspond to transitions out of D^- or D^0 states (or a combination of the two). In Figures 1(b) and 1(c) we also have summarized the magnitudes of the OP1 and OP2 defect bands in the dark annealed and light soaked states of each sample.

We find that for most samples, the magnitudes of each of the deduced defect bands, TH1, OP1, and OP2, increase after light soaking. However, the relative factors of these increases vary among the samples studied. In addition, the TH1 defect densities are slightly higher in the more recently grown 35at.% Ge samples (8257 and 8330) than the earlier samples (6558 and 6565) while the OP2 densities are significantly lower. Also, the recent sample pair exhibit slightly lower conductivity activation energies (by about 50meV in the annealed state) indicating a slightly greater n-type character to these two

FIG. 1. Comparison of the deep defect densities obtained for seven a-Si,Ge:H samples obtained from capacitance profiling (TH1), and from sub-band-gap optical spectra (OP1 and OP2) in both the dark annealed (solid bars) and light soaked states (shaded bars). The variation between TH1, OP1, and OP2 indicates that more than a single defect sub-band must be involved. We believe the OP2 band arises from D^+ states, while the TH1 and OP1 bands arise from D^- and/or D^0 states.

samples. This supports the assignment of D^+ to the OP2 defect band. Since the increase of OP1 and TH1 with light soaking is different among the samples, this suggests that both D^- and D^0 states are involved. We think it likely that the TH1 determined defect density is more heavily weighted toward D^- states than is the OP1 defect density.

The inferred presence of charged defect states in the a-Si,Ge:H alloys, and the fact that their ratios appear to change as a result of light soaking, is clearly very important regarding light induced degradation of photovoltaic devices fabricated from these alloys. Indeed, modeling of a-Si,Ge:H p-i-n cells based only upon the observed increase in deep defects after light soaking (in companion films) have failed to account for the observed changes in device performance. Because our experimental results indicate that there exist significant concentrations of charged defects even in the most intrinsic a-Si,Ge:H alloys, these definitely need to be included in future device modeling studies. Our plans for the near future regarding studies of a-Si,Ge:H include obtaining very lightly doped n and p-type samples so that we can more quantitatively determine the concentrations of deep defects in their different charge states.

Our second area of study has been concerned with the electronic properties of a-Si,Ge:H/a-Si:H heterojunctions. It is likely that the properties of this interface plays a key role in determining the performance and the stability of tandem and triple amorphous silicon based cells. A total of eight samples were obtained from United Solar Systems Corporation, consisting of a thinner (3000-5000Å) layer of a-Si:H next to a thicker layer of a-Si,Ge:H alloy with roughly 35at.% Ge. The opposite side of the a-Si:H layer was contacted either with a heavily doped p^+ crystalline Si substrate or a metal Schottky barrier.

We applied a filling pulse to place the junction nearest to the a-Si:H/a-Si,Ge:H interface into forward bias and then recorded the capacitance transients after restoring the initial reverse bias. Under these pulsing conditions all the samples, except those in which the interface was adjacent to the Schottky

barrier, exhibited a particular type of capacitance transient. As displayed in Fig. 2, the transients can be divided into two time regimes: a short time regime, in which the capacitance increases with time corresponding to a *loss* of negative charge (electron-emission type), and a long time regime, in which the capacitance decreases with time corresponding to a *gain* of negative charge (hole-emission type). If the filling pulse voltage is zero or slightly *negative* (i.e. still in reverse bias), the long time, hole-emission type behavior is not observed. This suggests that hole injection from p⁺-silicon is a necessary condition for the occurrence of this second type of transient. Also, the absence of the hole-emission type transients for the forward biased Schottky barrier contacts, where no hole injection can occur, strongly supports this conclusion.

We can also demonstrate that the hole-emission region of the capacitance transients are due to traps at the heterojunction interface. Through a simple analysis, the interface charge density can be shown to be

$$\Delta Q_{\text{int}}(t) = \frac{\epsilon^2 A^2 \rho_{\text{a-Si,Ge:H}}^{\text{ave}}}{2d} \left[\frac{1}{C_i^2} - \frac{1}{C(t)^2} \right], \quad (1)$$

where A is the active area, d is the thickness of the a-Si:H layer, $\rho_{\text{a-Si,Ge:H}}^{\text{ave}}$ is the average charge density in the depleted a-Si,Ge:H layer, and where C_i and $C(t)$ refer to the initial capacitance and the capacitance at time t, respectively. According to this analysis, if the capacitance transients are dominated by the emission of interface charge, then the right hand side of Eq. (1) should be independent of the applied bias provided it is large enough to allow complete depletion of the interface traps.

Figure 2(a) provides a comparison of the capacitance overshoots for one sample as a function of time for different values of the ambient bias under otherwise identical pulsing conditions. The calculated interface charge density from Eq. (1) corresponding to these transients is shown in Fig. 2(b). The value of $\rho_{\text{a-Si,Ge:H}}^{\text{ave}}$ for each sample was obtained from drive-level capacitance profiling within the a-Si,Ge:H

FIG. 2. (a). Capacitance transients for sample 7 at 370K using the same 1.6 volt, 300s filling pulse, but using different ambient bias voltages as indicated. (b) Calculated interface trap density derived using Eq. (1) for each transient in (a). The close overlap of these different curves confirms that the dominant traps are confined to a particular spatial location (the heterojunction interface).

layer (in this case $\rho_{\text{a-Si,Ge:H}}^{\text{ave}} \approx 2 \times 10^{16} \text{ cm}^{-3}$). The close overlap of these curves indicates that the charge emission is indeed occurring from within a very localized spatial region.

We also measured two samples that were identical except for the a-Si:H/a-Si,Ge:H interface treatment. From drive-level profiling, we determined that the density of states for the a-Si,Ge:H layer in both samples was nearly identical (about $1.5 \times 10^{16} \text{ cm}^{-3}$) while their deduced trap densities differed by a factor of 2.5. Since the only difference between these two samples was their interface preparation, this verifies that the observed traps are located very close to the interface.

For all eight samples studied in this fashion, we deduced interface defect densities within a factor of two of 10^{11} cm^{-2} . We also determined that holes trapped at these defects did not seem to recombine with free electrons. Therefore, while these states appear not to behave as recombination centers, such densities of trapped interface charges will significantly alter the electric field profiles in such devices and thus affect the quantum efficiencies. The control of these interfacial trapping states appears to be essential for device optimization.

Finally, during this year we also carried out comparison studies between a-Si:H samples grown by the glow discharge method either with 100% silane, or with silane diluted in H_2 or He gas. The samples were of a n-i-p configuration deposited on Cr coated glass, and were obtained through collaboration with the V. Perez-Mendez group (F. Zhong and W.S. Hong) at Lawrence Berkeley Laboratory. The defect densities in these samples were characterized by drive-level capacitance profiling measurements.

In Figure 3 we compare the light-induced degradation of one hydrogen diluted sample, one helium diluted sample, and the 100% silane sample. Samples were exposed for up to 300 hours to a 1.9eV red filtered tungsten-halogen light source at an intensity of 3.4 W/cm^2 . We observed a substantially lower degraded defect density in the hydrogen diluted sample at each exposure, as well as much earlier saturation in that case. Surprisingly, the standard and He diluted samples are nearly identical in their degradation properties. In constrast, *the hydrogen diluted sample exhibits at least a factor of five improvement compared to these other glow discharge a-Si:H samples*. Further studies of the degradation properties of a-Si:H grown using different dilutant gases will be continued into next year.

FIG. 3. Comparison of drive-level determined defect densities for samples 1 (hydrogen diluted, solid circles), 5 (helium diluted, solid triangles) and 6 (undiluted SiH_4 , open squares) as a function of light exposure. The total defect densities are estimated by multiplying these drive-level values by a factor of 1.5.

Title: **Advanced Processing Technology for High Efficiency Thin-Film
CuIn_x Ga_{1-x}Se₂ and CdTe Solar Cells; Heterojunction
Development and Optimization in Thin-Film Compound
Semiconductor Solar Cells**

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CuIn_x Ga_{1-x}Se₂

Objectives

The objectives of this project are to develop improved processing techniques for CuIn_x Ga_{1-x}Se₂ (CIGS) solar cells and to correlate performance and processing mechanisms.

Approach

Device properties are determined by two primary process variables, the precursor and the anneal profile. The precursor consists of layers of Cu, In, Ga, and Se which are deposited in various sequences. All of the precursor components are deposited at temperatures typically below 275° C. Fabrication is completed by annealing the precursor with a temperature ramp up to 550 C followed by a cooldown to room temperature. During the anneal profile Se flux is applied as an additional variable. There are virtually an infinite number of perturbations that can be made with these processing components. We have spent considerable effort exploring this deposition space, and from the understanding which we have developed based on this experience we have narrowed the field two primary approaches which we label PI and PII. These offer two different options for the incorporation of Ga and the optimization of performance. The key difference between the two is that in PI the Ga is deposited before the In, while in PII the In is deposited first. Since to first order In and Ga are thought to be interchangeable in a homogeneous CIGS lattice, by reversing the order in which they enter the lattice we examine to what extent this is found to be the case.

Results

An important aspect of the difference in performance between PI and PII is the quantum efficiency(QE) spectral response shown in figure 1. The resulting current densities for PI devices is very high(- 40 mA/cm²). This level of performance can be achieved on a consistent run to run basis. It is to be noted that the band gap of these devices, though containing significant Ga, is unchanged from CIS. This is due to the method of incorporation for Ga which causes it to accumulate in the rear of the device. This is felt to result in the formation of an effective back surface field which aids the collection of carriers. The slopes in the central portion of the QE curves for the PI devices are believed to be due to the influence of trace Ga in the space charge(SC) layer. As the Ga increases, the slope increases causing some loss in J_{sc}, although E_G has not changed.

PII devices allow much higher levels of Ga into the SC layer resulting in the band gap shift observed in figure 1. The increase in the slope in the central region is also consistent with increasing Ga incorporation.

The control and understanding of Ga incorporation has resulted in the achievement of 12% efficiency in PI devices which is the primary goal of the first year of this project. This result is for device IB which had J_{sc} of 39.2

mA/cm^2 , V_{oc} of .463 and FF of .66. Due to the band gap shift V_{oc} 's up to .57 have been achieved in PII devices. The accompanying loss of J_{sc} , however, thus far results in efficiencies in the 11% range. As we combine the virtues of these two approaches to Ga incorporation we expect efficiencies in the 15% range while still maintaining our manufacturing-friendly guidelines.

Figure 1. Quantum efficiency for type I and type II devices.

Heterojunction Characterization and Development

Objectives

The objectives of this project are to advance understanding of heterojunction formation and performance in CdTe and CIS devices and to use that understanding to guide further development of the technologies.

Results and Discussion

In last year's report we discussed the successful application of Shockley-Read-Hall (SRH) recombination theory to CdTe devices. The key variable affecting device performance for CdTe is the recombination lifetime near the metallurgical junction. Because of the similarities between CdTe and CIGS technology we expect SRH theory to apply equally to CIGS devices. An example of the ability of the theory to fit experimental data for CIGS is shown in figure 2. $I_{sc} - V_{oc}$ data is particularly useful in that it eliminates the series resistance and allows observation of the IV curve over a large voltage range. The two sets of data points are for increasing and decreasing voltage (intensity) to demonstrate reproducibility. The fit using the SRH model is accomplished using a combination of measured parameters and parameters from the literature. While the uncertainties in these parameters contribute some uncertainty to the determination of a given parameter, the range is fairly narrowed by the required self-consistency of fitting the data. In particular, these uncertainties are substantially eliminated when making comparisons between devices on the same substrate. As discussed above we have recently focused on the role of Ga. In making our devices we make a matrix of 25 devices on a single substrate in which the Ga level is systematically varied. By fitting data as in figure 2, for these we can determine the effects of Ga on the fundamental properties. An example for a PII device is shown in table 1. The key processing variable is the Se/Ga ratio which represents not only the amount of Ga that is incorporated but the environment of incorporation as well. We see a clear correlation between this

processing parameter, the recombination lifetime and ultimately the V_{oc} . We find that V_{oc} is more sensitive to the Se environment than to the Ga level itself. This kind of insight is invaluable in guiding our fabrication efforts and has contributed greatly to the progress we have made in performance. Ongoing refinements to these procedures are expected to further advance our understanding of the important links between processing, fundamental parameters and performance.

Figure 2 Fit to J_{sc} - V_{oc} data for a type I device. The dashed line is J_{sc} at one sun. The lower line is the theoretical curve without including shunting. The line through the data includes a shunt contribution to the current.

Relative Se/Ga		1.6	1.4	1.2	1.0
minority lifetime	10^{-9} s	2.8	2.0	0.71	0.42
V_{oc}		.53	.51	.46	.43

Table 1. Properties of a type II device versus relative Se/Ga flux.

CdTe

Objectives

The main objective of this project is to develop high efficiency CdTe solar cells based on processing conditions that are favorable for manufacturing purposes. This stems from the fact that while nearly 16% efficiencies have been achieved for laboratory devices, these were fabricated using processes that have certain disadvantages for a manufacturing environment: high processing temperatures and expensive borosilicate glass substrates. Another task is to evaluate alternative window layers/TCO's.

Results-Discussion

Inexpensive soda lime (SL) glass substrates are used for the fabrication of CdTe/CdS solar cells using a wide range of deposition conditions. Emphasis is placed on the substrate temperature during the deposition of CdTe by the closed-spaced sublimation (CSS) process. This is typically varied in the range of 450-600 °C. The CdS thickness is also a key device parameter since it determines the spectral response (SR) of the cells below 500 nm. A certain amount of the CdS films is usually consumed during the fabrication process leading to the formation of a CdSTe layer at the CdTe/CdS interface. The photovoltaic parameters of two typical CdTe cells fabricated on SL glass substrates are listed in table 2; these suggest that high efficiency cells can be prepared at low processing temperatures (<550 °C). Devices fabricated on SL glass using low processing temperatures have yielded near 14% efficiencies.

T Deposition	V _{OC} (mV)		FF, (%)		J _{SC} (mA/cm ²)	
Low	830	839	71	71	20.6	19.0
Low	832	841	71	74	20.8	20.3
Low	833	837	71	73	20.4	19.8
High	839	834	73	71	20.0	21.1
High	839	834	72	71	21.1	21
High	836	828	71	69	21.2	21

Table 2: The photovoltaic parameters of CdTe cells prepared at low and high processing temperatures on soda lime glass substrates.

The CdTe deposition temperature can be used as a means of controlling the final thickness of the CdS films. The SR of two cells prepared with CdS films of 600 and 700 Å thicknesses are shown in figure 3. The blue response of the two cells suggests that the final CdS thickness is the same. The open-circuit voltage and fill factor of the 700 Å device were higher by 50 mV and 8% respectively (than the 600 Å one). This result suggests that device performance can be enhanced by fabricating devices using CdS of a "large" starting thickness, and consuming part of this layer by using the appropriate processing steps.

The CSS process is also being used for the deposition of CdS films. This technology offers manufacturing advantages over the commonly used chemical bath deposition (CBD). The influence of temperature profiling and various ambients on the properties of the CSS-CdS films and the performance of devices have been studied. Solar cell efficiencies are greatly enhanced when the CSS-CdS films are prepared in O₂ containing ambients. Heat treatments of the CSS CdS have also been found to influence device performance. Solar cells prepared entirely by the CSS process have yielded efficiencies in excess of 14%.

Figure 3. The SR of CdTe cells prepared with CdS films of different starting CdS thicknesses.

Zinc selenide (ZnSe) films are also being deposited by CSS and used for the fabrication of CdTe/ZnSe solar cells. The most difficult aspect of these devices is controlling the extent of interdiffusion between the ZnSe and CdTe layers. Currently device performance is only at the 10% level. The best V_{oc}'s and ff's achieved are 780 mV and 65% respectively. Spectral response measurements indicated that J_{sc} for most CdTe/ZnSe cells is low due to inefficient collection. These measurements also suggested that once the collection problems are resolved the CdTe/ZnSe cells have the potential of achieving higher J_{sc}'s than the CdTe/CdS cells.

Title: High Efficiency Thin Film Cadmium Telluride Photovoltaic Cells

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Objectives

This project is focussed on improving the fundamental understanding of rf sputtering for the deposition of CdTe-related polycrystalline thin film photovoltaics with the goal of exceeding 14% AM1.5 efficiencies on soda-lime glass.

Technical Approaches

The University of Toledo effort emphasizes rf sputtering of both CdS and CdTe from compound semiconductor targets.¹ During the past year we realized a new performance high of 11.6% for our all-sputtered cells. See Fig. 1 below. This represents a record for cells prepared by sputtering of both the CdS and the CdTe layers.^{1,2,3} Continuing efforts were placed on cell fabrication with the goal of improving contact stability and using thinner CdS layers. We have also continued collaborative efforts with the CdTe Thin Film Team, including efforts toward understanding the limitations of thin CdS. This has included the fabrication of cells on borosilicate glass substrates from the University of South Florida with nominal CdS thicknesses of 300, 200, 100, 80, 60, 40, 20, and 0 nm. (See Ref. 4 and further discussion later in this report.)

During the past year a substantial effort was placed on studies of $\text{CdS}_x\text{Te}_{1-x}$ alloy films and on the CdS/CdTe interdiffused layers. Alloy films were prepared by pulsed laser deposition over the complete range of x-values. These films and interdiffused layers were studied by photoluminescence (PL) and Raman scattering, Rutherford backscattering (RBS), and by grazing incidence x-ray scattering (GIXS). See references 5-7. Dean Levi, *et. al.* have studied time-resolved PL and absorption in our films.⁸ Discussion of GIXS results was presented in the Thin-Film Teaming meeting of Nov. 17, 1997 and summarized in notes circulated from the DOE Center of Excellence Review Meeting on the Advanced Photovoltaic Project on Nov. 22, 1996. An extensive series of frequency-dependent C-V measurements is now being analyzed in the M.S. thesis work of E. Bykov.

Record Performance for an All-sputtered Cell

The best all-sputtered solar cell to date was one of our cells measured during the past year at NREL. The superstrate was $8 \Omega/\square$ soda-lime glass from LOF. The structure was glass/ SnO_2 :F/CdS(0.25 μm)/CdTe(1.8 μm)/Cu(4 nm)/Au(50 nm). The CdS and CdTe were sputtered sequentially in the same two-magnetron chamber, about 0.2 μm of CdCl_2 was deposited by pulsed laser deposition followed by 400 °C anneal for 20 minutes in air, followed by a deionized water rinse. The evaporated

Cu/Au contact structure was diffused for 30 minutes at 150 °C. The I-V performance is shown in Fig. 1. Note that the voltage and fill factor are good, but the current is limited by the relatively thick CdS layer. A major effort is underway to find ways of reducing the CdS thickness and still retain high fill factors and voltage in these sputtered cells on glass. See further results under teaming activities below.

A further limitation in these cells is the deterioration in the contact. We found the efficiency of cell SSC372-20 after four weeks to be 0.8% lower than initially. (The NREL test was done approximately three weeks after fabrication.) We have been collaborating with IEC and SCI, as well as exploring our own graphite contacts, to try to identify better and more stable contacting procedures for our sputtered CdTe.

CdTe Teaming Activity – thin CdS

As part of our contribution to the first of two recent rounds of teaming activity, we prepared four types of all-sputtered cells with CdS thicknesses of 300, 200, 100, and 60 nm. In the second round, we fabricated cells with 80, 20, and 0 nm of CdS. In both cases we prepared identical films on superstrates of Corning 7059 with SnO₂ deposited by the Univ. of South Florida, and on soda-lime glass superstrates from LOF with their 8 Ω/□ SnO₂:F. The films were deposited side-by-side in the sputter chamber. This gave us the opportunity to make a direct comparison of the two superstrates for a wide range of CdS thicknesses. The results are summarized in Tables 1 and 2 below. Table 1 shows measurements obtained at Colorado State University one to two months after cell fabrication. Table 2 shows a combination of measurements, some done in our lab immediately after fabrication and one set done at CSU.

Since we utilize an optical thickness monitor during growth, it is straightforward to control the CdS thickness. In addition, the sputtered CdTe grows easily on either type of SnO₂. The 1 mm 7059 superstrates are more transparent than the 3 mm LOF soda-lime. The USF coating is smoother and more transparent than the LOF and it is our understanding that the USF coating uses a final intrinsic layer of SnO₂. The availability of both types of cells with the wide range of CdS thicknesses presents an unusual opportunity to explore the role of CdS. It is known that optical absorption in the CdS window layer can severely limit the cell current and finding ways to reduce it is a major objective of the teaming activity. In addition, it is important to understand the importance of interdiffusion in optimizing the cell performance. In this regard it is particularly interesting to be able to prepare cells

University of Toledo CdS/CdTe

Sample: SSC-372#20 Temperature = 25.0°C
Feb 7, 1996 10:45 AM Area = 0.1150 cm²
ASTM E 892-87 Global Irradiance: 1000.0 Wm⁻²

$V_{oc} = 0.8056 \text{ V}$ $V_{max} = 0.6514 \text{ V}$
 $I_{sc} = 2.266 \text{ mA}$ $I_{max} = 2.053 \text{ mA}$
 $J_{sc} = 19.70 \text{ mAcm}^{-2}$ $P_{max} = 1.337 \text{ mW}$
Fill Factor = 73.27 % Efficiency = 11.6 %
10 min soak @ P_{max} , 6:13 cool, fast sweep, fan on

Fig. 1. I-V response of all-sputtered cell SSC372, contact 20.

with pure CdTe and no CdS layer at all. This we have done with the cells described in the two tables. Note that the tested cells had an area of 0.113 cm^2 and were selected from a structure with either 6 or 9 cells defined by the Cu/Au evaporation mask. It should be pointed out that our deposition temperature (380°C) and postdeposition processing has been optimized with the LOF substrates and there is no reason to believe that the fabrication process on the 7059/USF superstrates is fully optimized. We have made fewer than ten deposition runs on the 7059 superstrates.

Table 1. Comparison of cell performance on different substrates (round 1)

[cell I.D.] CdS thickness [cell I.D.]	superstrate type	$V_{oc}(\text{mV})$	$J_{sc}(\text{mA}/\text{cm}^2)$	FF(%)
[SSC303-14] 300 nm [SSC303-18]	7059/USF	790	19.5	70
	LOF 8 $\Omega/\square$	800	19.0	70
[SSC304-7] 200 nm [SSC304-12]	7059/USF	780	19.5	67
	LOF 8 $\Omega/\square$	755	20.0	65
[SSC305-14] 100 nm [SSC305-11]	7059/USF	780	22.5	68
	LOF 8 $\Omega/\square$	600	22.0	60
[SSC306-21] 60 nm [SSC306-17]	7059/USF	760	24	62
	LOF 8 $\Omega/\square$	490	23	60

Table 2. Comparison of sputtered cell performance on different substrates (round 2)

[cell I.D.] CdS thickness [cell I.D.]	superstrate type	$V_{oc}(\text{mV})$			$J_{sc}(\text{mA}/\text{cm}^2)$			FF(%)		
		day 1	day 5	day 30 [‡]	day 1	day 5	day 30 [‡]	day 1	day 5	day 30 [‡]
[SSC489-22] 80 nm [SSC489-14]	7059/USF	784	761	750	21.4	21.0	23.6	68.5	65.6	65
	LOF 8 $\Omega/\square$	623	595		19.9	20.3		59.5	58.5	
[SSC490-23] 20 nm [SSC490-13]	7059/USF	769	711	765	22.7	21.6	19.8	63.6	54.7	53
	LOF 8 $\Omega/\square$	511	435		19.9	19.7		64.4	61.2	
[SSC491-8] 0 nm [SSC491-24]	7059/USF	763	696*		20.1	19.2*		56.6	42.9*	
	LOF 8 $\Omega/\square$	473	414*		20.1	19.4*		57.4	57*	

* these cells were tested on day 2 ‡ measurement done > 30 days later at CSU

We find that the largest difference between the two types of superstrates is that the cells sputtered on 7059/USF had consistently higher V_{oc} than those on LOF. This voltage difference increased

as the CdS thickness decreased. Note that with 300 nm of CdS the V_{oc} for the two types of superstrates are essentially the same, ~ 800 mV. However, for 60 nm of CdS or less the V_{oc} for LOF superstrates is 490 mV or less whereas for the USF superstrates, the V_{oc} is 696 mV or higher.

Conclusions and future directions

We have recently brought on-line a second small system for rf sputtering of intrinsic SnO_2 . We shall be using this to apply a thin insulating layer to the standard LOF superstrates we have been using. Hopefully this will improve the performance of cells with thin (<100 nm) CdS, as was observed with the USF superstrates. The second major area of emphasis is on improved contact structures. We continue to collaborate with other thin-film partners on this issue, and are bringing additional capability with a three-gun DC sputtering system donated to us by Harris Semiconductor.

We believe that recent results, especially from the teaming activity, indicate that the sputtering process should be quite capable of reaching efficiencies $>14\%$, provided that the CdS can be thinned or removed entirely and stable contacts found. Furthermore, we feel that deposition speed is not a major problem since we demonstrated this year that the sputter deposition rate increases linearly with rf power at least up to 70 W into a 2-inch, unbacked target. At this power we measured a rate of $1 \mu\text{m}/12$ min for a target-substrate distance of three inches.

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Title: Optimization of Laser Scribing for Thin-film PV Modules

Organization: Department of Physics and Astronomy
The University of Toledo
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Lower Tier Subcontractors: Solar Cells Inc.
International Solar Electric Technologies

Objectives

This thin-film R & D partnership contract is designed to evaluate and optimize the use of new types of lasers and laser scribing processes to improve the reliability, performance, and cost-effectiveness of monolithically integrated polycrystalline thin-film photovoltaic modules. The project is being carried out with support from the lower-tier subcontractors and in collaboration with the CIS- and CdTe-based thin-film PV research teams.

Technical Approach

Materials for polycrystalline thin-film PV include CdTe, $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$, $\text{SnO}_2\text{:F}$, ZnO:Al , molybdenum and other metals. We find that the required energy density and the quality of the laser scribe in these thin-film materials is most dependent on two fundamental properties: 1) pulse duration and 2) wavelength. In order to obtain a wide range of these parameters, we initially chose four laser systems, with wavelengths and pulse durations given in brackets -- the flashlamp-pumped Nd:YAG laser (fp-YAG) [$\lambda=532$ & 1064 nm, $\tau_p=10$ nsec], the continuous-lamp-pumped Nd:YAG laser (cw-pulsed or cwp-YAG) [$532/1064$ nm, $90\text{--}600$ nsec], the XeCl excimer laser [308 nm, 15 nsec], and the copper-vapor laser [$511/578$ nm, 50 nsec]. Recently we have added the KrF excimer laser [248 nm, 25 nsec] to this list by performing studies at an applications lab of the manufacturer, Lambda Physik. Analysis of the scribe lines and ablation spots is being done by optical microscopy, SEM, stylus profilometry, and electrical isolation tests.

Laser systems

Initial work with the Cu vapor laser was done in an applications lab of C J Laser Corporation in Dayton, Ohio. More recent work is being done at the University of Dayton Research Institute. Our work with the continuous-lamp-pumped YAG has been done at Solar Cells Inc, in Toledo, OH, and we have used their stylus profilometer for quantitative analysis of scribe lines and spots. ISET has supplied us with samples of films of moly on glass, CIGS/moly/glass, and ZnO/glass, and is assisting with complete CIGS laser-scribed cell fabrication studies. The fp-YAG and the XeCl excimer lasers are in our lab at the University of Toledo. We have added the Lambda Physik KrF laser to our study because this system has the highest pulse energy of the excimer gases and it has achieved significant

acceptance in a number of industrial applications. In addition, we were able to use a beam delivery system incorporating a beam homogenizer and projection imaging onto the workpiece to test its potential as a system for scribing without beam scanning. See discussion below.

In addition to the fundamental properties of pulse duration and wavelength, we are addressing the issue of cost-effectiveness as determined by laser energy needed per unit scribe length, laser operating efficiency and cost, speed of scribe, suitability for multi-beam handling, optimum focussing, pulse-to-pulse amplitude fluctuations and beam profile fluctuations especially as these relate to the fundamentals of laser operation (gaseous vs. solid state media, longitudinal vs. transverse discharge, etc).

Ablation thresholds

We have studied the threshold energy densities for the onset of measurable surface damage for each of the five different laser systems. The results for the damage (vaporization) threshold are presented in Table 1.

Table 1: Threshold for Vaporization of Thin-Film Materials

$\lambda(\text{nm})@ \Delta t$	SnO_2 (J/cm ²)	CdTe (J/cm ²)	ZnO (J/cm ²)	CIS (J/cm ²)	Moly (J/cm ²)
1064 @ 10ns	2.4	0.65	3.9*	0.32	0.44
532 @ 10ns	4.5	0.10	3.5*	0.15	0.26
532 @ 90ns	5	0.22	12*	0.23	0.5
511, 578 @ 55ns	3.4	0.1	0.6*	0.1(CIGS)	1.0
308 @ 15ns	0.44	0.08	0.24	0.13(CIGS)	0.24
248 @ 25ns	0.22	<0.07	0.16	<0.08(CIGS)	0.32

* large shot-to-shot variations

Optimum energy densities for thin-film scribing

In addition to threshold energies, we have studied the vaporization depth as a function of pulse energy to identify the energy density needed to optimize the scribing rate. An example of the effect of increasing pulse energy density on the thickness of material removed is given in Fig. 1. These data show the depth of material vaporized per 90 nsec pulse of the cw lamp-pumped, frequency-doubled Nd:YAG laser for six different thin films. Data were from stylus profilometer traces across spots from single laser shots. Typical film thickness was about 2 μm except for SnO_2 , which was 0.5 μm , and the NREL CdTe which was about 5 μm . The peak energy density for our focussing conditions with this laser was $\sim 20 \text{ J/cm}^2$. For all of the films, except for the 5 μm thick CdTe, it was possible to reach complete removal of the film with a single pulse. (However, the highest energy does not yield the most efficient film removal.)

Although the vaporization depth rises with pulse energy, it is generally sublinear (note the semi-logarithmic plot) indicating that the most efficient vaporization occurs only slightly above the

threshold. Not surprisingly, the transparent conductors SnO_2 and ZnO yield high thresholds (5 and 10 J/cm^2 respectively) for this mid-visible wavelength. The two CdTe films, one sputtered and one deposited by closed space sublimation, show very similar behavior until the full $2 \mu\text{m}$ of the sputtered film is vaporized.

The Mo film vaporizes in layers, $0.3 \mu\text{m}$ at low energy, $1.0 \mu\text{m}$ with intermediate energy, and finally, with 20 J/cm^2 , one can punch through the full $1.4 \mu\text{m}$ in one shot. We understand that these correspond to the layers of film growth as the substrate is rotated in front of a sputtering source. Apparently a slight interfacial layer occurs for the short time it periodically receives no flux from the sputter source. This interface structure reveals itself in the layered vaporization behavior.

Fig. 1. Thickness vaporized per pulse vs. energy density at 532 nm and 90 nsec for six different thin films.

The case of ZnO on glass is anomalous, for 532 nm pulses, in that either the film was undisturbed or the entire film is blown off under the laser focal spot. In addition, we observe that often a second pulse on the same spot will vaporize the entire film even though the first pulse appears to leave no visible damage. We believe this is due to defect-assisted and/or non-linear absorption in the transparent ZnO . At 308 nm and at 248 nm, which are strongly absorbed, the ZnO vaporization depth increased gradually with energy, similar to the other strongly absorbing materials.

In Table 2 we summarize the measurements of the optimum energy densities for scribing, *i.e.*, the energy density for the highest rate of vaporization per pulse.

Beam delivery options

A common laser used for scribing (of Si wafers and ceramics, as well thin-film PV materials) is the cw-lamp pumped, Q-switched Nd:YAG. This laser system has the disadvantage that the pulse duration is relatively long, 90 ns for the lowest pulse repetition frequency (PRF) of 1 kHz and increasing to 600 ns at the highest PRF of 10 kHz. The typical pulse energy for a laser of this type is 1 mJ. The copper vapor laser at 8 kHz also produces pulse energies of about 1 mJ. Lasers with these pulse energies would be most efficiently used by focusing the 1 mJ pulse to a line image on the film, *e.g.*, $50 \mu\text{m} \times 1 \text{ mm}$. However, for a 120 cm long panel, scanning of the beam is necessary. With the higher pulse energies (500 mJ or more) available from the excimer lasers (available also from the flashlamp-pumped Nd:YAG, but at no more than 50 Hz PRF), it is possible to contemplate focussing to a line image which covers the full length of a 120 cm PV panel, *i.e.*, a line of $50 \mu\text{m} \times 120 \text{ cm}$. This type of configuration is facilitated further by the fact that the optimum energy densities for scribing with the excimer laser are well below 0.5 J/cm^2 , as opposed to the optimum energy densities of up to 2 J/cm^2 for the 90 ns pulse at 532 nm.

TABLE 2: Optimum Efficiency for Laser Scribing

$\lambda(\text{nm})@ \Delta t$	$\text{SnO}_2 (\mu\text{m})$	$\text{CdTe} (\mu\text{m})$	$\text{ZnO} (\mu\text{m})$	$\text{Cl(G)S} (\mu\text{m})$	$\text{Mo} (\mu\text{m})$
1064 @10ns	0.24 @ 5J/cm ²	0.47 @1.7J/cm ²	0.48* @1.7J/cm ²	0.40 @ 4J/cm ²	0.36 @ 1.7J/cm ²
532 @10ns	0.27@9 J/cm ²	0.23 @1.7J/cm ²	0.72* @ 0.9J/cm ²	0.23 @1.8J/cm ²	0.47@ 0.7J/cm ²
532 @90ns	0.49@7 J/cm ²	1.6@1.5J/cm ²	2.1* @12J/cm ²	0.86@3.6 J/cm ²	0.29@0.7J/cm ²
308 @15ns	0.09@1.2 J/cm ²	0.11@0.35J/cm ²	0.19 @ 1J/cm ²	0.25 @2.5J/cm ²	0.52@0.4J/cm ²

* highly variable

Conclusions and future directions

We have measured the threshold energy density for visible damage by six different laser systems on five different polycrystalline thin-film PV materials. Measurements of the optimum energy density for scribing by these laser systems have been completed with four of these laser systems. Results for the copper vapor laser and the KrF excimer laser are presently being analyzed. Before the end of this partnership project, we expect to analyze further the issues involved with projecting a line image for the full length or width of a large PV panel. Finally, we plan to assess the potential for pulsed diode laser pumped Nd:YAG laser systems as a scribing engine. These diode-pumped YAG systems have the same wavelengths, and similar PRFs as the cw lamp-pumped Nd:YAG, but have shorter pulse durations which do not stretch as the repetition frequency increases. In addition, they are more compact and operate more efficiently.

Acknowledgments

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Title: Alternative Window Schemes for CuInSe₂-Based Solar Cells

Organization: Electronic Materials Laboratory
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OBJECTIVES

The objectives of this program are: (1) to develop alternate heterojunction partner layers for high efficiency CuInSe₂-based thin film solar cells; and, (2) improve the understanding regarding the effects of these buffer layers and related processing upon cell performance.

TECHNICAL APPROACH

The program is structured into three tasks : (1) MOCVD growth of non-cadmium containing buffer layers; (2) Optimized processing of buffer layers for high efficiency solar cells; (3) Characterization of layers and devices. The general approach to these studies has consisted of utilizing substrates provided by industry and NREL, so that efforts could focus on buffer layer investigations. MOCVD growth of buffer layers is accomplished with a SPIRE 500XT reactor with added gas handling capabilities. Optimum processing parameters for candidate buffer layers are determined by characterizing Al/X/CIS test cell structures, where X refers to a heterojunction partner. Al film thicknesses in the range of 100 to 150 Å are utilized so that illuminated I-V characteristics can be obtained for the test structure. After buffer-layer growth parameters are determined, completed solar cell structures are fabricated and evaluated. Layers and devices are characterized at WSU and with the help of collaboration with NREL. Results for this past year are summarized according to buffer layer material. In particular, accomplishments for studies of buffer layers based on ZnO, ZnSe and InSe are discussed.

ZnO BUFFER LAYER STUDIES

ZnO Film Growth. Chemical vapor deposition of ZnO is done by reacting a zinc adduct with tetrahydrofuran. The zinc adduct is formed by reacting dimethylzinc and triethylamine. The approach to CVD growth of ZnO is distinguished from other approaches in two important ways, namely: (1) The zinc and oxygen precursors are both relatively large molecules; (2) and no extra oxygen or ions are involved in the deposition process.

Optimization Of ZnO Buffer Layers Optimization studies have concentrated on investigating the effects of substrate temperature (T_{sub}), as-deposited film resistivity and film thickness on test cell performance. Measurements of ZnO film thickness and resistivity are made on a film grown on a glass witness to provide an estimate of these properties of the film grown on CIS. Illuminated characteristics of test cells are measured by illuminating the device such that $J_{\text{sc}} \approx 40 \text{ mA/cm}^2$ for CIGSS substrates, and 36 mA/cm^2 for CIGS substrates. The cell efficiency may be regarded as an estimated active area, AM1.5G efficiency, assuming that one can add a top contact layer and collector grid without degrading the junction properties. Although aluminum is quite reactive, the test cells provide useful information regarding buffer layer properties since the

ZnO films are typically ≥ 500 Å thick, which makes the ZnO-Al interface relatively far from the ZnO-CIS interface.

Best results for ZnO buffer layers have been achieved with a two-step growth process. First, a layer on the order of 100 Å to 150 Å is grown at 250°C, followed by growth of 500 Å to a 1000 Å at 100°C. It is also important for the as-deposited film resistivity to be $> 10,000$ ohm-cm. ZnO films grown at 250°C have a smoother morphology compared to films deposited at 100°C. Thus, the 250°C step may provide good coverage but must be limited in time to minimize interdiffusion effects. Further studies are required in order to understand the significance of the two step approach. The necessity of the as-deposited resistivity being relatively large may be a basic requirement for direct ZnO/CIS cells. In particular, ZnO/CIS solar cells fabricated with low resistivity (.001 to .01 ohm-cm) ZnO in direct contact with CIS and related alloys generally lead to cells with low efficiencies. Based on modeling studies discussed below, one should be able to achieve efficiencies $> 10\%$ with the resistivity > 1.0 ohm-cm. Therefore, it appears that the resistivity requirement is related to processing.

Modeling Studies. Simulation studies were carried out with PC-1D for CIS cells with ZnO buffer layers, and with a low resistivity ZnO top contact layer. The main objective of the work was to determine if low efficiency n-ZnO/CIS cells could be understood by assuming a high surface recombination velocity (S), or by assuming a low value of recombination lifetime (τ) in the space charge region. Calculated efficiency versus buffer layer resistivity is plotted in Figure 1 for a range of values of S and τ . The simulation studies indicate that the low efficiencies observed for cells with low resistivity ZnO buffer layers may be caused by reduced values of τ resulting from processing.

Physical Characterization CIS cells with ZnO buffer layers have been characterized by spectroscopic ellipsometry. Data for pseudo-optical constants of a ZnO film grown by the two-step process are shown in Figure 2A along with a theoretical fit. The simulation is based on the layered structure depicted by Figure 2B. The ZnO buffer layer grown with the two step method apparently results in two layers, the top layer being approximately 300 Å with a bandgap of 3.3 eV, and the bottom layer adjacent to the CIS material approximately 600 Å with a bandgap of 2.6 eV. Whereas the top layer is apparently ZnO, the region adjacent to CIS is another compound with a bandgap intermediate between ZnO and CIS. A candidate material for the intermediate layer

Figure 1. Calculated efficiency vs ZnO buffer layer resistivity for a CIS cell for: (A) a range of values of surface recombination velocities and $\tau = 40$ psec; and (B) for a range of lifetimes and $S = 1E4$ cm/sec. ZnO Thickness = 300 Å.

Figure 2. Spectroscopic ellipsometry studies of ZnO/CIS structure: (A) Data for pseudooptical constants along with theoretical fit; (B) Assumed layer structure to achieve fit of data.

is ZnInSe_2 . Additional ellipsometric measurements are planned in conjunction with low angle X-ray diffraction measurements to confirm these results.

ZnO/CIS Solar Cells ZnO/CIS solar cells have been fabricated by first depositing a ZnO buffer layer onto a CIS (or related alloy) substrate, followed by deposition of a low resistivity ZnO top contact layer and collector grid. A total area efficiency of 11.3 % was previously reported for a cell fabricated with a Siemens CIGSS substrate. Collaboration with NREL this past year has allowed fabrication of cells with NREL CIGS material. It was determined that the two-step growth method was appropriate for NREL substrates. Figure 3 describes results for a cell fabricated using a NREL substrate. After depositing a highly resistive ZnO buffer layer (referred to as i-ZnO) onto a NREL substrate, the i-ZnO/CIGS structure was sent to NREL for deposition of a low resistance ZnO top contact layer, deposition of a collector grid and AR coating. These last two steps are typically done at WSU, but cell completion was done at NREL in this case. The total area efficiency was 12.7 % and the estimated active area efficiency was 13.4 %. These results apparently represent the best performance for a direct ZnO/CIGS cell.

ZnSe BUFFER LAYER STUDIES

Investigations of CIS cells based on ZnSe buffer layers continued, but at a lower level than the studies of ZnO layers. Test cells fabricated using ZnSe buffer layers exhibit exceptional properties. In particular, test cells based on Siemens CIS and CIGSS substrates, and NREL CIGS substrates all exhibit fill factors ≥ 0.7 , and relatively large values of open circuit voltage. To date, a process for depositing a top contact layer that allows one to complete a cell with properties approaching those of test cells has not been developed. Recently, an encouraging result was achieved, however. A ZnSe/CIS(Siemens) structure was sent to NREL for deposition of a conducting ZnO top contact layer by RF sputtering, and then returned to WSU for deposition of collector grids and MgF_2 . Illuminated characteristics measured at WSU are shown in Figure 4. Although the resulting cell performance is significantly less than the 12 to 13 % suggested by test cell studies, the completed cell exhibited improved properties over those previously obtained with other ZnO TCO deposition processes.

InSe BUFFER LAYER STUDIES

Investigation of InSe buffer layers was also initiated this past year. InSe films are grown by reacting H_2Se and ethyldimethylindium with substrate temperatures in the range of 300 to 400 °C. Test cell studies have shown promise. Raman spectroscopic analyses indicate that the crystallinity of the films improve as T_{sub} is increased from 300°C to 400°C. The Raman studies also suggest that the amount of the γ - In_2Se_3 phase increases with T_{sub} . This phase has a bandgap of approximately 2.0 eV.

ACKNOWLEDGEMENTS

We wish to thank Bolko von Roedern for his guidance as our contract monitor, Kannan Ramanathan and many other NREL personnel for their collaboration, and NREL and Siemens Solar for supplying substrates.

NREL CIGS
 WSU i-ZnO Buffer Layer
 NREL RF Sputtered
 ZnO TCO
 AREA = 0.464 sq. cm

 $I_{\text{sc}} = 14.46 \text{ mA}$
 $J_{\text{sc}} = 34.06 \text{ mA/sq.cm}$
 Fill Factor = 66.43 %
 $V_{\text{oc}} = 0.560 \text{ Volts}$
 Efficiency = 12.7 %

Figure 3. Illuminated I-V characteristics as measured by NREL for a completed ZnO/CIGS solar cell with a high resistivity ZnO buffer layer.

Siemens CIS
 WSU ZnSe Buffer Layer
 NREL RF Sputtered
 ZnO TCO
 AREA = 0.464 sq. cm

 $I_{\text{sc}} = 16.5 \text{ mA}$
 $J_{\text{sc}} = 36.44 \text{ mA/sq.cm}$
 Fill Factor = 62.15 %
 $V_{\text{oc}} = 0.420 \text{ Volts}$
 Efficiency = 9.51 %

Figure 4. Illuminated I-V characteristics measured by WSU for a completed ZnSe/CIS solar cell.

4.0 PHOTOVOLTAIC MANUFACTURING TECHNOLOGY (PVMAT) PROJECT—Introduction

C. Edwin Witt, Team Leader

The Photovoltaic Manufacturing Technology (PVMaT) Project was initiated in 1990 to help the U.S. photovoltaic (PV) industry extend its world leadership role in PV manufacturing and the commercial development of PV modules and systems. As previously described, the PVMaT Project is a government/industry research and development (R&D) partnership between the U.S. federal government (through the U.S. Department of Energy [DOE]) and members of the U.S. PV industry. PVMaT is designed to accomplish this by helping the U.S. PV industry improve manufacturing processes, accelerate manufacturing cost reductions for PV modules, improve commercial product performance, and lay the groundwork for a substantial scale-up in the capacity of U.S.-based PV manufacturing plants.

The PVMaT Project is being carried out in four separate phases, designed to address separate R&D requirements. These are Phase 1, Phase 2A, Phase 2B, Phase 3A, and Phase 4A. The detailed activities and accomplishments of each of the currently active subcontractors is covered in individual sections following this summary. Phase 1 evaluated 23 manufacturing problems and was completed in 1991.

PHASE 2

Phase 2 addressed process-specific module manufacturing problems of individual manufacturers. Phase 2A was open only to organizations that received awards under the Phase 1 solicitation. The seven 3-year subcontracts implemented in early 1992 were 41% cost-shared by the U.S. PV industrial participants. All of the Phase 2A subcontracted activities have been completed. Phase 2B was a solicitation open to all U.S. PV industrial firms, allowing organizations who had not been ready for the earlier Phase 2A procurement cycle, or who were not participants in Phase 1, to have a chance to "ramp up" and participate in this process-specific solution phase of the PVMaT Project.

Four 3-year Phase 2B subcontracts were selected from 13 proposals and awarded in late 1993. These subcontracts addressed process-specific individual subcontractors' module manufacturing problems. They included work in CdTe module manufacturing, the manufacture of Spheral Solar™ cells and modules, and cast polysilicon wafers, cells, and module manufacturing. These subcontracts represented new technological additions to the PVMaT Project, and were cost-shared at 52.1% by the subcontractors. Three of the four subcontracts (listed in Table 1) are active—Golden Photon, Solar Cells, and Solarex.

Table 1. PVMaT Phase 2B Subcontract Awards

<u>Subcontractor</u>	<u>Emphasis of Research</u>	<u>Principal Investigator</u>
Golden Photon	Commercial Scale-Up of Advanced Thin-Film PV	Terry Brog
Solar Cells, Inc.	High-Throughput Manufacturing Thin-Film CdTe Photovoltaic Modules	Dan Sandwisch
Solarex	Cast Polycrystalline Silicon PV Cell and Module Manufacturing Improvements	John Wohlgemuth
Texas Instruments	Photovoltaic Manufacturing Technology	Jim Skelly

PHASE 3A

Phase 3 of the PVMaT Project addressed R&D problems that are common to the PV industry as a whole through a teamed research approach. Two subcontracts were selected from seven proposers and awarded in January of 1993 (see Table 2). These subcontracts were cost-shared at 25% by the subcontractors. The Springborn subcontract is currently still active.

Table 2. PVMaT Phase 3A Subcontract Awards

<u>Subcontractor</u>	<u>Emphasis of Research</u>	<u>Principal Investigator</u>
Spire Corporation	Automated Solar Cell Assembly Teamed Process Research	Mike Nowlan
Springborn Testing and Research, Inc.	Development of Advanced PV Encapsulants	William Holley

PHASE 4A

Phase 4A, Product-Driven Manufacturing, is the most recent phase of the PVMaT Project. This is a broader approach at addressing the overall PVMaT goal of improved U.S. market share by meeting the market challenges. The solicitation included responses from individual or teamed U.S. PV and related industries addressing manufacturing of PV end products, as well as subelements of these products. Objectives include: stimulating a broader interest in the production of PV products; encouraging and supporting risk-taking by industry to explore new manufacturing options and ideas for improved PV products or components; encouraging system and product integration; and stimulating advances in balance of systems or developments in design leading to overall reduced system life-cycle costs of the PV end product. Cost reduction, improved efficiency, and manufacturing flexibility and broader market applications for PV systems as a

Table 3. PVMaT Phase 4A1 Subcontract Awards

<u>Subcontractor</u>	<u>Emphasis of Research</u>	<u>Principal Investigator</u>
Solar Design Associates, Inc.	The Development of Standardized, Low-Cost AC PV Systems	Steven Strong
Omnion Power Engineering Corp.	Three-Phase Power Conversion System for Utility-Interconnected PV	Hans Meyer
Utility Power Group	Development of a Low-Cost, Integrated, 15-kW AC Solar-Tracking Subarray for Grid-Connected PV Power Systems	Michael Stern
Solar Electric Specialties	Design, Fabrication, and Certification of Advanced Modular PV Power Systems	Glen Minyard
Trace Engineering	Modular, Bidirectional DC to AC Power Inverter Module for PV Applications	Christopher Freitas
Advanced Energy Systems	Next-Generation Three-Phase Inverters	Robert Wills
Ascension Technology	Manufacture of an AC PV Module	Ed Kern

whole are emphasized. The subcontracts in Phase 4A were divided into two parts, 4A1 and 4A2, and both are now completing their first year.

PHASE 4A1

Phase 4A1 addresses the product-driven system and component technology and includes manufacturing improvements directed toward innovative, low-cost, high-return, high-impact PV products. Proposals in this phase addressed manufacturing that was generally related to PV system components and aspects other than modules, system components such as inverters, and/or system integration efficiency and/or design improvements, with lesser focus on module manufacturing. In addition, proposals looked at issues in system/component integration to bring all elements together for a PV product that is offered on the market. Seven two-year subcontracts (listed in Table 3) were awarded from 31 proposals received. These subcontracts are cost-shared at 25% by the subcontractors.

Table 4. PVMaT Phase 4A2 Subcontract Awards

<u>Subcontractor</u>	<u>Emphasis of Research</u>	<u>Principal Investigator</u>
AstroPower, Inc.	Large-Area Silicon-Film Panels and Solar Cells	James Rand
ASE Americas, Inc.	Market-Driven Edge-Defined, Film-Fed Growth (EFG) Modules	Michael Kardauskas
Siemens Solar Industries	Photovoltaic Cz Silicon Module Improvements	Richard King
Iowa Thin-Film Technologies	Monolithic a-Si Modules on Continuous Polymer Substrates	Frank Jeffrey
Photovoltaic International	Manufacturing of the PVI Power Grid	Neil Kaminar

PHASE 4A2

Phase 4A2 is focused on product-driven PV module manufacturing technology. Subcontracts under this phase are directing their efforts at manufacturing flexibility and module manufacturing cost reduction for a wider range of PV products. Phase 4A2 consists of five three-year subcontracts (shown in Table 4), selected from 31 proposals. These subcontracted efforts include development of large-area silicon-film panel and cell manufacturing; EFG module manufacturing; improvements in CZ silicon modules; development of monolithic a-Si modules on continuous polymer substrates; and manufacturing of extruded concentrator modules. These subcontracts are cost-shared at 42% by the subcontractors.

PROGRESS IN THE PV INDUSTRY

It is important to put the technical progress that the U.S. PV industry is making into perspective. Based on the improvements in manufacturing processes, reductions in manufacturing costs, introduction of new products, and improvements in product performance, it would be expected that the U.S. PV industry would exhibit both a scale-up of its U.S.-based PV manufacturing capacity and a reduction in its production costs. This has indeed been the case.

At the beginning of Phase 2A subcontracted research, information was collected to establish both the current and projected capacities and module costs for the eight subcontractors. These data, shown in Fig. 1, represented both the diverse status of a still-maturing industry and the optimistic speculation of its members regarding the effects that the PVMaT Project would have after their PVMaT efforts were allowed to take effect. Additional information was collected from the twelve PV industrial participants in all phases of PVMaT that were in production in late 1996.

Figure 1 - 1993 PVMaT Projections

These most recent data, shown in Fig. 2, represent an update of previous projections regarding these subcontracted efforts. Data in this figure are based on each manufacturer's maximum production capacity during a given year, assuming they were to operate at maximum capacity. The "average" represents the average cost per watt of modules (weighted by each participant's capacity) produced by these twelve PVMaT industrial participants. Module cost estimates were then based on these manufacturing levels and included only those costs directly associated with the manufacturing of the modules (not, for example, marketing, administration, and sales). It should be noted that data associated with any particular point in time represent a potential capability. Actual manufacturing production levels may be lower (and concomitant costs higher) because of other considerations such as market conditions and available labor.

The PVMaT Project is currently finishing the first year of subcontracts under Phase 4A1 and 4A2, with research in Phase 2B concluding its third year and Phase 3A now being completed. At this time, it is apparent from Figs. 1 and 2, that the U.S. PV industry involved in the PVMaT Project has made significant progress toward reducing manufacturing costs and increasing PV module manufacturing capacity. "Average" module manufacturing costs have been reduced 36% and total manufacturing capacity for 12 PVMaT industrial participants with active lines has increased by a factor of more than 4. By 1998, projections are for a reduction in costs of 65% at \$1.64/Wp, and a factor of 14 increase in capacity by 1998 to 223 MW. It has also indicated in both the industries' future cost/capacity data and its technical projections that its optimism for continuing these improvements is high.

Figure 2 - PVMaT Manufacturing Cost/Capacity

Photovoltaic Manufacturing Technology (PVMaT) Subcontracts

**Title: Next Generation Three-Phase Inverters for
Application in Photovoltaic Hybrid Systems**
Organization: Advanced Energy Systems, Inc.
Wilton, NH 03086

Contributors: Dr. Robert Wills, P.E., Principal Investigator
Adam Wesley, Project Manager

Objectives: The overall objective of this subcontract is to develop a new generation of specialized inverters for the PV hybrid market. This new generation of inverters will incorporate the following features:

- ⊗ Digital Control
- ⊗ Design for Manufacture
- ⊗ Economies of Production
- ⊗ Remote Monitoring, Control, and Service Diagnostic Capability.

The resultant cost reductions should yield manufacturing costs under \$300/kW, down from current inverter costs on the order of \$1000/kW. The inverter cost is typically 10-20% of total installed photovoltaic system cost. As the price of photovoltaic modules decreases, inverter price becomes an increasingly important component of the total system price. The complete hybrid inverter, including the full control system, is projected to have a manufacturing cost well below \$450/kW. At the same time the output efficiency will be improved to greater than 93% and the total harmonic distortion (THD) will be reduced to less than 3%. Digital control will provide increased reliability, flexibility and self-test capability while core software modules and configurable application-level modules will reduce initial software costs as well as future upgrades. Integrated self-test capabilities, modular components, wide use of LED indicators and multilingual LCD Interface will lead to lower installation and service costs. With the use of generic power electronics and flexible software, integrated data logging, renewable control, utility SCADA links, and demand-side management capability will open multiple target markets. Together with higher efficiency and smarter control algorithms these factors will bring about an overall reduction in cost per kWh.

Description of Hybrid Inverter system: The hybrid inverter (HI) system is the control and command center of a total power system (see Figure 1 for a block diagram). The HI constantly monitors the load, the state of the energy storage system (rechargeable battery) and dispatches whichever generator source is the most appropriate for the load, given the setpoints that are pre-set at the factory (and user adjustable for changing conditions). Further, the bi-directional HI converts DC, available from the batteries or a PV array, into AC for the load; it also can rectify (change AC to DC) the power from the generator to recharge the battery bank, in the event the battery state of charge falls below a preset level. Sophisticated controls and intelligence are used to ensure that the power delivered by the various components of the total system is uniform and capable of fully satisfying the load under highly dynamic conditions and power factors. One of the key operating objectives is to operate the diesel generators only at their peak efficiency, thereby conserving fuel and minimizing maintenance costs.

Background: Several economic and social factors are driving the consideration of stand-alone renewable generating stations in remote and rural areas, to serve isolated loads or villages. On the economic side, renewable systems can save money by displacing fossil fuel use, reducing operation and maintenance costs. On the social side, many positive changes can result from providing reliable electric power to a community that otherwise would not have electricity. These include the ability to use the electricity to create new businesses, operate a health care facility, and provide light to a classroom. More than two

billion people live without ready access to electric power. The key issue is how to best serve their needs.

Figure 1: The Hybrid System

system, when it includes a diesel genset, can provide reliable power around the clock, to satisfy nearly any instantaneous load. Finally, in terms of operation and maintenance, the central system a single trained service staff, whereas the alternative is to have each system owner be trained – and responsible for their own system operation.

Experience has proven us correct:

AES has first hand experience with serving a variety of remote needs, including eco-tourism (a 120 kW, three phase hybrid inverter that controls two diesels and a PV array in Belize – the largest in Latin America, see Figure 2), village power (a 30 kW single phase unit at the source of the Amazon), and telecommunications (a 90 kW, three phase unit in Idaho for the US military). These experiences have served to point out in a

remarkably strong way, the need to advance the state of the art in stand alone systems, including the hybrid inverter. Specifically, we have learned a great deal from these installations, including the value in providing clear and simple operating instructions and interfaces, a highly reliable, easy to troubleshoot unit and remote communications, giving us access to the unit, from our facilities in Wilton. We also learned that all methods to improve reliability will ultimately pay off, relative to the costs of sending a repair team to such isolated sites.

The objectives of the PVMaT program, as described above, are perfectly consistent with the advances that we see as critical to the widespread deployment of hybrid systems.

Centralized system vs. discrete systems:

Village power systems can be implemented as either multiple discrete systems, *termed solar home systems*, or as village-scale central systems. While the central system requires some local distribution, it is often superior to independent small systems. The central system can provide power to larger loads, e.g., a village water pump or medical clinic; the central system is more flexible to changing and growing loads. Furthermore, the central

Figure 2: Eco-tourist Installation in Belize

The case for PVMaT funding: Despite the compelling set of arguments in favor of hybrid systems, there remain some very high barriers to commercialization. Foremost among them is money – the communities that can benefit most from electric power have the least ability to pay. Commercial and industrial agencies have a strong interest in short term rates of return (i.e., a high up front capital cost, typical with renewables systems, is hard to swallow). In addition, the markets are fragmented, geographically, politically and technically. Finally, the unique demands of these applications demand sophisticated solutions, in order to provide systems that are flexible to changing needs and appropriate for the given (lack of) infrastructure. Some would say that the market for hybrid systems is off in the future, and always will be. We are committed to the belief that the market should be developed and will be developed by those organizations and stakeholders who have the creativity to tackle the barriers and overcome them, one at a time. Creating the market, however, requires a substantial investment. Large companies are unwilling to make that investment now, due to their perception of market risk. Small companies don't have the investment capital available – unless they are fortunate enough to receive support from another source. In the present case, the PVMaT program funding is improving the product and preparing it for full commercialization. Without the support of NREL, this level of development couldn't happen. The product advances would come far more slowly, or not at all. Consequently, market development would be held back - i.e., the PVMaT funding is the necessary catalyst to develop the product capability that is the "admission ticket" to this vast market opportunity.

AES is creating the advanced hybrid system in conjunction with AES Ltd, our sister company in Western Australia. AES Ltd has provided background technology and engineering expertise, developed over the course of the past ten years; AES Inc. is providing advances in software, hardware design and key customer (market) input, as well as transferring full manufacturing capability to New Hampshire.

Approach: Remote PV-hybrid inverters are currently being manufactured by Advanced Energy Systems, LTD. in Perth, Western Australia. These inverters are bi-directional and capable of paralleling with one or two diesel generators. Termed STATIC POWER PACKS, they can operate either as inverters or as battery-chargers. At high peak load times, the inverter can augment generator output allowing a smaller genset to be used. At low load, the generators are stopped and the system runs on inverter power only. This greatly reduces generator maintenance costs and battery life-cycle costs.

AESI will utilize the current SPP design and work to increase its reliability and reduce its production cost by building on developments in other areas of emerging technology such as highly integrated demand-side management (DSM) controllers and smart insulated gate bipolar transistor (IGBT) modules developed for the auto and other high volume industries. AESI will use digital rather than analog control methods resulting in far fewer components, greater stability and reliability and greater flexibility (as control changes can be performed simply by loading a new program). And finally, AESI will evaluate inverter designs for manufacturing to meet the cost goals for U.S. production and manage the pilot manufacturing of the more reliable and efficient inverter.

Results: During FY96 several significant achievements were realized. Development of a new IGBT driver card followed the implementation of a digital inverter control module. The new card integrates a full-bridge drive circuit from the four boards previously needed onto one single board. The final design is significantly improved with respect to self protection and in its ability to operate from a bipolar battery bank. This increases the number of applications the inverter can interface with and allows the use of lower current IGBT devices, which in itself is a potential system cost saving. The inverter control card software has been completed to a point where it emulates precisely the functions of the existing three single-phase

control modules. The new controller also handles the control of cooling fans, current limiting with supervised shutdown and software-adjustable delays, and selectable operation at either 50Hz or 60Hz. Full power tests of the integrated control card evidenced a marked improvement in the THD to less than 3%. The operator interface is also improved. A revised specification for the layout of each display page was completed. The layout specification identifies all data and control functions which are accessible via the keypad interface.

The objective of reliable use of remote SCADA control interfacing was achieved. Remote communications with a standard Windows 95® interface was implemented. The new graphics pages included the Connect Screen which allows the user to select direct or modem site connection, System Control-mode Selection, Operational overview which provides real-time operating data, and Configuration which gives point editing and review. The graphical display of performance parameters and the display of warnings generated by the hybrid station are pages which are near completion.

The successful development of the Power Block design (see Figure 3) has resulted in the realization of several key advantages. The design makes possible component replacement without the use of test equipment. Further, the custom design of the magnetics has improved the no-load loss characteristics of the power stage when compared with the previous magnetics design. This produces an inverter of higher conversion efficiency over the typical operating range for a PV hybrid system.

The implementation of U.S. manufacturing of this inverter has been successful. In collaboration with WPI Power Systems, Warner, NH, Advanced Energy Systems,

Inc., will successfully meet the objective of delivering a prototype of the Next-Generation Three Phase Inverter in February, 1997. The final specifications for the prototype unit included a completed Bill of Materials (BOM), a complete set of Cut-Sheets which identifies dimensioned components from the BOM, multiple drawings of the Cabinet Layout, electrical schematics which identify the electrical connection of all printed circuit boards (PCBs), terminal definitions which indicate a terminal block and denotes connection points, and cable definitions. The completed design will result in a unit which is not only more reliable and efficient but also much more compact, taking 40% less volume and 30% less floor space than the previous design.

Figure 3: Power Block Schematic

Title: **Manufacture of an AC Photovoltaic Module**

Organization: Ascension Technology, Inc.
235 Bear Hill Road, Waltham, MA 02154

Contributors: M. C. Russell, C. K. P. Handleman

Objectives

Ascension Technology has developed a grid-tied module-scale inverter and integrated this inverter with a large-area PV module from ASE Americas. The result is an AC module, the *SunSine300*, that produces utility-compatible ac power. Among the advantages offered by the *SunSine300* are its flexibility, allowing grid-tied PV systems to be configured in small power increments. The objectives of Ascension Technology's work under NREL's PVMaT program have been to refine the inverter and its integration with the PV laminate, and prepare for manufacturing and commercialization of the *SunSine300* AC module.

Approach

Ascension Technology selected a simple inverter circuit topology that offers excellent potential for performance, safety and manufacturability. A custom cast-aluminum enclosure houses the inverter and attaches directly to the back of the PV laminate. A quick-connector makes the electrical connection between the inverter and the PV module's dc circuit, when the inverter assembly is mechanically attached to the PV laminate. An important characteristic of this design is that there are no dc wires and no dc voltage accessible to users. The *SunSine300* AC module is equipped with quick-connectors, developed under this project, that make AC field wiring between *SunSine300* AC modules safe and rapid.

To complete a *SunSine300* system, Ascension Technology advanced the design of our RoofJack™ mounting hardware for pitched, residential rooftop installations. The latest version of the RoofJacks™ increases their attachment strength, provides for concealment of module-to-module connectors and serves as an attachment point for the PV Source Circuit Protector (PVSCP™) -- Ascension Technology's UL-listed field wiring junction box. New versions of the PVSCP™ have also been developed, providing more convenient field-wiring options and other mechanical improvements, facilitating their use in *SunSine300* AC module systems.

Ascension Technology has developed the *SunSine300* AC PV module in partnership with 19 electric utilities and ASE Americas, a leading manufacturer of PV modules. Combined, these utilities have purchased approximately 120 *SunSine300* AC PV modules from our upcoming pilot production and will be operationally testing and evaluating them at sites around the country.

Results

As of this writing Ascension Technology is preparing for our first manufacturing run, scheduled for February 1997. *SunSine300* prototypes have passed FCC class B. A preliminary

investigation by Underwriters Laboratories turned up only minor issues that have been addressed in the version slated for the pilot production. The SunSine300 has passed DC Hi-pot tests and is currently undergoing a battery of testing in environmental chambers at ASE Americas. Field testing is underway at a variety of sites including NREL and Sandia National Laboratories.

The SunSine300 exhibits a dc-to-ac conversion efficiency greater than 90% over much of its operating range, and total current harmonic distortion has been measured well below 5% from 10% to full power. The SunSine300 is rated at 260 Watts ac, at standard test conditions (1,000 W/m², 25C cell temperature). The peak output is limited to 2.5 Amps ac at 120 Volts ac, or 300 Watts. Additional specifications are shown in Table 1 below.

Table 1

SPECIFICATIONS	
AC Output:	
Voltage	120 Volts AC
Power	260 Watts at STC*
Frequency	60 Hz
Current Distortion	<5%THD at rated power
Power Factor	>95%from 40 to 100% power
Ambient Temp.	-40 C (-40° F) to 50 C (122° F)
Size	74.5 x 50.5 x 2.5 Inches
Weight	122 lbs
Fully Automatic Operation, Protection and Reset:	
Maximum Power Point Tracking	
Morning and Evening Start-up and Shut-down	
Over/Under Voltage and Over/Under Frequency	
Active and Passive Anti-Islanding Protection	

* STC: Standard Test Conditions

Summary

The SunSine300 AC PV module represents an important advancement in PV system technology: (1) AC modules reduce the threshold cost for a grid-interactive PV system; a grid-tied PV system can be deployed with as few as one AC module, (2) Safety levels are increased; SunSine300 AC PV module systems have no DC wiring and, unlike traditional PV modules, the units are not energized until connected to the utility grid, (3) Installation is quick; wiring between SunSine300 AC modules is completed with factory-installed quick-connectors, (4) Systems are compliant with the National Electrical Code; the SunSine300s are also FCC compliant and are designed to be UL listed, (5) Systems will meet utility interface requirements; the SunSine300 is equipped with sophisticated anti-islanding features including a proprietary active method in addition to standard over/under voltage and over/under frequency detection. Manufacturing scale-up and commercialization are targeted for summer 1997.

Title: Market-Driven EFG Modules

Organization: ASE Americas, Billerica, Massachusetts

Contributors: M. Kardauskas, Principal Investigator; J. Kalejs, Program Manager; J. Cao, R. Gonsiorawski, C. O'Brien, E. Tornstrom

Objectives

We summarize here the progress made at ASE Americas Inc. during the first year of the planned 3 year program in Phase 4A2 on the development of technology to address photovoltaic module manufacturing flexibility and cost reduction for EFG wafer based products. The PVMaT program addresses advanced manufacturing technology for reduction of the thickness of polycrystalline silicon EFG wafers from 300 to 250 microns, improvement of EFG solar cell efficiency to produce cells with average efficiency of greater than 15% on 10 cm x 10 cm area wafers, and simplification of processes and reduction of costs in interconnect and module manufacturing. This work includes the development of a novel and new environmentally safe and reduced cost diffusion glass removal process for the solar cell manufacturing line. The overall goal of the program is to reduce EFG module manufacturing costs by 25%. We have identified module cost reductions of approximately 7% as a result of improvements made on the program in the first year. The significant technological advances made are described in the next three sections, representing the work in the three main tasks: Task 1: Wafers, Task 2: Cells, and Task 3: Modules.

Technical Developments

The EFG manufacturing line development program under PVMaT is based on growth and processing of EFG polycrystalline silicon wafers. EFG wafers are produced from octagon tubes. These tubes are closed shape crystals, with eight 10 cm faces and wall thickness about 300 microns, which are grown by the Edge-defined Film-fed Growth (EFG) process to a length of 4.6 meters. The tubes are cut by high speed lasers into 10 cm x 10 cm wafers. Other details of the wafer production may be found elsewhere [1]. EFG wafers are processed into solar cells using specially designed and optimized processes. ASE Americas, under its former name of Mobil Solar Energy Corporation, participated in Phase 1 and Phase 2A of PVMaT in programs to improve its manufacturing line and reduce module cost. The current PVMaT program goals will reduce costs in all three areas of the manufacturing line: wafer production, solar cell processing and module manufacture. The work in progress and results are described next.

Task 1: Wafers

The work in this task involved developing improvements to the EFG crystal growth process that will lead to increased as-grown quality of EFG wafers and so contribute to an increase in solar cell efficiency in Task 2, and to reduce wafer thickness while maintaining yield. During the first year of the program two unforeseen difficulties were encountered in the quality area which have hampered progress toward the 1998 goal of 15.5% EFG solar cell efficiency. First, a number of contamination problems on the line depressed solar cell efficiencies and interfered with experiments designed to demonstrate higher cell efficiencies. The availability of high quality

silicon feedstock was restricted. The problem of how to work with feedstock of variable quality, which was observed to limit the EFG solar cell efficiency, needed to be investigated. However, we have made progress toward the high efficiency goal. We achieved solar cell efficiency improvements of about 0.5% and this has contributed toward a cost reduction for EFG modules. The second difficulty encountered relates to the use of oxygen during the growth process to raise solar cell efficiency. Oxygen, when introduced most effectively, can raise cell efficiency by as much as 0.3- 0.5% absolute. However, we were not successful in optimizing oxygen levels in EFG wafers to date because the introduction of oxygen-bearing gases has interfered with crystal growth and reduced productivity and yield.

Highlights of Task 1: 1. We identified improved methods of purifying graphite components used in crystal growth. We have qualified alternative sources of graphite and vendors for purification and demonstrated consistent as-grown EFG wafer quality on the manufacturing line. Currently, the EFG as-grown wafer quality is stabilized at levels which are capable of producing average solar cell efficiencies of 14%. Efficiencies of 14.0-14.2% have been demonstrated on solar cell lots containing hundreds of solar cells representing one octagon tube, even without stabilized or optimized oxygen levels.

2. We have developed an improved process to handle and sort silicon feedstock pellets for crystal growth. The automated equipment to carry out this function is being qualified. This process will reduce the effects of varying pellet size on process productivity and quality, reduce costs in crystal growth by increasing silicon feedstock utilization, and reduce the potential for external contamination in preparing the feedstock, thus helping to increase wafer quality.

3. An outside vendor has designed an enclosure for the EFG furnace. It is currently under construction. The design will allow the EFG octagon to be grown to its full length in a totally enclosed space, and reduce the perturbations in material quality than arise from external ambient contamination brought into the furnace in the form of transition metals (dust) and oxygen.

The first of the above two improvements are estimated to result in a 3.5% decrease in module manufacturing costs in the manufacturing line.

Concerns in Task 1: We have made progress toward reducing damage in laser cutting to allow 250 micron thick wafers to be processed through the EFG line without a reduction in yield. As of this date, a number of 275 and 250 micron thick octagon tubes have been grown for yield studies. These generally can be processed with yields comparable to those on standard 300 micron thickness tubes. Thin tubes have lower yield on average because of occasional very thin regions in some tubes. Thus, they are currently not acceptable for production on a larger scale.

Two laser systems for improved cutting are under study. An improved CO₂ laser has become available. An initial trial was not successful because the first model available did not have sufficient power for the necessary high speed cutting required. The edge damage improvement demonstrated in a laboratory test could not be reproduced on the production floor. A second CO₂ laser system is being evaluated now which promises to be able to generate the power needed. This will be tried out in the first quarter of Phase 2. The second laser system being evaluated is the copper vapor laser. The initial test showed the laser selected had insufficient power for high speed cutting although it had greatly reduced edge damage. These experiments were deliberately done with a very low power laser which has potential to reduce costs for EFG wafer cutting. The higher power copper vapor lasers currently are too expensive and impractical

for production floor operation. Experiments are continuing with the low power copper vapor laser in order to attempt to improve its speed of cutting.

The effect of reduced quality of incoming silicon feedstock on the ability to achieve program goals on solar cell efficiency will be under study in Phase 2. Although peak solar cell efficiencies over 14% and meeting program goals have been demonstrated, degradation of efficiencies in later tubes is evident in many runs. This has several causes. The effects of impurities in the incoming feedstock need to be separated from those due to other causes, e.g., ambient ingress of impurities.

Task 2: Cells

Solar cell efficiency programs are essentially on schedule. Although some issues with impurity effects due to feedstock quality and oxygen need to be resolved, as discussed above, improved cell efficiencies continue to be demonstrated.

Highlights of Task 2: 1. A method to reduce fluorine ion effluent in etching of phosphorus glass by several orders of magnitude has been successfully demonstrated by a lower tier subcontractor, Bright Technology. In addition to reducing costs of the process step and in waste disposal, this method will significantly add to the environmental safety on the EFG cell line. Planning and design for development of a prototype station to try out on the EFG manufacturing line in 1997 are under way.

2. A process to apply a dielectric textured ZnO layer on an EFG solar cell with a silicon nitride underlayer has been successfully demonstrated for the first time at a lower tier subcontractor, Harvard University. The first ZnO layers did not lead to an increase in EFG solar cell efficiency, however, and studies are in progress to identify the cause for the shortfall.

3. Improvements in the solar cell processing on the EFG line have demonstrated that large batches of hundreds of cells are capable of exceeding 14%. We have achieved 14.3-14.5% efficiency on smaller R&D lots. These results must be transferred to manufacturing. We demonstrated CZ cell efficiencies averaging about 16%.

The efficiency improvements achieved in raising the absolute efficiency by 0.5% are estimated to contribute to a 3.5% reduction in module manufacturing costs.

Concerns in Task 2: The causes for the failure of the ZnO layer to produce efficiency increases on EFG cells comparable to the 0.5% absolute demonstrated on CZ material are not known. Studies at Harvard and at Sandia in the next Phase of the program will attempt to determine the causes for the shortfall and attempt to find processing variations to meet program objectives.

Task 3: Modules

Several tasks in the module program were delayed in starting as a result of a slower than anticipated ramp-up of the program because of staffing shortages, and delays in getting new equipment operational.

Highlights of Task 3: 1. We have completed a redesign of the module diode housing and electrical protection circuits. The new configuration simplifies manufacture, reduces materials cost and will enhance customer satisfaction with the leading product at ASE Americas, the large ASE 300-DG module.

2. We have identified a vendor for producing a new frame, which reduces material and labor costs in manufacturing. Final designs are being prepared by the vendor for prototype study in the Fifth Quarter.

3. We are studying several new encapsulants with potential advantages for EFG products. These are expected to reduce lamination times and enhance yields. We are planning to extensively test and qualify them for manufacturing in Phase 2.

The first two of the above improvements are expected to be introduced into the manufacturing line in the first half of 1997 and offer a potential of a 4% reduction in EFG module manufacturing costs in the second half of 1997.

Concerns in Task 3: Although the development of a lower cost frame and manufacturing process and of a new diode housing are successfully completed, other work is behind schedule. Demonstration of a useful new cell finger and busbar configuration and bonding approach with rear side interconnects was not successful. Several new configurations for fingers were fabricated and tested, but did not meet the criteria of the low resistance that is required. Additional process variations to reduce finger width and to bring front side contacts around to the back of the cell are under study.

Summary

The initial phase of the PVMaT program at ASE Americas has led to a 7% reduction in module manufacturing costs. This occurred in the wafer and cell tasks: we demonstrated an EFG cell efficiency improvement of 0.5% as a result of quality improvements in the as-grown EFG wafer, arising from better controls on graphite purification. Thinner octagons, down to 250 microns, have been grown, but the laser cutting process is not sufficiently improved to allow regular processing in manufacturing. Improvements in cell processing have produced R&D EFG lots of a few hundred cells with over 14% efficiencies, and we are studying means to introduce these modifications into the manufacturing line operation. Another 4% of cost reductions has been identified in the module area with redesign of the frame and the diode housing, and these changes will be implemented in the manufacturing line in 1997.

In other tasks in wafers, equipment for automated sorting of silicon feedstock has been qualified. a design for an enclosure for the EFG furnace has been completed, It will allow growth of the EFG tube into a controlled ambient. This enclosure is now being constructed and will be tested early in Phase 2. In the cell task, a new process for removing phosphorus glass has been demonstrated. A prototype unit is being built for testing in production. A process to deposit a textured ZnO layer on the silicon nitride to enhance light trapping at the front of the cell has been developed. It currently is being studied to determine its potential for raising EFG solar cell efficiency.

This work has been supported in part by DOE/NREL subcontract No. ZAF-6-14271-13.

Reference

[1] M.J. Kardauskas, M.D. Rosenblum, B.H. Mackintosh and J.P. Kalejs, "The Coming of Age of a New PV Wafer Technology- Some Apects of EFG Polycrystalline Silicon Sheet Manufacture", 25th IEEE PVSC, 1996, pp. 383-388.

Title: **Large-Area Silicon-FilmTM Manufacturing**

Organization: AstroPower, Inc.
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Newark, DE 19716-2000

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Introduction

The Silicon-FilmTM process is on an accelerated path to large-scale manufacturing. A key element in that development is optimizing the specific geometry of both the Silicon-FilmTM sheet and the resulting solar cell. That decision has been influenced by cost factors, engineering concerns, and marketing issues. Optimizing the solar cell size first focused on sheet nominally 15 cm wide. This sheet generated solar cells with areas of 240 cm² and 675 cm². Most recently a new sheet fabrication machine was constructed that produces Silicon-FilmTM wafers with a width in excess of 30 cm. The results of testing have indicated that there is no fundamental limit to the width of sheet generated by the Silicon-FilmTM wafer process. This new wide material has led to prototype solar cells with areas of 300, 400 and 1800 cm². Significant advances in solar cell processing have been developed to fabricate devices of this size, including emitter diffusion and application of the anti-reflection coating.

The existing Silicon-FilmTM manufacturing process is based on solar cells with an area of 240 cm² (the solar cell is referred to as the AP-225). Efficiencies in excess of 12% have been demonstrated on these large area cells. Smaller, laboratory devices have demonstrated efficiencies of 14.6% (see Figure 1).

In support of the move to large-scale production, development work has been underway to determine the optimum width of the Silicon-FilmTM sheet. The sheet presently in production is nominally 15 cm wide. Advantages to increased sheet width include reduced capital costs, improved material utilization, and the capability to increase solar cell size. Increased solar cell size has the advantage of higher power per piece with fixed cost for handling during solar cell and module fabrication. A critical element in the optimization process is the capability of cutting finished solar cells into smaller sizes for different applications, as illustrated in Figure 2.

Processing Developments

The flexibility in substrate size has led to the need for advances in producing emitters and applying anti-reflection coatings. In contrast to "traditional" solar cell manufacturing, based on

integrated-circuit technologies, these next-generation Silicon-Film™ solar cell processes are inherently free of substrate size boundary conditions. The use of low-cost, environmentally responsible precursors and industrial coating application equipment with proven reliability also make these advanced processes particularly attractive to large-scale adaptation.

Large area Silicon-Film™ emitter production is accomplished by continuous-feed application of a phosphorous-based coating. This is followed by thermal cycling, using conditions approaching those encountered in rapid thermal processing (RTP). The resulting emitter sheet resistance is uniform to within 10% over the full device area. Wafer deglazing is straightforward, and requires no specialized equipment or chemicals.

For large-area anti-reflection coatings, simple liquid precursors are applied using commercial coating equipment to form an oxide layer which is index-matched to module encapsulants. Advances made in this technology include the enhanced ability to chemically vary the index of refraction, and the improvement in coating characteristics using conductive and radiative heating methods.

Improvements in the characterization of Silicon-Film™ material have been made by using a RFPCD lifetime measurement technique developed by Dr. Richard Ahrenkiel of NREL. The measurement method allows a contactless measurement of the minority carrier lifetime in grown material with little or no sample preparation.

Device Performance

A summary of the solar cells being evaluated is shown in Table 1. Some of the devices have been tested at NREL (see Note). Testing of these large devices has required the use of special apparatus. One such testing jig is presently being evaluated by NREL with AP-225 and AP-300 solar cells. A second jig has been fabricated for testing the AP-1800 solar cell and will be supplied to NREL for performance testing.

Summary

The Silicon-Film™ solar cell manufacturing process is presently in pilot production with a sheet nominally 15 cm wide. In planning for large-scale manufacturing, an effort has been undertaken to determine the limits to the sheet width. A new Silicon-Film™ sheet producing facility was constructed that has successfully demonstrated sheets in excess of 30 cm wide. The wider sheet has allowed us to evaluate a number of different solar cell sizes. The largest Silicon-Film™ solar cell presently under evaluation has an area of 1800 cm².

$V_{oc} = 0.5966 \text{ V}$	$V_{max} = 0.5086 \text{ V}$
$I_{sc} = 30.14 \text{ mA}$	$I_{max} = 28.63 \text{ mA}$
$J_{sc} = 30.14 \text{ mA/cm}^2$	$P_{max} = 14.56 \text{ mW}$
$FF = 81.00\%$	$Eff = 14.6\%$

FIGURE 1. Current-voltage curve for a 1-cm², Silicon-Film™ solar cell with an energy conversion efficiency of 14.6%.

FIGURE 2. Flexibility of a 30 cm x 60 cm solar cell in meeting several different PV markets.

TABLE 1. Summary of device data on different size solar cells.

Product	Area	Power	Efficiency	Note
Laboratory Solar Cells	1.0 cm ²	14.6 mW	14.6%	(1)
AP-225 Solar Cell	240 cm ²	2.93 W	12.2%	(1)
AP-300 Solar Cell	311 cm ²	3.48 W	11.2%	(2)
AP-400 Solar Cell	412 cm ²			(3)
AP-6 75 Solar Cell	676 cm ²	7.87 W	11.6%	(1)
AP-1800 Solar Cell	1800 cm ²			(3)

(1) NREL test , (2) AstroPower test, (3) Fabricated, but not yet tested

Advanced Polymer PV System

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Abstract. During this first year of a two year sub-contract from NREL under PVMat, a project to lower module manufacturing and related systems costs has been pursued. A novel backskin material has been developed which allows for a frameless module with a wide variety of simpler and lower cost mounting possibilities. Using rapid prototyping techniques and extensive feedback from potential customers, a new junction box has been designed. Preliminary work has been done towards the development of a new encapsulant. This new encapsulant, in turn, will enable the development of a continuous non-vacuum lamination method and the foundation for this was also established. The net result of all of this, when successfully deployed, will be a cost reduction of at least \$0.50/watt for both module making and systems installation cost.

INTRODUCTION

Evergreen Solar, Inc. (Evergreen) is a new solar cell company which was started in the fall of 1994. In order to reduce the costs of making crystalline silicon solar cells and modules, Evergreen is developing novel technology in each of the three principal areas involved in PV manufacture: (1) wafers or substrates; (2) cell making; and (3) modules and systems. For (1) Evergreen is developing String Ribbon [1,2,3], a method for producing silicon sheet in the form of continuous ribbon from the melt. For cell making, Evergreen is developing what we believe will be the lowest cost and simplest process in the industry for crystalline silicon. The third area, modules and systems, is the subject of this paper. In September of 1995, Evergreen began a two year PVMat subcontract (#ZAF-5-14271-09) which had the following objectives:

- (1) Development of a novel backskin material which would then result in a frameless module.
- (2) Reduced systems cost. This included development of novel mounting methods utilizing such a frameless module and the design of a better junction box.
- (3) Development of a new encapsulant material which could be laminated in air.

- (4) Development of a non-vacuum, continuous lamination method utilizing this new encapsulant.

In this paper we report on progress made in this project during the first year of this sub-contract. We will focus on work done under objectives (1) and (2) above.

DEVELOPMENT OF A NOVEL BACKSKIN MATERIAL

The theme underlying Evergreen's PVMat contract is that the explosive growth of low cost but high performance polymers fueled by the huge markets these materials serve, offers interesting opportunities for photovoltaics. These are possibilities which PV, by itself, would not generate given the present size of the PV market vis-a-vis typical polymer markets and quantities. Of course these materials are not usually exactly in a form or precise composition which makes them immediately usable for PV. Thus, one thrust of Evergreen's PVMat contract has been to develop the necessary modifications to be able to utilize such materials.

For the development of a novel backskin material, the following criteria were used. It had to be a material of lower cost than the conventional Tedlar laminate which is about \$1/sq. ft., but without sacrificing any of the desirable properties of Tedlar backskin. To avoid any possibility of puncture, it should be thicker than the approximately 9 mils thickness of the Tedlar backskin. It had to be a material which could be formed and molded in the lamination process in such a way that a frameless module design would be viable, especially regarding bonding to all adjacent surfaces and protecting the glass edges of the module. And finally, it should be a material which would be expected to pass all the PV module tests as well as the UL requirements.

After an extensive search of possible resin suppliers, a material based on modified polyolefins was chosen. This material basically satisfied all the above criteria. Following its selection, 40 mil sheet was prepared from it.

One of the earliest concerns with this novel backskin material was its resistance to thermal creep. In architectural applications, for example, it is possible for modules to reach temperatures as high as 90° C. Accordingly, a number of tests were used to assure that the thermal creep resistance of this material was satisfactory.

In the first such test, 1" x 6" strips of the material were subjected to 85°C under a nominal load for 45 days. The nominal load was that estimated for typical field operating conditions. In the second set of more stringent tests, 1" x 6" strips with nominal loading were heated to temperatures exceeding 250°C for periods of several hours. In both cases, no significant thermal creep was measured.

FRAMELESS MODULE

The development of the novel backskin material paved the way for a frameless module in which the backskin material is also employed as an edge protector for the glass superstrate and then wraps around the edge to form a frameless module. In this case, the sealing of the module and the edge seal of the backskin material, as well as the wraparound edge, are all formed in the lamination process itself. So, at the end of the lamination step, a frameless module with edge seal and wraparound edging emerges.

The backskin material which was eventually chosen also exhibited excellent bonding capabilities to glass, metals, and other polymers. Fig. 1 shows the top portion of an Evergreen module using string ribbon solar cells and the new backskin. The edge protection of the front glass and the wraparound features of the backskin can be seen.

FIGURE 1. A String Ribbon frameless module

Several tests were employed to determine the integrity of the bond between the backskin material and the glass superstrate. The principal test was done in an environmental chamber. It was decided to use humidity freeze, since this was viewed as one of the most stringent of the test protocols for PV modules. The humidity freeze cycle is 85°C at 85% R.H. for 20 hours, followed by cooling down to -40°C. The standard protocol calls for 10 such cycles. We decided to see if we could test the glass/backskin bond to failure and found that even after 100 such cycles the bond integrity showed no weakening.

The strength of this bond, we did find, was contingent on the lamination temperature. Too low a temperature could produce a weaker bond.

The major advantage of the frameless module was that "slide bars" of metal or polymer could readily be bonded to the backskin in such a way as to allow the module to then be slid into place along two pieces of "C" channel. With such a possibility, the need for any mounting screws or nuts and bolts could be eliminated. Fig. 2 shows aluminum slide bars on the back of an Evergreen module. In the case of the aluminum/backskin material bond integrity, both

extensive humidity freeze and creep tests under load were performed to test bond strength and reliability. Fig. 3a shows the set-up used for thermal creep testing. Samples were tested for 45 days at 85°C with a load estimated at more than twice that for any actual in practice loads and demonstrated no measurable creep. Fig. 3b shows how static load testing was done. In this case the weights on the sample were such as to approximate twice the maximum estimated loading a module would ever experience with this mounting configuration. The results in this case were also excellent and indicated clearly that the bond strength was high and likely to remain so under use.

FIGURE 2. Edgewise view of a frameless Evergreen module showing the new junction box and, just below it, the aluminum slide bar.

REDUCED SYSTEMS COSTS

In addition to fostering the capability for a frameless module, the novel backskin also permitted a large variety of lower cost mounting possibilities. In particular, it is possible to attach either metal or plastic mounting components of many possible configurations. Fig. 3 shows the back of a module with aluminum mounting "slide bars." These slide bars allow the module to be mounted onto "C" channel by simply sliding the module onto two pieces of "C" channel. Such a mounting configuration requires no screws, is rapid, and consequently low in labor cost. Fig. 4 shows several modules mounted this way in an outdoor suburban Boston location.

FIGURE 3A. Thermal creep test arrangement for the new backskin material.

FIGURE 3B. Set up for static load testing of the aluminum slide rail for the frameless module.

FIGURE 4. Four Evergreen frameless modules mounted onto a simple C Channel and aluminum tubing structure.

IMPROVED JUNCTION BOX

A portion of the PVMat program was devoted to marketing studies of the novel frameless module and mounting arrangements. In the course of this, Evergreen also obtained feedback concerning junction boxes from a number of potential customers and integrators. As a result, Evergreen decided to design a new junction box which would incorporate the most desired features which emerged from this marketing study.

Using the techniques now widely practiced for injection molded polymer parts, Evergreen embarked on a rapid prototyping method which used 3-dimensional modeling, continual feedback for several design iterations, and then stereolithography and a laser sensitive polymeric material to form prototypes. The prototypes were then used in a final feedback loop and then an injection mold was ordered. Fig. 5 shows the junction box and lid. Here the junction box has an extension to mount onto an aluminum frame. The j-box can also be made without this extension if the j-box is mounted away from the module edges.

This new junction box had the following features: a size large enough for comfortable field wiring; a hinged lid which stays open in any position and a single captive screw; field and factory wiring clearly separated; a molded in terminal strip, 600 V d.c. rated; conduit capable with 4 knock-outs; built-in fuse capability; multiple module attachment possibilities—onto or away from an aluminum frame when there is such a frame; and spare terminals for multiple module wiring configurations.

FIGURE 5. Evergreen's new junction box.

NEW ENCAPSULANT AND LAMINATION PROCESS

As of this writing, Evergreen has just begun testing of the new encapsulant material which can be laminated in air. We are also in the final stages of a prototype continuous lamination machine which will utilize such an encapsulant.

SUMMARY

The initial reception to Evergreen's frameless module, mounting system, and junction box has been very positive both among potential customers, integrators and even thin-film PV makers. In this brief report, we have summarized some of the work which led up to this during the first year of a two year PVMat contract. Given the progress made so far, the prognosis for reaching the cost goal reduction of \$0.50/watt seems very positive.

ACKNOWLEDGMENTS

We wish to thank Holly Thomas of NREL for her continued support and encouragement in this work which was done under PVMat contract #ZAF-5-14271-09. The assistance of Joseph Fava and Jennifer Martz at Evergreen is also gratefully acknowledged.

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Title: PVMaT Improvements for Commercial Production of Thin-Film CdTe Modules

Organization: Golden Photon, Inc.
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Contributors: Jeffrey Phillips and Terry Brog, Ph.D.

Abstract. Golden Photon, Inc., of Golden, Colorado, has developed and refined a process for fabricating thin-film cadmium telluride-based photovoltaic devices. Golden Photon invested a considerable amount of effort in 1996 to implement processing improvements related to process scaling as part of PVMaT. These processing improvements have brought about increases in both product stability and wattage, while other process improvements resulted in a sizable increase in through-process yields. This paper contains a summary of these activities and the gains made at Golden Photon, Inc., in 1996 for PVMaT.

Golden Photon, Inc. (GPI), a subsidiary of ACX Technologies, has been investing in both cadmium telluride (CdTe) technology and the production of photovoltaic (PV) modules for approximately five years. These modules are fabricated via a proprietary thin-film spray deposition process onto LOF glass substrates. As part of the Photovoltaic Manufacturing Technology (PVMaT) contract with NREL, GPI has attempted to scale this process from the prototype manufacturing facility at 4545 McIntyre St., Golden, CO, to a 10-MW facility. GPI has identified various obstacles, however, which must be overcome before any process scaling will occur, and spent considerable time and effort in 1996 to correct these problems.

GPI has compiled multiple successes in calendar year 1996 related to the manufacture and scale-up of thin-film CdS/CdTe PV modules. These successes were the result of identifying process improvements and implementing them into the standard production process. These process improvements have resulted in (1) reduced module degradation over time; (2) higher average wattage output; and (3) increased production process yields. The combination of these factors helps to drive down the costs associated with the manufacturing of these thin-film PV modules while providing a reliable product to the solar industry. Discoveries that led to these improvements are discussed below.

In 1996, GPI scaled its production process from approximately 1200 panels per month to 1900 panels per month. This was done although many of the modules produced during this time showed considerable degradation ($\approx 30\%$) from the initial wattage after an 8-week outdoor exposure. Other panels, however, showed only moderate losses in wattage (refer to Figures 1 and 2). Because of this inconsistency in batch performance, R&D and Process Engineering were asked to identify variables in the process that were the source for module degradation. This needed to be corrected before any continuation in process scaling.

The results from this study determined that a major contributor to the batchwise variation in degradation mechanism was a nonhomogeneous CdTe microstructure across individual panels and between batches. This was determined from scanning electron microscopy characterization with samples analyzed after the CdTe recrystallization process. Some batches had a consistent microstructure across a panel and from panel to panel whereas other batches had a wide range of microstructural inhomogeneity across a panel. GPI evaluated and implemented an improved recrystallization thermal profile that has yielded a more reproducible CdTe microstructure and reduced

degradation (refer to Figures 1 and 2). This improvement has also led to a World Record Small Cell Efficiency for CdS/CdTe thin-films on soda-lime-glass of 14.7%.

The second area targeted at GPI for PV manufacturing was to increase module wattage output. At the end of 1995, the average wattage by batch was approximately 21 watts. This represented considerable improvement from the beginning of the year, but fell short of the wattage goals established by GPI Operations Management. The targeted goals were to show a continual wattage increase with time, but this has not been realized in production. In 1996, Operations and R&D were tasked by GPI management to identify mechanisms responsible for the lower wattage observed and to implement a pathway for improving the wattage to the targeted levels. Modest gains in wattage output were made throughout 1996 (refer to Figure 3), but a primary breakthrough came with the discovery of the nonuniformity and small grained nature of the CdTe microstructure. The process improvement discussed above that led to improved module stability also resulted in an increase of approximately 1.5 Watts in the average module output.

The improved CdTe morphology alone, however, was not the sole contributor to improvements in the maximum module output (refer to Figure 4). The maximum wattage panel produced each month was observed to fluctuate between 28 Watts and 31 Watts (measurement based on GPI internal testing). The reduced wattage observed in February 1996 was attributed to material contamination, and Operations has implemented an improved characterization plan to screen raw materials prior to use. The wattage output, however, showed considerable increase from 1995 where the maximum wattage panels rarely exceeded 26 Watts. This sizable increase has been partly attributed to better control over film deposition (film quality and thickness) and the testing and implementation of a superior CdTe dopant incorporation technique. GPI believes that setting up process controls at other key stages in the process will result in a continued increase in the average and maximum wattage values.

The third area of interest at GPI towards PVMaT was increasing the total throughput process yields. In 1995, throughput process yields ranged from approximately 35% to 60%. Most of the yield losses were associated with glass breakage with a secondary issue being low wattage modules. Operations supervisors, consultants, and engineers targeted two key stages for improving the total process yields. These were tin oxide deposition and cadmium sulfide deposition. These films are deposited onto a soda-lime-glass substrate using a spray deposition process that can lead to lower yields from glass breakage. In 1995, these individual processes demonstrated yields that ranged from 50% to 95%, but could not be controlled to acceptable levels. Routine furnace maintenance showed improvements, but these could not be maintained over time.

From analyzing the problem, it became apparent that ambient atmospheric conditions outside these furnaces played an integral role in the individual process yields. For example, air drafts into the production zone could create disturbances in these film deposition furnaces causing the glass to fracture. The glass breakage would throw off the heat balance from zone to zone leading to greater temperature instability. GPI has since installed an air heating system for both furnaces that minimize the impact of outside interference and has increased the yields for these furnaces to greater than 95%. This has resulted in throughput process yields typically exceeding 70% and sometimes achieving 80%. The 80% average yield is now the target set by Operations Management.

In January 1996, GPI was producing PV modules with an overate output of 20 watts and at a rate of approximately 1200 modules per month. The total process yield of completed modules was approximately 50%.

- Implementation of a Statistical Process Control plan identified numerous areas of process

variability. Through more rigorous process measurement, specification analysis and subsequent specification changes, machine modifications and process changes directly led to yield improvements in GPI's cell interconnection operation as well as improvements in module output and total process yield.

- A complete redesign of GPI's encapsulation scheme resulted in significant raw material and labor savings.
- An Incoming Raw Material and Pre-Qualification plan was implemented to screen raw materials prior to use by Operations.

By June 1996, the average module output had increased to almost 26 watts, and GPI's productivity had increased to more than 1900 modules per month. The final process yield had also increased to greater than 75% with costs decreased by approximately 20%. Although these milestones were impressive, module degradation continued to be a major obstacle for product liability and continued production. In July, GPI shifted its principle focus from scaling the process towards gaining a better understanding of mechanisms that led to module degradation. The team assembled by GPI has shown significant successes as evidenced by a marked decrease in module degradation and a significant increase in module output.

GPI has demonstrated multiple successes in 1996 in the area of manufacturing photovoltaic modules in accordance with PVMaT guidelines. GPI scientists, engineers, operators, and management have devoted efforts towards identifying mechanisms responsible for panel degradation, limiting wattage output, and limiting process yields. Initial results indicate that GPI is making considerable progress as evidenced by higher wattage modules, more stable modules, and higher process yields. GPI has implemented key process improvements into its standard production practices and increased initial wattage by approximately 4 to 5 watts per module. These modules are also more stable based on internal testing at GPI. Finally, variables that contributed to reducing the overall process yield were studied, identified, and corrected in GPI's manufacturing process. This has resulted in a significant increase in the process yields and helped to lower the costs associated with manufacturing scale up. GPI continues to investigate factors to improve wattage and stability so it can continually successfully scale its thin-film photovoltaic production line.

Figure 1. Golden Photon Batch to Batch Degradation.

Figure 2. Percentage of Wattage Loss for Numerous Production Batches.

Figure 3. Golden Photon's Average Monthly Wattage.

Figure 4. Golden Photon Maximum Wattage Panel by Month.

Figure 5. Golden Photon Average Production Yield by Month.

Title: **Monolithic Amorphous Silicon Modules on Continuous Polymer Substrates**

Organization: **Iowa Thin Films Technologies, Inc., Ames, IA**

Contributors: **F.R. Jeffrey, Principal Investigator; D. Grimmer; S. Martens, H. Shanks, and M. Noack, Investigators**

Objective

The overall goal is to develop the most cost effective PV manufacturing process possible. To this end Iowa Thin Film Technologies, Inc. has chosen a roll based manufacturing process with continuous deposition and monolithic integration.

The objective of this subcontract over its three year duration is to improve overall module performance, increase the throughput of the metalization, a-Si deposition, laser-scribing, and welding processes and to reduce the overall module manufacturing costs of the ITF production line by 68%.

Approach

This subcontract consists of three one-year phases which began in July, 1995. This report covers most of the first year and the beginning of the second. The first year activities were divided into four task efforts designed to: replace the ITF TiN layer with a less absorbing ZnO layer; design and implement a web steering system for feeding the web onto the printer platen; establish new laser operating parameters to optimize the laser beam scan speed; and develop a new insulating ink printing and roll based laminating process for the ITF production line.

Second year activities are divided into five task efforts designed to: increase the throughput of the metalization, a-Si deposition, laser-scribing and printer processes; design and implement baffles for the isolation of metal deposition regions; investigation of the limits on the ZnO deposition rate; develop new machine control programs; identify new laser operating parameters to optimize the laser beam scan speed; integrate a new, water based insulating ink into the patterning process; and automate the final process steps of busbar attachment and web cutting.

Research Results (10/1/95-9/30/96)

Work undertaken during this segment of the program was designed to meet the goals of reducing the overall module manufacturing costs of the ITF production line by improving manufacturing throughput and performance of the manufactured devices. The following efforts and achievements were the focus of work carried out during Phase I and the first quarter of Phase II:

Sputtering high quality Zn(Al)O The capability of sputtering a high quality Zn(Al)O was developed during this period. A wide range of variations were investigated to allow ITF to implement this material as a reflection enhancement layer in devices. However, all efforts resulted in an increase in shunt defects in the devices. Work will continue on this task throughout Phase II.

ZnO top contact deposition Increased deposition rates for the ZnO top contact deposition were successfully implemented. Preliminary work was done on implementing single pass operation of this system. As a result of efforts under this task, a throughput increase of 50% has been achieved.

Registration and ink line improvements To allow a reduction in area loss due to interconnects, improvement in registration and ink line width were required. A new alignment process and sensor were developed to improve the speed and accuracy of registration for the patterning processes. This technique proved highly successful and has been fully implemented on the scriber. The sensors have been installed on the printer and implementation of the new process is in progress. This development has improved registration reproducibility from 100 μ m to 10 μ m. A new Silver ink composition has been developed which allows finer print lines and lower series resistance. This has allowed an overall improvement in area utilization of 8%. In addition, throughput improvements of 30% on the scriber and 70% on the printer have been realized.

Insulator inks Water based insulator inks were evaluated for compatibility with our process. One candidate was found which shows promise.

Roll based lamination Use of roll based lamination was investigated and tested as a means to reduce the cost of assembly with promising results. Straight roll lamination capability using pressure sensitive adhesives and thermally activated bonding was developed. This process works well with a range of candidate materials. Laminated assemblies will be life tested to determine long range stability. This approach yields at least a 4-fold increase in throughput. Use of the standard EVA/Tefzel encapsulant with a roll laminator was evaluated. This process requires a post bake following rolling. The best method for this post bake is still under investigation.

Conclusions

ITFT has succeeded in replacing the ITF TiN layer with a less absorbing ZnO layer; designing and implementing a web steering system for feeding the web onto the printer platen; establishing new laser operating parameters to optimize the laser beam scan speed; and developing a new insulating ink printing and roll based laminating process for the ITF production line.

During the next year ITF will focus on the following: continued efforts at implementing the back reflector; optimization of performance and deposition rates in the new tandem machine; development of single pass capability in the TCO and metalization systems; implementation of the new alignment process on the printer; and development of an automated cutting and busbar attachment system to go with the roll laminator.

Title: **Three-Phase Power Conversion System for
Utility Interconnected PV Applications**

Organization: **Omnion Power Engineering Corporation
2010 Energy Drive, P.O. Box 879
East Troy, WI 53120**

Contributors: **D. G. Porter, Principal Investigator; H. Meyer and W. Leang**

Objectives

The objective of this contract is to make advancements in three major areas of three-phase utility interconnected, photovoltaic power conversion: cost, reliability, and performance. The total manufacturing cost of a nominal 100-kilowatt power conversion system (PCS) will be reduced from approximately \$0.50/watt to \$0.25/watt when built in production lots of 100 units. A design goal of 40,000 hours mean time between failures (MTBF) has been established for this development. Using soft-switching technology, three performance goals have been established to 1) improve converter efficiency from 95.5% to 96.5%, 2) meet FCC regulations for electromagnetic interference, and 3) reduce audible noise to below 60 decibels.

Approach

In Phase I of the contract Omnion will develop the product specification with input from a customer user group. The draft product specification shall be prepared based on Omnion's understanding of customer preferences and current technological trends. Omnion will design and build a prototype 100-kilowatt, three-phase power conversion system working with Soft Switching Technologies Corp. (SST) which incorporates a soft switching resonant DC link converter. The PCS will be demonstrated and the product specifications reviewed with the customer/user group.

During Phase II, Omnion will finalize the revised and repackaged design for the 100-kilowatt PCS product (Series 3400). Omnion will also conduct tests on modified manufacturing equipment and conduct a pre-production run of the prototype 100-kilowatt PCS. At the conclusion of Phase II, Omnion will have a production-model PCS with UL certification.

Results

Significant progress in Phase I has been made during FY96. Discussion will be focused on the two main tasks of Phase I: specification development and prototype design and fabrication.

Specification Development

Specification for the core resonant converter was developed in conjunction with SST. Product specifications for the PCS were also developed. Representative Omnion product specifications and specifications from recent major procurements (PVUSA, Team-Up, and Sacramento Municipal Utility District) were collected to serve as references.

Review of the product specification with key customers/users was initiated. Omnion sales/marketing and engineering personnel conducted these interviews. To facilitate presenting the design and focusing the reviewer's attention on specific features, three documents were provided to each reviewer: 1) A system one-line drawing, 2) A system specification, and 3) A matrix comparing the specification requirements of recent industry procurements. Walking each reviewer through the matrix and referring to the one-line diagram or system specification when necessary proved to be an efficient method for obtaining detailed input. Each interview lasted between two and three hours. Customer/user feedback regarding features and qualities were incorporated in the PCS specification.

A review and analysis of field failures experienced with Omnion's Series 3200 hard-switched IGBT product was initiated in March and completed in June 1996. Proper identification of past problems was helpful in solidifying the design of the Series 3400 product.

Prototype Design and Fabrication

The core resonant converter was developed in conjunction with SST. A breadboard core module was designed and tested by SST at full voltage and current in December 1995. SST then shifted their focus to designing of final control boards and the prototype. During this development phase of the core resonant converter, monthly progress review meetings were held with SST personnel. A prototype core resonant converter was delivered by SST in September of 1996.

Design work was initiated on the Analog Interface printed circuit board in January 1996. This board is used to convert high voltage signals to logic levels for input to the Master Control board. Work was also initiated in January on the system schematic and bill of materials. Work on the Master Control printed circuit board was initiated in February and completed in September. The Master Control is responsible for overall system control and, specifically, control of the core resonant converter module. A state diagram was prepared to facilitate writing of the software. Software design was initiated in September. The prototype bill of material was released by engineering in June. In stock materials were staged while other items were given to purchasing for procurement.

System packaging work was initiated in February. Packaging, control design, and core resonant converter module design are all highly interrelated, and therefore require some level of simultaneous consideration. Progress made at SST on the final packaging of the core resonant converter module enabled Omnion to move forward with system packaging in August. A modular T-slotted aluminum frame system, with aluminum side panels, was selected to readily permit optimization of component location within the enclosure. A preliminary cabinet layout was completed in September.

A quality audit on the core resonant converter was conducted by Omnion's quality assurance personnel. The report was shared with SST to enable improvements to be implemented on future units.

The core resonant converter module received from SST was tested in October. It was operated in parallel with Omnion's utility service to ensure proper functioning. It performed well in all respects.

Summary

Under Phase I, the following was accomplished:

- An advanced product specification was drafted to guide prototype design and development.
- Field failure data with Omnion's hard switched IGBT technology hardware was analyzed to better understand where design improvements were needed.
- Product specifications were presented and reviewed with key customers/users.
- A working product specification was drafted to serve as a baseline in the development of the new power conversion system.
- The core resonant converter technology was developed in conjunction with SST.
- A 100 kilowatt prototype power conversion system was designed.
- Prototype system package was designed.
- Interaction with vendors to optimize component selection and specifications was initiated.
- Preparation of design documentation was initiated.
- The prototype core resonant converter was built, and preliminary testing was initiated.
- Assembly of a 100 kilowatt prototype power conversion system was initiated.

These accomplishments will provide the framework for the completion of Phase I, and the smooth transition into Phase II of the contract.

Title: PVMaT Improvements in the Manufacturing of the PVI Powergrid™, Year-One Annual Report

Organization: Photovoltaics International, LLC (PVI) 171 Commercial Street
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Objectives

The goals for PVI's PVMaT program are to reduce the cost of manufacturing the Powergrid, to demonstrate large volume production, and to reduce the use of volatile organic compounds (VOC) and hazardous materials (hazmat) in manufacturing. Successful completion of PVI's PVMaT program will result in a reduction in the cost of the Powergrid of approximately three dollars per Watt. The goal for year-one was to produce engineering designs for an advanced lens and module side extrusion system, a second generation automated receiver assembly station, low-cost frame members, and a low VOC and hazmat module assembly process. Details of the first year activities can be seen in the Phase 1 Technical Reportⁱ

Approach

An advanced acrylic extrusion system was designed that could be used for the production of both high quality lenses and for module sides. The extrusion tooling was designed, built and tested off-site. In addition, some parts of the extrusion system, such as the puller, were completed and tested. Results of these tests were used to refine the design of the extrusion system.

A second generation automated assembly station was designed. All aspects of the design were verified in proof-of-concept tests. The tests used actual hardware where possible. Results of the testing were used to refine the design where needed.

A low-cost, roll-formed steel panel frame was designed. Prototype frames were assembled and tested. Costing was done for the frame members and the tooling.

A low-VOC, hazmat module was designed and prototypical modules built. A process for ethylene vinyl acetate (EVA) encapsulating receivers was developed that eliminated the silicone encapsulate which contributes the majority of VOC and hazmat in present module production.

The new EVA formulations are less sensitive to UV light and the acrylic used in the PVI lens blocks the high energy UVⁱⁱ. This enables EVA to be used in the PVI concentrator receiver.

A small vacuum oven was built to test the EVA materials and processes. Experiments were conducted to determine a process that gave a good bond with no air inclusions. Different EVA formulations were also tried. Several small test

receivers were built and subjected to UV radiation, thermal cycling, and freeze-humidity cyclingⁱⁱⁱ.

Results

Advanced Extrusion System

An advanced extrusion system was designed. The system borrows heavily from the medical device industry, which demands close tolerance on extruded parts, such as catheters. The system is computer controlled with provision for data acquisition and analysis. Sensors are designed into the system for on-line sensing of lens dimensions and transmission as well as the normal extrusion parameters such as extrudate temperature and pressure.

A post-extrusion roll forming concept was developed and proof-of-concept tests performed. The testing showed very accurate fidelity.

Sheet extrusion technology was used for the die design. This allows easy adjustment during running and easy and inexpensive changing of the die geometry. A "coat-hanger" type manifold was used. A "cold-shoe" type vacuum former was used to curve the lens after extrusion.

A die, manifold, and cold-shoe was designed, built and tested off-site, see Figure 1. Many modifications were done to the die plate over the year, each one requiring extensive testing. All of this testing was used to refine the design of the extrusion system, die, after-forming equipment, controls, and instrumentation.

Figure 1. PVI Lens Die and Cold-Shoe

The same extrusion system and manifold will be used for production of module sides. A die plate was made for the sides and tested. Preliminary testing indicated that the same manifold could be used for both products. This will save considerable cost in development and production. The die plate will be developed when the extrusion system is installed at PVI.

Automated Receiver Assembly Station

An automated receiver assembly station was designed, see Figure 2. The design uses a pick-and-place robot to load two assembly "nests" with cells and leads. The cell assemblies are soldered using IR lamps. The robot removes the completed cell assemblies and places them on the heat sinks where the series connections are made using laser soldering. Our special adhesive system bonds the cell assemblies to the heat sinks.

Figure 2, Automated Receiver Assembly Station

The IR lamp soldering was found to be a quick and reliable process, if certain design features and process variables are used. Also, under correct process parameters, laser soldering of the series connections was found to be a reliable and clean process.

The design throughput for the automated receiver assembly station is one cell per 15 to 20 second. This equates to 4 to 5 MW/yr for this machine. By parallel processing of cell assemblies, the production of one machine is expected to increase to 50 MW/yr.

The automated receiver assembly station was designed to be modular. This allows accommodation of changes and refinement of the different components.

Low-Cost Panel Frame

A roll-formed, galvanized, sheet-steel panel frame was designed and prototypes made. Aluminum extrusions with identical section stiffness were used for prototype frames. The design was modified based on tests of the prototype frames. We plan to develop the tooling and introduce roll-formed into production in the second year.

Low VOC and Hazmat Module Manufacturing

With the correct temperature and vacuum cycles, serviceable EVA encapsulated receivers were made with Tefzel® covers. A two chamber vacuum oven was needed, using a flexible diaphragm between the chambers. Both chambers were initially evacuated. After the EVA melted, atmospheric pressure was introduced to the top chamber to press the diaphragm onto the EVA/Tefzel sandwich.

Less than 10% degradation in performance of the test receivers was measured after temperature and freeze-humidity cycling. The samples that were tested under UV lamps showed negligible yellowing when the sheet of acrylic lens material was on top of the samples. Samples that did not have the acrylic sheet showed yellowing.

Summary

All design work was completed during Phase 1. The designs will be implemented in Phase 2 and initial testing and refinement will be completed. Final testing and demonstrations will be completed in Phase 3.

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Title: Photovoltaic Cz Silicon Module Improvements

Organization: Siemens Solar Industries, 4650 Adohr Lane, Camarillo, CA 93012

Contributors: R. R. King, principal investigator, T. L. Jester and K. W. Mitchell

Introduction

The objective of the DOE/NREL Photovoltaic Manufacturing Technology (PVMaT) subcontract with Siemens Solar Industries (SSI) is to continue the advancement of module design and manufacturing methods at SSI in order to achieve an 18% reduction in module cost per watt at the end of three phases of work, with each phase lasting a year. Phase I of this subcontract began in November 1995. The approaches for reaching this cost reduction goal are to analyze existing module cost structure and explore new module configurations which address the highest cost components, investigate the reduction of labor and improvement of yield, and to implement statistical process control (SPC) in module manufacturing.

Module Cost Analysis and Design

A first step toward reducing the cost per watt at the module level is to gain a thorough understanding of the present factors which dominate cost. Analysis of the cost structure of module manufacturing at SSI has allowed specific strategies and module designs for reducing the most significant costs to be formulated. These improvements in module configuration have been introduced into production in the SSI Camarillo plant during Phase I of the contract, or exist as prototypes with production scheduled to start during Phase II. Fig. 1 shows the detail of the module direct material costs. There are many contributors, but the frames and junction boxes are the module direct materials with the greatest cost per watt. In May 1996, a new junction box design entered production, combining improved versatility for PV module users, and a cost that is 0.05 \$/W lower for present module sizes. Production of laminates with 72 103-mm semi-square cells, rather than the more usual 36, began in the SSI Camarillo plant in August 1996. The larger module size and power (110 W) lower the \$/W components from the junction box and module manufacturing labor, and from the frames due to the smaller perimeter-to-area ratio, resulting in a 4% reduction in module \$/W relative to 36-cell modules.

Fig. 2 shows a new module configuration that uses 150-mm round cells in a 36-cell package. Prototypes of this module have been built during Phase I of this contract and shipped to NREL. The cost per watt is expected to be significantly lower for this type of module for a variety of reasons. The larger cell substrates used translate to an increase in surface area per wire saw run, and reduction of handling and equipment costs per watt for a given MW/year production level. The round shape of the 150-mm cell makes more efficient use of the Cz ingot by eliminating slabbing of the ingot. The large module size also means that handling and equipment costs per watt will be reduced for a given MW/year production level. All told, this module configuration with 150-mm round cells is projected to be capable of a 19% reduction in cost per watt.

Yield and Productivity Improvements

Manufacturing yield is a powerful driver of the cost of cells used in a module, the cost of module direct materials, and of the cost of module manufacturing labor. Close monitoring of yield and categorization of various types of loss in the wafering, cell fabrication, and module fabrication areas reveal that

mechanical breakage is the dominant type of yield loss. Consequently, most efforts have been aimed at reducing this component of yield loss, through improved tracking, better wafer handling equipment, operator education and involvement, and by experimentation to find the root causes of wafer breakage and its dependence on material properties. Fig. 3 is a chart of the force required to break single-crystal Cz Si and multicrystalline Si wafers measured at 6 different points in the cell fabrication sequence. Throughout the cell process, the breakage force of mc-Si is fairly similar to that of single-crystal SSI Cz. As sawn, the wafers are 50-60% weaker than after texture etching (after Step 1). One explanation is that microfractures or other irregularities on the as-sawn wafer surface can serve as nucleation sites for larger fractures when the wafer is stressed. The fracture nucleation sites on the as-sawn wafer are likely to be removed or their density decreased by the wet etching solutions.

Manufacturing Systems to Improve Module Reliability

The SSI Camarillo plant received ISO 9001 certification in March 1996. This is a major milestone in the pursuit of quality manufacturing systems, and represents a very substantial effort by the company to establish and document procedures, operator work instructions, maintenance and calibration schedules, conduct operator training, etc. The benefit is a profoundly improved system to ensure manufacturing compliance and control of its processes. It is, however, only a beginning.

A goal of the PVMaT program at SSI is the identification of key processes in the fabrication sequence, *e.g.*, wafer thickness variation, wafer cleaning, emitter sheet resistance, cell fill factor, incidence of wafer edge chips, solder bond pull strength, lamination defects, etc., and implementation of SPC charting at each key step at the end of Phase II. SPC methods are now in use at many sites in the plant, baseline data is being gathered, and a feedback mechanism for early detection of out-of-control process conditions exists. Fig. 4 shows an example of a shift in the average value of automatic soldering yield, and distribution tightening, coupled to events in the line.

Summary

Cost drivers for Cz Si solar cell modules have been identified. Cell size and shape, material usage, module size, and cell and module yields have an especially strong influence on cost. Specific module designs to address cost issues have been implemented. Broader changes to the module configuration based on the 150-mm-diameter round cell are in progress during Phases II and III. Wafer breakage is the mechanism which dominates cell yields. Breakage is being reduced by understanding root causes, improved tracking of data, and by operator involvement. The development of systems to ensure compliance and control of module manufacturing includes ISO 9001 certification received by SSI in March 1996, and the ongoing implementation of SPC methods at key control points in manufacturing. As a result of yield gains and other improvements, a 5% reduction in cost per watt at the module level was achieved through September 1996. Based on large prototype modules built with 150-mm-diameter round cells, a 19% reduction in module cost per watt is projected.

Acknowledgments

Many people have contributed to the work under this contract. Thanks are due especially to Rick Mitchell, NREL technical monitor, to Dave Bender, Ruben Balanga, Mark Crowder, Jean Hummel, Dave Jeffrey, Waltraut Klein, Greg Mihalik, Maria Tsimanis, Von Walters, Elena Woodard, Eugene Yamamoto, and others in the Engineering, Quality, and Finance groups at SSI. This work was funded in part by DOE/NREL Subcontract # ZAF-5-14271-12.

Fig. 1 Cost/watt for direct material in the module fabrication area.

Fig. 2 Large-area SM100 prototype module using 150-mm-diameter cells has a reduced cell contribution to \$/W, as well as reduced frame and junction box \$/W components.

Fig. 3 Wafer breakage force of multicrystalline-Si (mc-Si) and SSI Cz Si, as measured by a stylus for wafers resting on two horizontal rails. The error bars indicate ± 1 standard deviation in the data.

Fig. 4 Charting of automatic soldering yield provides feedback mechanism to gauge the effect of process changes.

Title: Technology Support for Initiation of High Throughput Processing of Thin-Film CdTe PV Modules

Organization: Solar Cells Inc., 1702 N. Westwood, Toledo, OH 43607

Contributors: R. A. Sasala, R. C. Powell, and G. L. Dorer

Objectives

The goal of Solar Cells Inc. is to develop the technology to produce photovoltaic modules in volumes sufficient to compete with the economics of conventional electric technologies. CdTe is the material of choice due to its demonstrated good performance both in the laboratory and in pilot production manufacturing. Furthermore, the deposition methods under development are consistent with eventual integration with a commercial scale glass float line. This approach shapes the direction of research and the priority that experiments are performed. SCI is investigating processes which shorten and/or simplify deposition and post-deposition procedures, flow in a logical manufacturing sequence and permit in-situ processing of all deposited layers. As such, research is focused on developing an improved deposition apparatus, elimination of wet post-deposition processes, interconnection improvement, continued improvement of efficiency and further verification of stability.

Approach and Results

CdTe deposition: SCI has tested a full-scale continuous-feed deposition apparatus. In this system, CdTe or CdS is sublimated continuously and the vapors are transported to the glass with the aid of an inert carrier gas. Films have been deposited at pressures between 2 and 50 torr with growth rates exceeding rates achieved with our pilot production deposition system. Film thickness uniformity in the direction of glass travel has been excellent, typically $\pm 5\%$. Cross web thickness uniformity has been found to depend on distributor geometry, gas flow and pressure.

The new deposition equipment provides a new level of control over film growth, particularly the local deposition rate, material utilization and film uniformity. Currently, the continuous sublimation system has been used to deposit onto a discontinuous stream of glass. Even under these conditions, films of both CdTe and CdS with microstructures similar to standard CSS material have been deposited. Electronic properties have been tested by combining CSS CdS with VTD CdTe and vice versa. Small area devices have shown promising results. For example, 9% devices have been made using CSS CdS with VT CdTe. We believe that the continuous feed VTD system combined with a continuous stream of glass will produce steady state conditions and very reproducible films.

Chloride treatment: Work on implementing the chloride treatment for manufacturing has focused on elimination of wet processes and reduction of treatment time. The work focused on the use of vapor CdCl_2 and HCl as chlorine sources.

The goal of the vapor CdCl_2 experiments was to determine the minimum treatment time interval which would produce the effect of a full standard wet CdCl_2 treatment. While there were some 9% efficient devices made with a treatment time as low as 60 s, consistent results required a minimum treatment time of 300 s. The 300 s treatment consistently produced devices in the 10 % range but did not produce open-circuit voltages as high as the standard treatment. Prevention of residue formation is accomplished by maintaining a sufficient substrate temperature during or after treatment.

The HCl treatments were conducted at atmospheric pressure with a mostly inert ambient. The process control variables for the experiment include the substrate temperature, the HCl concentration and treatment time. HCl treatments tended to produce devices with higher V_{oc} 's than the vapor $CdCl_2$ method and 800 to 820 mV were typical. Device efficiencies over 10% were routinely produced. Similar to vapor $CdCl_2$ treatments we find 300 s to be the approximate minimum treatment time for reproducible high quality devices.

Interfacial layer: Formation of a low-loss contact to p-type CdTe requires special processing. It has been found that surface preparation of the CdTe is critical for fabrication of high quality devices. Most of the traditional surface treatments have included wet etch steps which create a Te-rich layer on the CdTe surface. However, dry vapor processing is preferred for manufacturing. Thus, work has been performed on replacing the wet etch with direct deposition of Te. Initial efficiencies similar to standard wet treated devices have been observed in devices on which Te has been deposited with a variety of techniques including rf and magnetron sputtering, e-beam evaporation, and close-space sublimation. In fact, near record mini-module performance has been achieved with a deposited Te interfacial layer.

Recent work has focused on CSS deposition of Te. Because of the relatively high vapor pressure of Te, high deposition rates are readily achieved by simple sublimation. Deposition rates as high as 500 Å/s have been observed and have been used to produce 10% efficient devices with characteristics similar to devices with sputtered Te films. Consequently, it appears that Te can be easily deposited in a manner similar to our CdS and CdTe deposition technology (VTD) and will not require more costly sputtering or e-beam evaporation.

Interconnection: As an alternative interconnection technique, SCI is refining its patented "dot matrix"(6) interconnect structure. The basic principle behind dot matrix is to use a second metal in parallel with the TCO but isolated from the contact in intimate contact with the CdTe. The electrical connection between the TCO and the second back metal is made through a matrix of dots which are isolated from the semiconductors and first back metal. There are several advantages of the dot matrix technique when optimized. One is that the dots can occupy less space per unit area than the three laser scribes which results in a higher total area efficiency. Another is that the cell width is limited by the sheet resistance of the second back metal rather than the TCO. This permits the choice of cell width based upon the desired output voltage and not minimum I^2R loss of the TCO. It also permits the use of a higher sheet resistance TCO which is both less expensive and has a higher optical transmission which leads to a higher efficiency. Another advantage of the dot matrix technique is that it can be made to be self registering.

To date, SCI has successfully made a 9.3% efficient (in-house measurement) 64 cm² interconnected mini-modules with 4 cm wide cells in the laboratory and is working on improved methodologies for the full size modules.

Efficiency improvements : Analysis has shown that increased photocurrent could substantially increase device efficiency. The major current losses are due to absorption in glass and low collection of carriers from light absorbed in the CdS (wavelengths below 520 nm). Since there has been little success in improving the collection efficiency of the CdS, the improvement strategy has been to minimize the window absorption by thinning the CdS. While this approach has resulted in increased current densities, reduced open-circuit voltage has lead to only marginal efficiency improvements. However, the deposition of an intrinsic SnO_2 layer on top of the $SnO_2:F$ permits the use of thin CdS without loss in V_{oc} . An example of this is the SCI record 1 cm² cells which were recently made on 3mm thick low haze LOF TEC8 glass. The I-V curve taken at NREL for this device is shown in Figure 1. The CdS

thickness of this sample was approximately 400 Å yet it still produced an open-circuit voltage near 840 mV, which is close to the SCI record with thick CdS. In addition to the high V_{oc} , the short-circuit current density of 22.3 mA/cm² is as high as has been made previously on soda lime glass at SCI. The J_{sc} is higher than normal because of the reduced thickness of the CdS and glass.

Stability: Stable CdTe-based photovoltaic modules have been made with our standard pilot production process. The stability of modules made using a particular process can only be ensured with long-term testing. Indoor continuous light soaking has been conducted for >20000 hours on many samples. However, it has been shown that >5000 hours is the minimal testing recommended. Without such testing, erroneous conclusions about the superiority of a particular fabrication recipe can be made. The recommendation applies to individual cells as well as to modules. Elevating temperatures beyond normal operating conditions by 20 to 35° C in light soaking may be effective in accelerating degradation but can only be used for recipe comparisons at this time.

$V_{oc} = 0.8340 \text{ V}$
 $I_{sc} = 22.54 \text{ mA}$
 $J_{sc} = 22.31 \text{ mAcm}^{-2}$
 Fill Factor = 69.73 %

$V_{max} = 0.6659 \text{ V}$
 $I_{max} = 19.69 \text{ mA}$
 $P_{max} = 13.11 \text{ mW}$
 Efficiency = 13.0 %

Figure 1. SCI record 1 cm² device made with a 400 Å CdS window layer and an intrinsic SnO₂ buffer layer.

Outdoor Array Data: While stability data for indoor tests are very important in device design and development, it alone is insufficient to predict module performance in the field. SCI has detailed performance data on twenty-four months of data on our Westwood facility 1.2 kW array. Data includes current voltage data as well as illumination intensity and temperature data to permit the normalization of both intensity and temperature variations from standard reporting conditions. Figure 2 shows the array data with the normalized power corrected for temperature away from 25 °C and this normalized output agrees with the initial array rating of 1200 watts. With the temperature correction, the data shows good stability for its 2 years of testing.

Figure 2. Power output of SCI Westwood 1.2 kW array normalized for intensity variations and corrected for temperature variations from 25 °C.

Title: Development of Standardized, Low-Cost AC PV Systems

Organization: Solar Design Associates, Inc. (Prime), Harvard, MA 01451;
Advanced Energy Systems, Inc., Wilton, NH 03086; Solarex,
Frederick, MD 21701

Contributors: Steven J. Strong, Solar Design Associates; Dr. John H. Wohlgemuth,
Solarex; Dr. Robert H. Wills, Advanced Energy Systems

Objectives

The objectives of this program are to improve the reliability and safety and reduce the cost of installed photovoltaic (PV) systems by creating standardized, pre-engineered components and an enhanced, low-cost modular inverter. These advances will be combined with the new, large-area Solarex MSX-240 PV module to create standard, modular ac PV "building blocks" for the U.S., Japanese, and European markets, where identical units can be combined to create PV systems of virtually any capacity, to suit virtually any application.

Approach

Research into the critical development areas of PV modules with integrated, dedicated inverters is a promising avenue of investigation for making PV systems easier to install, more reliable, safer, and more cost effective. Success in this effort will benefit the PV industry, in general, and the building-integrated PV market, in particular.

The approach to this research involves a collaboration among national laboratories, an inverter manufacturer, a PV manufacturer, and a systems integrator, pursuing seven specific tasks ranging from a review of array mounting systems, to the design and manufacture of digital module-integrated inverters, to the field testing of these units in the United States, Europe, and Japan.

Results

Work during the first year of this 2-year effort consisted of the following tasks:

Task 1: Systematic examination of past and present PV systems design and installation practices, with the goal of producing cheaper, more manufacturable products; simpler, standardized designs; and, ultimately, the delivery of a lower cost ac PV system to the customer.

In addition, this study included a detailed review of building code requirements on PV module mounting systems for sloped and flat roofs and develop generic design criteria to address these requirements.

Task 2: SDA and Solarex developed innovative, low-cost methods of array mounting and structural support for sloped and flat roofs of residential and commercial buildings as well as ground-mounted arrays using pre-engineered, standardized components and large-area Solarex MSX-240 modules.

Task 3: The development of an enhanced digital micro inverter, using the SDA analog modular

inverter developed under the PV:Bonus program as a basis for the new design. Solarex supported the digital development effort by reviewing the performance of the early analog inverter, and performing qualification, environmental and performance tests on the new digital version. Input from this testing, as well as testing by Sandia and Underwriters Laboratories, was used in the development of the new digital design and its support structures.

Task 4: Solarex and SDA were to define and develop innovative, low-cost methods of module-to-module electrical interconnection, array wiring, string interconnection, lightning protection and array grounding for systems on residential and commercial buildings as well as ground mounted arrays through the use of pre-engineered, standardized components.

Task 5: Solarex was to work with SDA to combine the results of Tasks 1-4 to create standardized, modular ac PV systems that can be packaged as kits by Solarex. Solarex worked with SDA to define the "building blocks" for these kits, incorporating comments from potential customer and develop prototype systems.

One of the first steps in creation of a standardized, modular system is to obtain UL Certification for the major building blocks.

Task 6 and Task 7: Development and testing of units for the Japanese and European markets.

Fig 1: The ac module concept

Figure 2 shows the ac module output power on May 1, 1996. The most striking feature is that individual modules act independently—east-facing S/N 79 starts up in the morning and drops to diffuse-only at noon. West-facing #84 starts to see direct beam after noon and #86, being vertical, sees less intensity than the tilted modules. Clearly, only an independent module-integrated inverter approach could work with so many orientations.

Fig. 2: Alternating Current Module Output Power (W) vs. Time of Day

Fig. 3: PV Module MPPT Voltage

The maximum power tracking (MPPT) capability of the inverters can be seen in Figure 3. Note that, as expected, the PV voltage drops as module temperature rises. Lower and shaded modules run at higher voltages.

Finally, inverter temperature shows warmer temperatures while operating at higher powers—as expected (east is warmer in the morning and west is warmer in the afternoon). Also note that the south-tilted #83 is just starting to current limit its output due to a 65°C (150°F) maximum temperature setpoint—if this setpoint is reached, the inverter backs off on PV current and the operating point rises above MPP (Figure 4).

Summary

The following points summarize the work performed during the first year of the contract:

Fig. 6: Inverter Temperature

- Performed a system-level review of present practice in PV systems design and components with input from utilities active in PV
- Performed a detailed review of building code requirements on PV module mounting systems and developed generic design criteria to address these requirements
- Completed design of standardized PV system mounting systems for sloped roof, flat roof, and ground mounting
- Built prototypes of the three mounting systems—sloped roof, flat roof, and ground mounting
- Selected a hard-wiring system and a quick-connect system for electrical connection of the ac modules
- Successfully completed mechanical loading tests on frameless MSX-240 module
- Completed design and prototyping of the advanced digital modular inverter
- Completed initial testing and qualification of the advanced digital inverter
- Completed an initial production run of enhanced digital inverters
- Completed initial discussions with UL for UL certification of the modular inverter
- Completed discussions with UL and agreed on test program for UL certification of MSX-240 module in the mounting systems designed for this program.
- Developed a preliminary qualification test sequence for modular inverter.
- Delivered two Solarex ac modules for testing and evaluation: one to NREL and one to Sandia.

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Title: Design, Fabrication and Certification of Advanced Modular PV Power Systems

Organization: Solar Electric Specialties Company, Willits, California 95490

Contributors: Glen E. Minyard and Timothy J. Lambarski

Abstract

The Design, Fabrication and Certification of Advanced Modular PV Power Systems contract is a Photovoltaic Manufacturing Technology (PVMaT) cost-shared contract under Phase 4A1 for Product Driven System and Component Technologies. Phase 4A1 has the goals to improve the cost-effectiveness and manufacturing efficiency of PV end-products, optimize manufacturing and packaging methods, and generally improve balance-of-system performance, integration and manufacturing. This contract has the specific goal to reduce the installed PV system life cycle costs to the customer with the ultimate goal of increasing PV system marketability and customer acceptance.

The specific objectives of the project are to develop certified, standardized, modular, pre-engineered products lines of our main stand-alone systems, the Modular Autonomous PV Power Supply (MAPPS) and PV-Generator Hybrid System (Photogenet). To date, we have designed a 200 W MAPPS and a 1 kW Photogenet and are in the process of having the MAPPS certified by Underwriters Laboratories (UL Listed) and approved for hazardous locations by Factory Mutual (FM). We have also developed a manufacturing plan for product line expansion for the MAPPS. The Photogenet will be fabricated in February 1997 and will also be UL Listed. Functionality testing will be performed at NREL and Sandia with the intentions of providing verification of performance and reliability and of developing test-based performance specifications. In addition to an expansion on the goals, objectives and status of the project, specific accomplishments and benefits are also presented in this paper.

Background

Although most PV system integration companies advertise standard product lines, most PV systems sold today are still custom designed based on general product line designs. The fact that most systems houses have system product lines attests to the need to make the specifications simple and standardized so that they can be more easily understood by the potential customer and marketed by the sales engineer. This contract makes a concerted attempt to increase standardization and modularity as we see in other product categories such as computers whether for consumers or commercial applications. There will always be a need for custom designs, but true cost savings and customer acceptance require that systems be more technology transparent. "Turn it on and watch it work."

In addition, up until now no PV power systems have been certified by agencies outside the PV industry such as Underwriters Laboratories (UL) or Factory Mutual (FM). We are seeing a trend toward certification in components such as PV modules, charge controllers and inverters. More companies are getting their PV products UL or ETL Listed or FM Approved for hazardous locations. This project represents the first effort to have whole PV power systems certified.

Program Goals and Objectives

The stated goal of the Design, Fabrication and Certification of Advanced Modular PV Power Systems contract is to significantly reduce the installed PV system life cycle costs to the customer. This is part of an overall goal of improving PV system marketability and customer acceptance. In line with the philosophy presented above, SES is attempting to make with happen by developing certified, standardized, modular, pre-engineered products lines of our main stand-alone systems, the Modular Autonomous PV Power Supply (MAPPS) and PV-Generator Hybrid System (Photogenaset).

The technical and cost advantages of this approach are 1) shorter production lead times, 2) higher overall quality and system reliability, 3) decreased management and engineering time, 4) lower overhead and inventory costs, and 5) lower installation labor and material costs. The marketing advantages are that the systems can be specified and described more easily by the sales engineers and the customer can more easily assess the options and choose the system he needs. A corollary to this is greater customer acceptance of the PV solution and greater confidence among lending institutions.

Definition of Terms

The MAPPS is a small, stand-alone, low voltage DC power supply consisting of PV modules, a mount, a charge controller and batteries. These systems range from a single, small module unit to units with several, large modules. The rated power encompasses 20 W to about 300-400 W. The system voltages are 12, 24 and 48 V. They may also have an optional, small, DC-AC inverter for 120 Vac output.

The Photogenaset is a mid-sized, stand-alone, AC power supply with engine generator for load and battery charging backup. It consists of PV modules, a mounting structure, a charge controller, batteries, a DC-AC inverter, an engine generator and a container. These systems range from under 1 kW to about 10 kW.

Status of Activities

The task structure of the contract calls for development and fabrication of a 200 W MAPPS and a 1 kW Photogenaset as the first prototypes for these respective product lines, certification of the prototypes and product lines, and functionality testing of the prototypes at NREL and Sandia. Within the charter was also room for development of new or improved components for the systems to improve performance and reliability while reducing costs or to facilitate certification.

The sizes of the prototypes were chosen for their high sales potential and manageable size and cost for fabrication and certification. The purpose of the functionality testing is to provide verification of performance and reliability and to develop test-based performance specifications.

MAPPS Status

To date we have completed the design of the 200 W MAPPS and procured the components. We have developed a new enclosure for the batteries and control assembly. This enclosure costs less than the previous design and makes better use of internal space while providing a separate compartment for the control assembly. The design makes use of only UL Listed or UL Recognized components. We are also developing a new microprocessor-based controller for small systems. We expect to have this controller UL Listed when it is completed. It will be used as an option when greater control flexibility or remote monitoring is needed.

We have established the contracts for obtaining UL Listing the MAPPS and FM Approval Listing for use in hazardous locations. These locations, as defined in Article 500 of the National Electrical Code [1], have environments with incendiary gases present. The battery enclosure is currently undergoing a rain spray test at UL after which we will provide the electrical components for completing the evaluation. Following completion of the UL evaluation, the MAPPS will be sent to FM for its evaluation.

A second unit is being built for the functionality testing program. We are developing the test requirements and protocol in concert with NREL and expect the testing to begin in January 1997. We have also developed a manufacturing plan for development and certification of the MAPPS product line and expect to complete this effort by the end of the PVMaT contract.

Photogenaset Status

To date we have completed the design of the 1 kW Photogenaset. The design incorporates a multi-platform layout. The Photogenaset can be provided with either a skid-mounted building or in a trailer for mobile applications. We have attempted to make maximum use of UL Listed components; however, we are evaluating alternatives to the generator and inverter to facilitate Listing and reduce Listing evaluation costs. Because of the complexity of the Photogenaset, the cost of Listing will be much higher than that for the MAPPS. We have obtained quotes from both UL and ETL (Electrical Testing Laboratories) to assess the costs and benefits of each. We expect to complete fabrication of the 1 kW prototype by the end of February by which time it will be scheduled for Listing evaluation and functionality testing.

Current and Expected Accomplishments

To recap current accomplishments, we have: 1) a UL-certifiable 200 W MAPPS with upgraded assembly process controls and installation instructions; 2) an understanding of certifications issues and requirements [2]; 3) a manufacturing plan for a standardized, modular MAPPS product line [3]; 4) a 1 kW Photogenaset design with a multi-platform layout; and 5) an improved, lower cost MAPPS battery enclosure.

Expected near term accomplishments include 1) UL Listing of the 200 W MAPPS; 2) a SES microprocessor-based small charge controller; 3) FM Approval of the 200 W MAPPS; and 4) an

increased-reliability, UL certifiable 1 kW Photogenet. Prior to the end of the contract we expect to accomplish the following: 1) A standardized, UL Listed, MAPPS product line; 2) a certified 1 kW Photogenet; 3) a manufacturing plan for a standardized, modular Photogenet product; 4) functionality test results on both the MAPPS and Photogenet; and 5) test-based performance specifications.

We believe this PVMaT contract will provide important advances in PV power supply market penetration through lower costs, higher reliability, product standardization and product certification.

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Figure 1. MAPPS Block Diagram

Figure 2. Photogenet Block Diagram

Title **Cast Polycrystalline Silicon Photovoltaic Module Manufacturing Technology Improvements**

Organization Solarex, A Business Unit of Amoco/Enron Solar

Contributors J. H. Wohlgemuth, Program Manager; F. Artiglieri, M. Brisson, M. Conway, J. Creager, T. Koval, M. Narayanan, , T. Tomlinson, M. Roy and D. Whitehouse of Solarex; B. Huff, M. Diver, R. Fernandez and D. Vanecek of ARRI

Objectives

The objectives of this three-year program are to advance Solarex's cast polycrystalline silicon manufacturing technology, reduce module production cost in half, increase module performance and expand commercial production capacity by a factor of three. Key components of this program are: 1) Casting of larger ingots; 2) Use of wire saws to cut thinner, larger wafers with less kerf loss; 3) Transfer of high efficiency cell processes to manufacturing; 4) Increased automation; 5) Development of frameless module mounting systems; and 6) Automated handling of large thin cells and wafers.

Approach and Accomplishments

Casting

The original goal of the casting task was to develop the ability to cast ingots that yield four, 15 cm by 15 cm bricks with at least equivalent material quality as was achieved for the standard size. Modifications were necessary to the chamber so it would hold more silicon, and to the heaters and insulation. A laboratory process was developed, yielding equivalent quality ingots. Most of Solarex's products are still based on the use of 11.4 cm by 11.4 cm solar cells, so an effort was undertaken to develop casting for even larger ingots that would produce 9 - 11.4 cm by 11.4 cm bricks. These "mongo" ingots required further changes in the insulation and receiver, but utilized the same casting stations as modified for PVMaT ingots. The process for casting mongo ingots was successfully developed in the laboratory. It has been transferred to production with more than two thirds of the casting stations now modified to cast mongo ingots.

Analysis of the production data shows that mongo ingots have an equivalent yield of useable cast silicon to the smaller mega ingots. In addition there is no statistical difference in average cell efficiency between the mega and mongo processes. Casting of larger mongo ingots has been used to double Solarex's casting capacity at approximately 20% of the cost that would have been required, if the same amount of capacity was added by purchasing new casting stations.

Wire Saw

The goal of the wire saw task is to develop the wire saw technology for cutting 15 cm by 15 cm polycrystalline wafers on 400 μ m centers at lower cost per cut than achieved on the ID saws. Solarex is utilizing HCT wire saws in this program. The wire saw has successfully demonstrated the ability to cut a variety of wafer sizes including 11.4 cm by 11.4 cm; 11.4 cm by 15.2 cm; and 15.2 cm by 15.2 cm on centers from 500 μ m down to 400 μ m. The saw has been operated in a production mode, producing more wafers than 16 ID saws, at better yields and lower per wafer cost than the ID saws. This saw has been so successful that Solarex has added additional HCT wire saws.

After wafers have been cut on the wire saw they must be removed from the hold down plate, placed in cassettes and cleaned. It is necessary to develop an automated process to reduce cost and increase yield especially as the thickness of the wafers decreases. The Automation and Robotics Research Institute (ARRI) at the University of Texas at Arlington, working as a subcontractor to Solarex on this project, has designed, built and tested prototype equipment to destack wet wafers into cassettes. The prototype worked very well for both dry and wet wafers. A full production machine will be built based on this design.

Cell Process

The goal of the cell task is to increase cell efficiencies to 15%, while decreasing the cost per watt at the module level. The developed process must be compatible with automated manufacturing at large volumes. Previous laboratory experiments demonstrated that an aluminum paste back surface field (BSF) can increase cell efficiency by approximately 5%. (1) BSF manufacturing trials have been completed, with more than 40,000 BSF cells produced with all processes except BSF performed in production using production processes, equipment and personnel. The average cell efficiency for all of the BSF cells was 5% higher than for the non-BSF cells produced during the same time period. The BSF process has now been transferred to manufacturing for use on approximately one-third of all the cells produced. This will be expanded to 100% of the cells once the necessary equipment is in house.

One method of reducing the cost of PV modules is to cut thinner wafers, so cell process developments like BSF should be compatible with the use of thinner wafers. To evaluate the effect of the BSF process on wafer thickness, cells were fabricated on wafers with thickness between 200 and 300 μm . Thinner non-BSF cells are less efficient, but thinner BSF cells are more efficient. The 5% efficiency gain observed for BSF cells with today's cell thickness increases to approximately 10% for the thinner cells now under development. (2)

A method to mechanically texture polycrystalline silicon has been developed during the program. Matched polycrystalline wafers were processed with and without mechanical texturing. Mechanical texturing resulted in a 3% gain in encapsulated cell efficiency. Efforts are now underway to develop a large area tool as part of a cost effective texturing process.

Back surface fields, mechanical texturing and phosphorus gettering all increase cell efficiencies. An integrated cell process sequence has been developed to include these efficiency enhancing processes in a cost effective manner. The best cells in this group met the program efficiency goal of 15%. (3)

Module Assembly

The initial goal of this task was to modify Solarex's present module assembly system to increase throughput by 100% and decrease the labor requirement by 50%. This has now been modified by Solarex requirements to increase the assembly capacity by 200% instead of 100%. Solarex subcontracted ARRI to review and model the automated module assembly system in operation at the beginning of this PVMaT Program and to make recommendations for improving the equipment and/or process flow. The first step in this task was the development of a process flow chart detailing all of the module assembly steps. ARRI used this information to model and analyze the manufacturing process. As a short term goal the changes necessary to increase production capacity by 40% were identified and implemented.

In 1995 Solarex publicly announced plans to triple the capacity of the polycrystalline plant by 1999. This became the new goal for the module assembly task. ARRI used AT&T's discrete event simulation package

called Witness to evaluate expansion scenarios. The Witness software provided an analysis of the capacity and resource requirements for the different scenarios. A new factory concept was developed that allowed for incremental increases to meet the shorter term capacity requirements and that could ultimately result in the required tripling of module assembly capacity. The plan was based on replacing the back solder robots with XY positioners to increase the number of solder bonds made at one time from 2 to 4, thereby increasing the throughput by nearly a factor of two. This modification has now been implemented and the XY positioners are operating at the throughput level predicted.

The new factory configuration and Solarex's projected module build plan through 1999 were then used as inputs to the Witness program. As the volume of products ramps up, the model predicts when the various pieces of equipment reach maximum capacity. This analysis was utilized to develop a capital investment budget. The implementation of this plan is now underway with capacity double what it was at the beginning of the PVMaT program, with a second doubling scheduled to be completed by 1999.

Frameless Module Development

The goal of this task is to develop and qualify a frameless module design incorporating a lower cost back sheet material (less than \$0.05/square foot) and user friendly, low cost electrical termination (less than \$1.00/module). Since PVMaT is designed for large systems, the modules were designed to mount directly onto the support structure without integral frames. The first step has been the design of a compatible support structure and the identification of 3M Very High Bond Tape for mounting the modules to the structure. This system was used on several large arrays, but major problems were encountered relative to the use of the tape. The problems appear to be related to either incorrect application by the installers or situations where the modules are mounted in such a way that there is a continual pressure on the beams. The failure mode is separation of the module from the beam. While correct assembly may alleviate this problem, it is likely that actual systems will not be assembled perfectly. We have therefore switched from using the tape to using RTV as the main adhesive. The modules are panelized several days before installation, so the RTV can cure.

A key component in frameless module design is the backsheet, since the electrical termination and the support system itself must adhere to the backsheet. This also offered an opportunity to reduce cost from the backsheet being used at Solarex. A number of candidate materials were selected for evaluation. Sample modules were subjected to a set of environmental qualification tests, in-house simulated UL fire tests, and exposure to 2 year equivalent UV. The only material that met all of the technical requirements was Tedlar. Based on the PVMaT results, Solarex switched manufacturing to a single layer Tedlar backsheet. However, Tedlar will not meet the \$0.05/square foot cost goal of this PVMaT program, although it does represent a significant reduction in cost over the material that was used before the PVMaT program.

Rather than use expensive junction boxes or connectors, the electrical connection from module to module will be made using pig tail wires with crimp connectors and shrinkable tubing insulation. This system has successfully passed IEC-1215 and IEEE-1262 without measurable change in internal resistance or leakage current during wet hi-pot testing at 2750 volts. This electrical termination system meets the technical requirements and the cost goals of the program.

Automated Cell Handling

The goal of the automated cell handling task is to develop automated handling equipment for 200 μm thick 15 cm by 15 cm polycrystalline silicon wafers and cells with a high yield (less than 0.1% breakage per

process handling step) at a throughput rate of at least 12 cells or wafers per minute. ARRI is also supporting Solarex in this task. ARRI performed a set of wafer fracture experiments to measure the mechanical strength of typical cast polycrystalline wafers. (4) A finite element model was then developed to determine the distribution of stress and deflection in a wafer and to determine the probability of breakage of that wafer under the specified load. The model was used to simulate a typical wafer handling situation, to estimate the maximum load that can be applied during handling and the corresponding probability of breakage.

ARRI also performed a study of commercial and academic information sources related to the handling of silicon wafers. The purpose of this search was to gain an understanding of the wafer handling methods that are commercially available, or documented in the open research literature. Almost all of the wafer handling equipment has been developed for the semiconductor industry, where contamination prevention is one of the most important parameters in the design. This has led to a preference for vacuum grippers that are allowed to come in full contact with the "back" face of the wafer, which is simply a featureless substrate. Non-vacuum methods involve arms that "push" the wafers in and out of their slot in the cassette, and are typically used in transfer and inspection operations. The typical gripper design in semiconductor wafer sorting and transfer machines consists of flat prongs with embedded vacuum ports flush with the surface or slightly below it. This provides a greater surface-to-surface contact between the gripper and the wafer than using vacuum cups alone, which likely helps to restrict movement of the wafer during transport and minimizes breakage due to bending of the wafer. Vacuum sensors are used to detect that the wafer is latched onto the jaws. These concepts are now being utilized in discussions with handling equipment manufacturers.

Conclusions

This PVMaT Program has led to the development of and/or improvements in processes, products and equipment. The following developments from this program have already been implemented in manufacturing: 1) Casting of larger ingots; 2) Use of wire saws; 3) Addition of a back surface field on a significant fraction of all production cells; 4) Introduction of a larger cell (11.4 cm by 15.2 cm); 5) Doubling of production capacity in the module assembly area; and 6) Use of a lower cost back sheet. We expect that more PVMaT development efforts will be transferred to manufacturing in the near future.

At this time we believe that all of the major objectives of this PVMaT program (reduction of production costs, improved performance and tripling of capacity) will be met. Our preliminary analysis indicates that through the year 2000, Solarex will save \$5.00 for every dollar it invested in PVMaT and our customers will save approximately \$7.00 for every dollar that NREL invested in this PVMaT Program.

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Title: Full Scale Testing of Modules Prepared with
Experimental EVA-Based Encapsulants

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Objectives

EVA resin-based encapsulant is employed extensively by module manufacturers worldwide, has been in commercial use since 1981¹, and has proven dependable from the standpoint of production, module fabrication, and end-use. Despite the widespread acceptance of EVA resin-based A9918P and similar formulations for PV, some module producers and end-users have reported cases of browning with field-aged modules. While isolated, these reports raised serious concern as to the long term reliability of EVA resin-based encapsulants.

During Phase I of this PVMaT 3A program, STR conducted problem definition using literature search, field survey, and accelerated U.V. aging (AAS) studies to evaluate the influence of compositional, processing, and operating parameters on A9918P discoloration.² Also, instrumental analysis was used to verify suspected chemical mechanisms of degradation.^{3,4,5}

During Phase II STR developed approaches for stabilizing the EVA-based encapsulant against discoloration/degradation, including reformulated systems. These "stabilization strategies" were evaluated by AAS using xenon-arc Weather-Ometer and EMMA (equatorial mount with mirrors for acceleration; accelerated outdoor weathering) with periodic measurements of Yellowness Index (ASTM D1925) as an indication of the onset of browning. One result of this work was the development of four experimental EVA-based encapsulants - three "standard cure" (X9903P, X9923P, and X9933P) and one "fast cure" (X15303P) which demonstrated greatly reduced discoloration on AAS.^{3,6,7}

The Phase III objective is to demonstrate the functional adequacy of these various stabilization strategies under end use conditions and in qualification tests using full-size modules.

Technical Approach

STR extruded pilot quantities of all four experimental EVA-based encapsulants plus controls. Rolls of nominal 0.018 inch thick sheet were supplied to various PVMaT project team members who: 1) Prepared full-size, nominal 50 watt modules for qualification testing and field testing in Arizona and 2) Prepared "mini-modules" (2.5 inch x 2.75 inch and 2.5 inch x 5.5 inch) using

small cells or half cells and the team members' normal materials of construction for superstrate, interconnects, and backing. Participating team members include: ASE Americas, Astropower, Ebara Solar, Photocomm, Siemens Solar, Solec International, Solarex, and United Solar Systems.

Module approach: Module manufacturer team members supplied Arizona State University's Center for Energy Systems Research (ASU/CESR), in most cases, six modules each representing three of the four possible experimental encapsulants. These modules, 80 in all, were used by ASU/CESR for qualification testing per IEEE 1262.

In addition, several team members supplied ASU/CESR six to eight modules, two each representing three or four out of five experimental "stabilization strategies." The strategies included the four experimental encapsulants plus the conventional "fast cure." All of these modules have cerium oxide-containing low iron glass as the superstrate.

These modules, 36 in all, were installed for ASU/CESR on a dedicated Martin Marietta two-axis tracker at the STAR facility by Arizona Public Service in Tempe. All modules were a nominal 50 watts with outside dimensions not exceeding 20 x 50 inches and were fitted with fixed resistive loads such that each module would operate within $\pm 10\%$ of its peak power point. The peak power point represents a typical day in March (i.e. near the mean annual average temperature).

Also, a thermocouple was installed on the back of each module, and each was photographed to provide a visual record.

Module current-voltage (I-V) curves are being taken at regular intervals for each module, and data, including I_{sc} , V_{oc} , P_m , and ff are being collected at actual test conditions and translated into standard conditions. In addition, such pertinent weather data as minimum and maximum ambient temperatures, global solar radiation in the plane of the array (kWh/m^2), and direct normal solar radiation (kWh/m^2) are being collected.

ASU conducted thermal mapping in early October by taking an infrared thermal image of each module at the peak power point ($\pm 10\%$) and another with the module short circuited.

Mini-module approach: Each mini-module was provided with leads through the backing material and was connected to a 1 ohm resistor. The back of each mini-module was insulated with a layer of Mylar, and the assembly mounted in a sample holder. This allowed the mini-modules to operate at a fixed resistive load during accelerated U.V. aging.

The samples were placed in an Atlas Ci35A xenon-arc Weather-Ometer and exposed at a nominal "two suns" ($0.55 \text{ watts}/m^2/nm @ 340 \text{ nm}$), 90°C over the cells, and $>95\%$ R.H. A total of more than 40 manufacturer/encapsulant/superstrate combinations were evaluated, including A9918P encapsulated controls. To date, the mini-modules have been exposed for six months at

continuous temperature and irradiance. They are being inspected every two weeks for discoloration, cell or interconnect/encapsulant interactions, etc.

Test results

Qualification testing: Testing is being done per IEEE 1262. The following provides status as of November: **Pretests:** completed; **Sequence A:** roughly half completed; 200 thermal cycles were started on September 23 and will have been completed by November 18; **Sequence B:** completed; **Sequence C:** completed; and **Final Inspection & Test:** will be started on November 25 and completed by December 20, including all documentation.

Thus far one experimental encapsulant, X9933P turned bright yellow during 1000 hours of damp heat. Otherwise, there have been no encapsulant-related failures.

Field testing of modules, data acquisition and analysis: Under direction of ASU a two-axis tracker and controller were installed at the STAR facility, Arizona Public Service, in Tempe. The system was "debugged" and is tracking in the two-axis mode. All 34 modules were installed by the end of August.

Photos were taken of all modules for a permanent visual record and were transferred to diskette for easy reference and archiving. I-V curves were taken on September 6 for baseline electrical performance, and a second set was taken in early October.

Thermal image mapping was completed on October 1. Peter Bliven, president of PBA Instruments and an expert in thermal imaging, collected and processed the data. IR data were taken with the modules at peak power and again short circuited. Some shorted modules exhibited hot spot heating with one hot cell reaching 86.6 °C; nine other modules had "hot" cells that ranged in temperature from 70.1 to 78.3° C. These same cells with a resistive load operated at about 65° C.

Hard copy (color images) as well as computer files of the data were generated at both peak power and under short circuit conditions.

Information will continue to be collected periodically until the end of the subcontract. After that it is the intention of STR, in cooperation with ASU, to continue the field testing indefinitely.

Accelerated aging of mini-modules: For the past six months, samples have been exposed under continuous conditions to a nominal two-suns and 90° C cell temperature in a xenon-arc Weather-Ometer. One team member prepared mini-modules with Tefzel cover film, and one set of mini-modules from each team member was prepared with cerium oxide-containing glass. Otherwise, all mini-modules used non-cerium low iron glass to provide "worst-case" conditions.

After 26 weeks of exposure, most of the A9918P encapsulated controls using low iron glass superstrate have turned brown over the cells, in the same manner as seen in our survey of fielded modules in the West and Southwest. With the exception of samples made with one experimental encapsulant, X9933P, all mini-modules prepared with experimental grades, as well as with 15295P and cerium-oxide containing glass, showed no browning over the cells.

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Title: **Modular, Bi-Directional Power Inverters for Photovoltaic Applications**

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Abstract. Description of the next generation of power inverters for both utility connected and off-grid photovoltaic applications. Includes explanation of the benefits gained by using modular connected "building block" power sections for inverters up to 50 kVA of continuous power rating. Intended applications include both single and three phase power systems both with and without energy storage systems (batteries). Also includes a summary of the work completed using this modular inverter approach with a current production power inverter design under a Phase 4A1 PV-MaT contract.

WHY A "MODULAR" POWER INVERTER?

Trace Engineering is in the process of developing a "modular" power inverter for use in a wide range of power conversion applications. The inverter module will be able to be used alone or as a "building block" for the construction of larger power inverters. The use of this modular approach will provide the following benefits:

- **The modular power inverter approach reduces inverter cost**

The basic power section components (transistor switches, transformer, control board and chassis) will be used for both small, single inverter applications and larger, single and three phase applications. This allows larger inverter applications to benefit from the substantially higher manufacturing volume of smaller sized inverters. Currently, for every 20 kVA or higher power inverter sold, thousands of smaller inverters (under 5 kVA) are sold. The present non-PV inverter market far exceeds the current and near term PV inverter markets. The modular approach allows PV applications to benefit from the volume of other markets.

- **The modular power inverter approach improves inverter reliability**

The modular approach allows the mass production of a common "core" technology. This reduces the amount of "one off" designs required. The higher volume will allow greater use of statistical analysis methods and more expensive automated testing systems.

- **The modular power inverter approach improves system reliability**

The use of inverter modules also allows the ability to incorporate N+1 redundancy into the design of a system (allows tolerance of one inverter module failure without loss of the system operation). The inverter modules will be "hot swappable" allowing servicing or upgrading to occur without shutting the system down. The use of a proven "building block" for new applications will result in improved product quality and faster time to market.

- **The modular power inverter approach improves inverter efficiency**

The efficiency of the individual modular inverter power section will be similar to existing designs. For larger inverter systems, the modular power inverter approach will provide a substantial increase in power conversion efficiency. This is achieved by operating only the number of inverter modules required by the load being powered. The additional inverter

modules are turned on to keep each of the inverter modules at the highest efficiency point possible. When only a small load is being powered, any excess inverter modules will be turned off to eliminate their "tare" or "idle" power consumption. This ability is important for many non-utility connected, or off-grid, applications where the AC loads on the system vary substantially over the course of a day, or for applications where the AC loads cycle on and off frequently, such as with air conditioner or some water pumping applications.

- **The modular power inverter approach improves system efficiency**

The use of inverter modules allows the installation of only as much inverter as is required for the application. Future growth can be accommodated, eliminating the need for installation of oversized power inverters. The modular design can also accommodate different inverter capacity per phase, allowing higher efficiency on systems where imbalanced distribution systems are encountered. If higher conversion efficiency is required, more inverter modules can be added to improve the high power efficiency.

INVERTER VS. SYSTEM EFFICIENCY

The performance of a PV system using an inverter is not as simple as one might assume. The overall efficiency depends upon the inverter topology selected, the loads being powered and the usage patterns of the loads.

Inverter efficiency is a product of two inverter characteristics - the inverters "through-put" efficiency and its "idle / tare / no-load" power consumption. The through-put efficiency depends upon the inverters topology - such as the switching frequency and transformer design and operation. With many inverter designs, the idle power consumption dominates the losses at low power and the I^2R losses dominate at high power. Some high frequency inverters loose the majority of the power in the actual switching process. They often have their peak efficiency must closer to their full continuous power rating, but have poorer low power efficiency.

Trace Engineering currently offers a 4 kVA low frequency sinewave inverter design which features a low idle current draw (less than 16 watts with no load) that has a typical efficiency curve as shown in FIGURE 1. Many high frequency switching inverter designs often have a higher idle current draw and have a resulting efficiency curve as shown in FIGURE 2.

FIGURE 1. Low idle current design.

FIGURE 2. High idle current design.

Both of the inverters can be described as "high efficiency" and can even have the same peak and full load efficiency points. Depending upon the load level and load patterns, the system efficiency might be very different. If the loads are continuous and at a high power level, than the inverter shown in **FIGURE 2** would be acceptable. If the loads are comprised of a lower continuous base load and short periods of higher loads, the inverter in **FIGURE 1** could result in a higher system efficiency.

FIGURE 1 is typical for a low frequency transformer based off-grid inverter. **FIGURE 2** is more typical of a utility connected high frequency switching type inverter.

Note that the two efficiency curves have the same peak and full capacity efficiency.

MODULAR POWER INVERTER EFFICIENCY

The efficiency of a modular power inverter can be significantly better than either of the two previous examples. This improved efficiency is due to the operation of the modular inverter system and is not dependent upon achieving a higher efficiency for the inverter module itself. **FIGURE 3** shows the efficiency of a single inverter module. **FIGURE 4** shows the resulting efficiency of a modular inverter system made up of five of the same inverter modules.

FIGURE 3. Single inverter module

FIGURE 4. Modular inverter system.

The improved efficiency of the modular inverter system is achieved by turning off the unnecessary inverter modules when the inverter system is operating at low output level. The inverter modules are turned on as the loads increase one at a time in order to maximize the operating efficiency. The dashed line represents the resulting efficiency if all of the inverter modules were operated continuously.

If better efficiency is needed at high power levels, additional inverter modules can be added. More inverter modules will not reduce the low power efficiency since they are turned off at low power levels.

Note that the two efficiency curves have the same peak and full capacity efficiency.

UTILITY CONNECTED VS. OFF-GRID SYSTEMS

For utility connected systems the efficiency at high power levels is usually viewed as being more important than the efficiency at low power levels. This is often based on the primary value of the system being a "peaking" source during periods of heavy utility demand. This perspective is common with utilities.

If the system is privately owned and/or is "net" metered, then the overall energy production of the PV system may be viewed as being more important. This means that the efficiency over the course of the day at variable operating power levels will be the most important characteristic. Therefore, the efficiency at low and mid-point power levels must also be considered.

In off-grid applications the pattern of loads must be considered when evaluating the expected performance of a inverter system. For most residential and commercial PV applications, the inverter may operate at low power levels for extended periods of time. It is common to have the inverter only reach full power occasionally. If the amount of time spent at high power levels is low, then the efficiency at full power is not as important.

In many off-grid applications, selecting an inverter size may be difficult due to lack of accurate information on the loads and usage. The modular inverter system allows expansion of the inverter system after installation. It also allows easier expansion of the system in the future as loads increase or finances permit.

The modular inverter system also allows installation of differing amounts of inverter capacity per phase to better match the loads connected. This may allow reduced inverter cost in some cases. For example, it is not uncommon for a three phase system to have imbalanced loads on one of the phases. With a modular inverter system, one phase of a three phase system could be installed with the additional capacity. With standard inverter designs, all three phases would have to be increased. The resulting larger inverter size would have higher idle power consumption and could operate at significantly lower overall efficiency.

The greater production volume of the non-PV markets inverters will allow cost reductions since the base inverter design and components are similar. The higher production volume will allow more investment into the manufacturing methods and will result in higher reliability due to the ability to implement advanced test and evaluation methods for the design.

INVERTER EFFICIENCY WITH INDUCTIVE LOADS

When an inverter is directly powering an inductive loads such as motors, the efficiency of the inverter is even more important. With an inductive load, the inverter has to process more power than the motor consumes, causing an additional reduction to the operating efficiency. When large inductive loads are to be powered for significant periods of time, a larger inverter should be considered. Using a larger inverter will improve the resulting system efficiency while operating the heavy load. If the larger inverter has substantially higher idle power consumption, then overall system efficiency would be significantly lower with the larger inverter.

The modular power inverter system allows "oversizing" of the inverter to allow efficient operation of inductive loads without the loss of overall system efficiency. No significant additional loss is incurred by having a larger inverter installed. It furthermore allows tuning of each system to achieve maximum efficiency for its particular loads, usage patterns and capacity requirements. This fine tuning of the system can occur after the original installation has been completed.

MODULAR VS. CO-INVERTER APPROACHES

One solution used in some of the high idle current inverter designs to remedy the poor low power level efficiency has been to include in the design a smaller "co" inverter. At low power levels the main inverter is turned off and the loads are connected to the smaller inverter. The size of this smaller inverter is from 1% to 10% of the main inverter continuous rating.

This approach does result in a significant improvement in the low power level efficiency. Often, the efficiency peaks and then drops off and then peaks again at the main inverter's optimum efficiency. Depending upon the capacity of the co-inverter, the drop when switched to the main inverter may be significant. FIGURE 5 shows a typical efficiency curve for a co-inverter equipped power inverter.

FIGURE 5. Co-inverter system.

Co-inverters add complexity to the design of the inverter. It can be difficult to design the inverter to allow the co-inverter to be offered as an option. This approach does not provide the flexibility benefits provided by the modular inverter approach. It is useful on smaller, single inverter applications where the modular inverter system can not be utilized.

The co-inverter also adds significant cost. The cost reduction benefits of the modular inverter's common power section design and components is not realized with this approach. The importance of efficiency at low power levels is much more important for inverters used in PV applications than inverters used in other applications.

Co-inverters also do not provide a means for hot swapping of individual inverter modules or provide redundancy in the event of a single unit failure.

DEVELOPMENT OF A MODULAR INVERTER SYSTEM

Trace Engineering has been actively developing this modular inverter concept for the last two years. This research and development program has been supported by a PV-MaT Phase 4A1 contract. This support has been very important and has enable much greater progress to occur compared to developing the system with our own internal company resources.

This work has been divided into two separate efforts - one team working on the development of the 2 kVA power inverter module, and a second team working on the interface and overall control of the multiple inverter modules. The inverter module team evaluated and prototyped several inverter topologies not previously used. The selected topology is based on a high frequency design not previously used by Trace Engineering. The second team has been developing the modular approach using a current generation inverter (our SW series) as the inverter module. This will allow implementation of the modular inverter system sooner. The 2 kVA inverter module is expected to enter limited production in late 1997 and have full volume production in early 1998. Developing the modular inverter with the existing production inverter will reduce problems by using a well understood and proven "base" technology.

The first application of the SW series based modular inverter will be shipping in December as a 15 kVA three phase power system. The first 10 kVA single phase applications SW series based modular inverters are expected to ship in February of 1997. Larger modular inverter systems are expected to be available in the summer of 1997.

ACKNOWLEDGMENTS

Trace Engineering would like to thank NREL and Sandia National Labs for their support of this modular inverter concept. The progress achieved has been significantly accelerated through the financial support of a PV-MaT Phase 4A1 contract. Sandia National Labs has been very helpful by allowing use of their test equipment both at Albuquerque and in the field.

Much of the information presented here has been developed through the work of several Trace engineers: Steve Johnston, Greg Thomas, Mike Frost and Milt Rice.

Title: **Development Of A Low Cost Integrated 20 KW A.C. Solar Tracking Sub-Array For Grid-Connected PV Power System Applications**

Organization: Utility Power Group, Los Angeles, California

Contributors: M. Stern, Principal Investigator; R. West, G. Fourer, W. Whalen, M. VanLoo, and G. Duran

Introduction

Utility Power Group has achieved a significant reduction in the installed cost of grid-connected PV systems. The two part technical approach focused on 1) The utilization of a large area factory assembled PV panel, and 2) The integration and packaging of all sub-array power conversion and control functions within a single factory produced enclosure. Eight engineering prototype 15kW ac single axis solar tracking sub-arrays were designed, fabricated, and installed at the Sacramento Municipal Utility District's Hedge Substation site in 1996 and are being evaluated for performance and reliability. A number of design enhancements will be implemented in 1997 and demonstrated by the field deployment and operation of over twenty advanced sub-array PV power systems.

Objective

The overall objective of Utility Power Group's two year PVMaT Phase 4A1 sub-array development effort is to achieve a 20% reduction in the installed cost of PV power systems. Given UPG's focus on BOS costs and assuming such costs represent 40% of the total cost of an installed PV power system, UPG's overall objective could be re-stated as seeking to achieve a 50% reduction in BOS costs.

Approach

The technical approach employed by UPG towards achievement of the above objective is based upon the following lessons learned during the construction or installation of a number of PV power systems:

- Factory assembly provides cost savings over field assembly.
- Reducing the number of components reduces installation cost.
- Design simplicity reduces the cost of construction materials.
- Reproducibility of tasks reduces the cost of construction labor.
- Modularity reduces the cost of design and project management.

These lessons led UPG to select modularity and component integration as the two primary design criteria to be utilized. A modular alternating current ("ac") sub-array design simplifies the generation of specific and custom PV system design packages and reduce incremental

administrative and project management costs. Redundancy and reliability are PV system operational cost factors which benefit from modularity and the reduced number of components associated with increased functional integration.

Based upon the above lessons learned and design criteria, UPG began development of an integrated and modular 15 kW ac sub-array in compliance with the 1996 National Electrical Code and applicable standards of Underwriters Laboratories.

Specifically, UPG is developing:

1. A large area Modular Panel (MP) which is factory assembled and tested by Utility Power Group utilizing production optimized and reliability tested PV laminates manufactured by Siemens Solar Industries.
2. An Integrated Power Processing Unit (IPPU) combining all sub-array electrical functions such as power collection, system protection, direct current ("dc") to ac conversion, and single axis solar tracking, into a single field deployable unit factory assembled and tested by Utility Power Group.

Modular Panel Development

The factory assembled PV panels developed by UPG in conjunction with Siemens Solar Industries (SSI) are specifically designed for high voltage power system applications and provides the following cost saving advantages:

1. Elimination of redundant structural frames on individual PV modules.
2. Simplification of the panel support structure.
3. Reduction of labor associated with field installation of panels.

UPG has completed development of the POWERGLASS™ Model 11M55 Modular Panel which with an STC rating of 606 Wdc, is believed to be the highest power UL listed PV panel in the world.

IPPU Development

The Integrated Power Processing Unit ("IPPU") developed by UPG provides significant BOS cost reduction through the integration and optimization of all electronic and electrical PV power system operations. To facilitate fabrication, testing, assembly, and field maintenance of the IPPU, UPG segmented the design into four sub-assemblies each utilizing high power printed circuit board (PCB) technology to perform a number of integrated functions. (Table 1).

With this approach, UPG has not only integrated all sub-array functions into a single unit, but also has developed a d.c. to a.c. inverter with a higher conversion efficiency and a higher switching frequency than any other commercially available inverter.

TABLE 1. IPPU Sub-Assemblies and Functions

<u>DC Interface PCB Assembly</u>	
PV sub-circuit conductor termination	
PV sub-circuit conductor protection	
Visible dc disconnect	
Blocking (paralleling) diodes	
Lightning transient protection	
Crowbar function	
DC contactor	
DC current sense, regulation and DAS	
DC ground fault current sense	
DC bus precharge and discharge	
<u>AC Interface PCB Assembly</u>	
3-phase utility conductor interface	
Fused power distribution	
AC contactor (bridge isolation)	
Regulated low voltage control power supply	
Tracker drive motor relays and interface	
Utility voltage sense	
Output inductor interface	
Output EMI filter	
DAS interface point	
<u>Bridge / Regulator PCB Assembly</u>	
20khz 3-phase ultra fast IGBT bridge	
Opto isolated IGBT drivers	
Digitally synthesized sine wave reference	
Phase locked loop line sync circuit	
Output sine wave current sense	
DC voltage sense	
Bus voltage regulation	
Fast line-overcurrent detection	
<u>Control PCB Assembly</u>	
Start, wake-up, disable and stop logic	
Machine state logic	
Diagnostics and fault detection	
Lowpower (nightly shutdown)	
Overpower, overvoltage bus	
Line synchronization error	
Frequency out of tolerance	
Utility voltage imbalance, blown fuse	
Utility undervoltage	
Utility overvoltage	
System fault, output current imbalance	
Control logic fault, undervoltage	
Overtemperature	
DC ground fault	
Tracker drive fault	
Disable, local or remote	
Electrical max. power point tracking	
DC power calculator	
LCD display driver	
Tracker drive logic and user interface	
<u>DAS Board Option</u>	
Machine state information	
Fault delineation	
3-phase AC power calculator	
Analog a/d conversion	
AC line voltage	
AC current by phase	
AC power	
DC voltage	
DC current	
DC power	
Remote enable/disable interface	
Isolated RS485 link to modem	

RESULTS

UPG successfully completed the design, fabrication, and installation of a modular and integrated 15 kW a.c. solar tracking PV power system sub-array which exceeded the 20% cost reduction goal. Eight (8) sub-arrays were supplied to the Sacramento Municipal Utility District in 1996 for evaluation (Figure 2) and UPG has received orders for an additional forty-two (42) units to be constructed in 1997. Table 2 compares the major field tasks required to construct a nominal 100 kW grid connected PV power system before and after the development of UPG's integrated sub-array. Modularity and integration are combined to significantly reduce the number of discrete field construction operations required, simplify design documentation, and permit standardization of key components.

TABLE 2. Before and After Comparison of Major Field Tasks.

	Major Field Tasks: Before Integrated Sub-Array Development		Major Field Tasks: After Integrated Sub-Array Development
1	Electrical Design	1	Modular Design Package
2	Mechanical and Structural Design	2	Site Mobilization
3	Site Mobilization	3	Site Preparation
4	Site Preparation	4	Support Pole Hole Augering
5	Support Pole Hole Augering	5	Support Pole Installation
6	Support Pole Installation	6	Drill Tracker Drive Assy Mtg Holes
7	Install Conduit Junction Boxes	7	Drill Torque Tube Bearing Mtg Holes
8	Install Tracker Motor Junction Boxes	8	Install Torque Tube Bearing Plates
9	Conduit Trenching	9	Install IPPU Assemblies
10	Dig & Form Electrical Equip Pad	10	Conduit Trenching
11	Electrical Equip Concrete Pad Form	11	Lay Conduit
12	Lay Conduit	12	Set Pre-Cast Xfmr Pad and Xfmr
13	Backfill Conduit Trenches	13	Pull Conduit and Torque Tube Wires
14	Pour Concrete Electrical Equip Pad	14	Backfill Conduit Trenches
15	Drill Torque Tube Bearing Mtg Holes	15	Install Torque Tubes
16	Drill Tracker Drive Assy Mtg Holes	16	Install PV Panels
17	Install Torque Tube Bearing Plates	17	Connect All Wires
18	Install Tracker Drive Assemblies	18	Test IPPU's
19	Install Torque Tubes	19	Sub-Array Start-Up
20	Install Struts	20	
21	Install PV Module Rails	21	
22	Install PV Modules	22	
23	Install Row Junction Boxes	23	
24	Install Tracker Limit Junction Boxes	24	
25	Install Inverter	25	
26	Install Transformer	26	
27	Install DC Interface Enclosures	27	
28	Install Tracker Control Enclosure	28	
29	Wire PV Modules	29	
30	Pull Conduit and Torque Tube Wires	30	
31	Connect All Wires	31	
32	Test Source Circuits	32	
33	Test Sub-Arrays	33	
34	Test Inverter	34	
35	Test Tracker Controller and Motors	35	
36	System Start-Up	36	

Acknowledgment

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5.0 PHOTOVOLTAIC MODULE AND SYSTEM PERFORMANCE AND ENGINEERING PROJECT—Introduction

Richard DeBlasio

Objectives

The objective of this project was to conduct module and systems development through state-of-the-art photovoltaic module and system research, engineering, testing, evaluation, and analysis activities. The objective included providing technical results, solutions to technical issues, technical assistance, and coordination for the development of PV standards, codes, and criteria for test and evaluation procedures. The objective further included maintaining and enhancing supporting facilities and capabilities that are consistent with the DOE National Photovoltaic Program, complementary to other DOE PV projects, and that will ensure that capabilities and facilities are available resources for cooperative research and utilization by the U.S. PV research and development community.

Technical Approach

The project primarily included NREL in-house activities and a few subcontracts. The project was organized within the primary areas shown in Figure 1 below. Major project meetings included the NREL PV Standards and Codes Forum (June 1996) and the NREL/SNL 9th PV Performance and Reliability Workshop (September 1996). One of DOE's 5-year plan goals was achieved ahead of schedule by the project regarding the development of a comprehensive module qualification test with the publication of the Institute of Electrical and Electronics Engineers (IEEE) Standard 1262, "IEEE Recommended Practice for Qualification of PV Modules." The following paragraphs provide an introductory description of the PV Module and System Performance and Engineering Project activities for FY 1996.

Figure 1. PV Module and System Performance and Engineering Project Activities

NREL Outdoor Test Facility. This past year, NREL completed the fit-up and installation of project equipment at the Outdoor Test Facility (OTF) laboratory building. The 10,000-square-foot OTF accommodates nearly all the laboratories utilized by the PV Module and System Performance and Engineering Project, collocating and consolidating activities and equipment from four other NREL locations. The OTF lies adjacent to the existing PV outdoor test site, and those field-deployed PV modules and systems are now connected to monitoring and control systems housed in the OTF (Outdoor Test and Measurement Laboratory). The OTF also has an adjacent south-facing pad, and roof-mounted array structures for additional experiments and measurement systems.

Modules mounted on the roof, representing all current and advanced PV material technologies, are continuously monitored for energy production. The measurement data is being used to validate module energy rating methodology models under consideration by the IEEE SCC21 Standards committee. The fit-up was completed in FY 1996 as planned and within budget.

PV Efficiency Measurements—Standard Reporting Conditions. The performance of photovoltaic devices of all sizes and technologies was evaluated by providing secondary calibrations of PV cells and modules, efficiency measurements with respect to standard reporting conditions, efficiency verification of subcontract deliverables, and current-voltage (I-V) measurements under varying temperature, spectral irradiance and total irradiance. Capabilities also support the entire PV community by providing information on PV measurement equipment and systems appropriate for the end user, I-V measurement procedures, and measurement uncertainty analysis, and being committed to obtaining the lowest possible uncertainty in the measurement of the standardized PV performance of single and multijunction cells and modules. Included in the uncertainty analysis are the determination of potential artifacts in the I-V results because of equipment or procedures, and realistic estimates of the elemental error sources.

Reliability Science of Encapsulated PV Cells and Modules focused on polymeric materials and formulations that will provide optimal module performance and protection from the environment for a 30-year life. The objectives were to identify, understand, and mitigate the causes of materials change, and to identify new or improved materials. The objectives included using accelerated life testing, real-time testing, and developing data analysis methods for correlation and understanding service lifetime limitations. Also included were identifying and testing superstrate materials for improving photostability, and testing commercially available adhesive films for simplifying the encapsulation process.

PV Module Exploratory Qualification Testing objectives were to investigate, understand, and improve PV module long-term performance and reliability. The approach included developing and validating test methods and procedures, and performing module exploratory/qualification and reliability tests on PV modules, as well as on R&D prototypes and contract deliverables, with special emphasis on thin-film photovoltaic technologies. Activities include working to establish a correlation between indoor (artificial, accelerated) test results and outdoor (natural, real-time) exposure as related to reliability, stability, and weathering issues. In addition, theoretical and experimental studies were undertaken on PV module lifetime prediction from accelerated testing. Further, the work with the NREL failure analysis group was aimed at developing methods and techniques to perform failure analysis on PV modules, establishing means of determining the mechanisms of failure, and then obtaining possible solutions to these module performance and/or reliability problems.

PV Component Diagnostics and Failure Analysis is concerned with conducting and documenting module and system reliability and failure activities. Data is obtained from operating systems, demonstration or prototype units, qualification and exploratory tests, research results, dedicated studies, and from the literature. Dedicated activities were pursued to uncover and reproduce identified failure mechanisms, to validate proposed hypotheses, to explore areas that are believed to be of high priority for long-term PV reliability, to recommend new tests for screening or qualification, and to develop better understanding for improved reliability and design. The cause of PV module failure is determined through nondestructive and destructive evaluation procedures. From these evaluations, more basic materials determinations can be confirmed and probable causes and mechanisms can be proposed. System-level concerns are addressed with emphasis extending outward from the module interface.

PV Module and System Technology Validation encompassed activities for testing, monitoring, and evaluating state-of-the-art and emerging photovoltaic technologies on the module and system level. Technology development and validation are also supported by analyzing the performance and reliability of PV modules and systems in support of the DOE National Photovoltaic Program. The approach included maintaining a database

on performance and reliability, performing thin-film module stability testing outdoors with comparison to indoor light-soak experiments, and researching and developing performance evaluation methodologies for modules, e.g., seasonal performance, spectral measurements, and techniques for evaluating modules on instantaneous power output and energy production. System performance activities also included supporting the Photovoltaics for Utility-Scale Applications Project, Federal Energy Management Program, Photovoltaics for Manufacturing Technology, and PV Building Opportunities in the United States projects, and international commitments such as the DOE-South Africa and DOE-India and China activities.

PV Solar Radiometric Measurements and Evaluation directly supported characterizing, measuring, testing, designing, and understanding the performance of PV cells, submodules, modules, and systems. That is pursued by providing scientific and engineering understanding of incident solar and artificial irradiance, and through developing instruments and/or measurement methods. The approach focused on providing integrated technical support, e.g., developing and providing broadband and spectral radiometric measurements, and instrument calibrations, characterization, and utilization to assist PV performance measurements. The approach included operation of reference radiometric sensors, calibration of solar simulators and other optical instrumentation, and development and operation of a reference meteorological and irradiance system at NREL.

PV Standards and Codes Development activities focused on providing coordination of the consensus development of PV standards, codes, and criteria for test and evaluation procedures, e.g., annually, NREL holds a PV Standards and Codes Forum. The coordination included participating and performing major leadership roles in the IEEE Standards Coordinating Committee 21 and in the ASTM Subcommittee E44.09, conducting round-robin cell and module test method verification, developing criteria for module certification and test facility accreditation through the PV community with balanced industry representation and subcontract support, revising the National Electrical Code Article 690, developing PV energy rating standards, and working in the international arena, e.g., through the NREL-managed Solar Energy Industries Association (SEIA) subcontract for International Electrotechnical Commission TC-82 secretariat and U.S. Technical Advisory Group coordination of international PV standards development. Additionally, NREL staff coordinated the PEP'93 intercomparison of reference cell calibrations and cell performance measurements.

PV Module and System Performance and Engineering In-House Research

Title: **Photovoltaic Component Diagnostics and Failure Analysis**

Organization: **Center for Performance Engineering and Reliability**

Contributors: **T.J. McMahon, Module Lead; and T.S. Basso, System Lead**

Objectives

The objectives were to conduct and document module and system reliability and failure activities. The purposes were to provide technical results, recommendations or solutions to technical issues, technical assistance, and technical inputs. These are intended for the development of PV standards, codes, criteria for test and evaluation procedures, and design input.

Technical Approach

Module- and system-level concerns will be addressed through working relationships with the industry, users, and other colleagues. Results were generally considered confidential, usually disclosing only generic data in the open literature. Collaboration with manufacturers individually or with teaming arrangements (e.g., CdTe Team) was helpful in achieving our objective.

Module and system reliability performance data were obtained from operating systems, demonstration or prototype units, qualification and exploratory tests, research results, dedicated studies, and from the literature. These data were used to establish a comprehensive database for individual module and array/system component performance with emphasis on reliability and operational characteristics. Analyses will be performed, including the correlation of real-time exposure testing, accelerated testing, and deployed system results. Dedicated tasks were pursued to uncover and reproduce identified failure mechanisms, to validate proposed hypotheses, to explore areas that are believed to be of high priority for long-term PV reliability, to recommend new tests for screening or qualification, and to develop better understanding for improved reliability and design.

The cause of PV module failure will be determined through nondestructive and destructive evaluation procedures. Nondestructive testing (NDT) includes measuring individual cells of modules using methods such as the newly devised two-terminal shunt resistance measurement technique, ac small-spot photocurrent technique for internal series resistance, and laser scanning. After NDT, module de-encapsulation may be done, or samples may be cored or cut from the module, to allow further evaluation of the suspect areas. This allows further characterization such as chemical analyses, microscopy, and spectroscopy. From these evaluations, more basic materials determinations can be confirmed and probable causes and mechanisms can be proposed.

Results

We continued to use our nonintrusive "two-terminal method" for measuring the shunt resistance of the individual cells within a series-connected module. Low shunt-resistance values indicate which

cells may have manufacturing flaws or degraded after qualification testing. These values allow you to know at any light level which, if any, of the cells in the series-connected module will degrade the module output due to low shunt resistance. In a recent study, a Spire simulator was used to measure module efficiency and the intensity was varied with sheets of vellum. The PSpice circuit simulation and analysis program was used here to quantitatively predict the effect of cell shunt resistance on module performance at different light levels, and it was compared to the Spire results. In a paper presented at the *IEEE Spec. Conf.* [Reference 1] we explained how the cell shunt resistances are measured and how the energy rating of a module is ultimately impacted, because the efficiency of a module is reduced, especially at lower illumination levels.

During this past summer, a student participating in the HBCU program tried to validate an alternate method for measuring these cell shunt resistances. The student used a chopped light spot (usually from a HeNe laser) [Reference 2]. She found that in order to have any correlation between the real cell shunt resistance and the value determined with the spot scan method, the spot power must be less than 50 μW and lower resistance cells were difficult, if not impossible, to measure. We prefer to use the method described in Reference 1; its strength lies in accurately measuring lower shunt resistance cells.

Baseline shunt resistance measurements of cells in representative modules being deployed in the field were made. These measurements allow us to separate manufacturing flaws that affect the initial performance from flaws that degrade the performance during environmental stress tests. This past year we baselined modules from Advanced Photovoltaic Systems, Solarex, Suncorp, Solar Cells, Inc., and Sovlux. All modules showed manufacturing flaws and some showed serious flaws that showed up during qualification testing. We provided test reports to manufacturers or NREL colleagues.

As team leader of the CdTe Stability Team, T. McMahon formulated a robust test plan for the accelerated screening tests to be conducted on CdTe cells and mini-modules to be completed with alternate back-contact recipes. Traditionally, some CdTe cells degrade because the back contact to CdTe becomes non-ohmic; after developing high series resistance it further degrades into a reverse diode. Only two candidate cell structures were submitted for evaluation and stress testing, an encapsulated set of seven cells from SCI and an unencapsulated device from USF.

We set up a solar cell internal resistance measurement based on the newly developed technique of A. Delahoy [Reference 3] to measure back-contact degradation. This is a new method to determine the internal series resistance (vertical rather than lateral components) of thin-film solar cells. The method involves illumination of a small area of the cell with light sufficiently intense to make the internal resistance easily observable. It works particularly well on CIS and CI(G)S cells with small internal series resistance values with RA products between 10^{-1} and 10^4 ohm cm^2 . These values would be difficult to measure with standard techniques. We expect this technique to be especially valuable for spotting small changes in back-contact resistance during accelerated stress testing and in identifying the source of any increased series resistance. Possible sources of internal resistance are the semiconductor/back-contact interface (the resistance may be ohmic or junction-like), and the bulk resistance of the film's neutral region or the CdS (photoconductivity can make these resistances light-dependent).

Data measured on CdTe cells, however, showed a large drop in photogenerated current with decreasing spot diameters that was not seen with CIS and CIGS cells [Reference 4]. We modeled the CdTe results on a 13.7% USF cell using a PSpice circuit simulation by including a shunted diode in series with the standard solar cell circuit. The modeling of ac photocurrents on the USF cell yielded a saturation current of 0.3 A/cm² and quality factor of 4. The interesting twist is that these are not back-to-back diodes as one would expect from the detrimental back-contact diode, but rather it is serially connected in the same directions. This diode is not real; it does, however, simulate the loss in cell photocurrent as the CdTe diode is driven toward flatband.

Conclusions

We continued to apply our two-terminal, nondestructive, module cell-shunt-resistance measurement technique, showing how it is useful for supporting qualification testing, failure analysis, and module cell performance characterization. This shunt resistance measurement technique will continue to be used at NREL, is readily available for others to implement, and is preferred to the method of Reference 2 because low-resistance cells are easily measured.

CdTe Team activities will continue with the internal series-resistance measurement continuing on cell structures and development of a methodology for a CdTe module lifetime prediction.

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Title: PV Efficiency Measurements—Standard Reporting Conditions

Organization: Center for Measurement and Characterization

Contributors: K.A. Emery, Team Leader; S. Rummel, H. Field, D. Dunlavy
Y. Caiyem (vacant 1-10/96)

Objectives

The performance of photovoltaic (PV) devices of all sizes and technologies was evaluated by this activity. This team supports the entire PV community by providing secondary calibrations of photovoltaic modules and cells, efficiency measurements with respect to a given set of standard reporting conditions, efficiency verification of contract deliverables, current versus voltage (I-V) measurements under varying temperature, spectral irradiance and total irradiance. Support was provided for in-house programs in device fabrication, module stability, module reliability, PV systems, and alternative rating methods by performing baseline testing, specialized measurements and other assistance when required. This activity also supports the entire PV community by providing information on PV measurement equipment and systems that are appropriate for the end user, I-V measurement procedures, and uncertainty analysis. Included in the uncertainty analysis are the determination of potential artifacts in the I-V results because of equipment or procedures, and realistic estimates of the elemental error sources. This activity was committed to obtaining the lowest possible uncertainty in the measurement of the standardized PV performance of single- and multi-junction cell and modules.

Technical Approach

The photovoltaic current versus voltage characteristics are measured with respect to standard terrestrial reporting conditions (25°C temperature, 1000 Wm⁻² total irradiance and ASTM E892 global reference spectrum). The intensity of the Spectrolab X-25 solar simulator (30 cm square beam) was adjusted until the measured short-circuit current of a reference cell was equal to its calibration value corrected for spectral mismatch. The current versus voltage characteristics are then measured using four-terminal Kelvin connections to the PV device with a custom data acquisition system designed to give a random error of less than 0.1% and a nonrandom error of less than 1%. The I-V system had a voltage range of ± 50 V (0.1 μ V resolution) and ± 8 A to ± 1 pA. These procedures have been shown to be valid for any given tabular reference spectrum including AM0 and the ASTM direct normal reference spectrum. Because of the wide current and voltage range the system was also used for concentrator and dark I-V measurements. For two-terminal multi-junction devices the spectrum of the Spectrolab model X-25 solar simulator was adjusted, using a special filter plate developed at NREL, until each junction was producing the correct photo-current. The I-V system was also used for examining the effects of premeasurement conditions, bias rate, maximum power versus illumination time, V_{oc} versus time, and I_{sc} versus time on the PV performance.

The filter spectral response system uses periodic monochromatic light directed through one of 51 10-nm bandwidth interference filters covering the spectral range from 290 to 1900 nm. The system was capable of providing steady-state light bias levels up to 2 A and voltage bias levels from 1 mV to 40 V. The intensity of the bias light was normally adjusted to give the short-circuit current under standard reporting conditions. The custom operational amplifier-based data acquisition system allowed for a wide range of gains (1 to 10⁶). The intense light from the 1000-W lamp illuminating the 5-cm diameter filters allows for small cells to large modules to be

illuminated with adequate signal to noise. The uncertainty in the relative spectral response as a function of wavelength was less than $\pm 5\%$. The data can be made absolute by forcing the integrated quantum efficiency to agree with the measured spectral response. The absolute spectral response can also be measured directly with this system, giving an uncertainty of $\pm 10\%$. The limiting factor in the uncertainty was the $\pm 5\%$ - 10% spatial nonuniformity of the monochromatic beam. The second grating monochrometer-based system had a wavelength range from 300-10,000 nm with a 1-nm wavelength resolution and ~ 5 -nm bandwidth. The grating system was designed for accurate absolute spectral response measurements by illuminating a small 1-mm by 3-mm rectangular area and measuring the power of the entire beam. The system used all reflective optics so chromatic aberrations and beam wander with wavelength were not present. The grating system used an operational amplifier for the current-to-voltage conversion, allowing a 15-V voltage bias range with 0.1 mV being the normal configuration. A lock-in amplifier was used to detect the ac signal. The system was capable of broadband or filtered light bias for multi-junction or nonlinear devices. Both systems rely on accurate pyroelectric detectors for the measurement of the light power.

The efficiency versus concentration measurements are measured with an unfiltered 1000-W Xe-arc light source that was focused to a small area, and with the one-sun data acquisition system described above. Using the cells I_{sc} measured at one sun (ASTM E891-87 direct normal reference spectrum at a total 1-sun irradiance of 1000 Wm^{-2}) and assuming linearity in the current with total irradiance, the I-V characteristics were measured. Using a technique developed at NREL, the space charge region temperature can be accurately set to a given value even though large temperature gradients ($>10^\circ\text{C}$) may exist between the plate temperature and junction temperature. The procedure involved setting the sample temperature to the reference temperature, e.g., 25°C , without illumination (no heat load). Using a high-speed shutter and voltmeter, the open-circuit voltage was sampled (1000 readings/sec). The highest measured V_{oc} was then taken to be the V_{oc} under concentration. The thermoelectrically controlled vacuum plate was then cooled until this V_{oc} was reached. This same procedure was used in the Spectrolab X-25 system for samples on thermally insulating substrates where temperature gradients of 5° - 10°C are typical.

The primary reference cell calibration procedure involved measuring the short-circuit current, total irradiance, and spectral irradiance at the same time outdoors with the same 5 field of view. The total irradiance was measured with a primary absolute cavity radiometer, and the spectral irradiance was measured with a LICOR LI-1800 spectroradiometer. The uncorrected average calibration value $\langle CV_u \rangle$ was calculated for the 30 I_{sc} and E_{tot} readings taken during the 30 seconds required to measure $E_s(\lambda)$. The atmospheric constraint for a valid calibration value was that the range (maximum to minimum) over the 30-second time period in I_{sc} be less than 0.25%, in E_{tot} be less than 0.07%, and in $\langle CV_u \rangle$ be less than 0.1%. Once a valid $\langle CV_u \rangle$ was obtained the short-circuit current was corrected for temperature to 25°C and the spectrally corrected calibration value CV was computed. Since the measurement of $E_s(\lambda)$ does not encompass the limits of the reference spectrum, the measured spectrum was extended using a computer model developed by the group to encompass the range of the reference spectrum (300-4000 nm). The calibration value CV was computed at least 20 times for at least 3 separate days giving a single primary calibration value. This procedure had been shown to have a total uncertainty of less than 1% by rigorous uncertainty analysis, intercomparison with primary AM0 standards and other intercomparisons.

The I-V characteristics of modules were routinely evaluated using the Spire 240A solar simulator. This system had a 0-100 V and 0-20 A range for a 61 cm $\times$ 122 cm area. The Spectrolab large-area pulsed solar simulator (LAPSS) produces a one-sun beam of light 2 m $\times$ 2 m area and could illuminate a 4 m $\times$ 4 m area. The Spectrolab data acquisition system has a 0-100 V, 0-40 A measurement range. The system has been used to

evaluate the I-V characteristics of modules. The concentrator lamp housing has been used to measure the performance as a function of concentration for several GaInP/GaAs concentrator cells fabricated at NREL to 1500 suns. The concentrator lamp housing allows measurement to 2000 suns.

During FY 1996 standardized Outdoor module I-V measurements were performed on a variety of one-sun modules using our variable-tilt test bed. For flat-plate modules, the total irradiance was measured with an Eppley pyranometer and a crystal-Si reference cell in a module package mounted in the plane-of-array. A normal incidence pyrheliometer calibrated against NREL's cavity radiometers was used to measure the direct normal irradiance for concentrator modules. The module temperature was measured with a temperature sensor attached to the back surface of the module. The spectral irradiance was measured during the I-V measurement using a LICOR LI-1800 spectroradiometer with a Teflon dome and temperature-controlled detector. Meteorological parameters at the time of measurement, including direct-to-diffuse ratio, wind speed, wind direction, barometric pressure, air temperature, and relative humidity are stored with the data. The outdoor I-V measurement system was capable of handling devices with a voltage and current range of 300 V and 40 A maximum, to 0.01 mV and 1 A minimum.

Results

During FY 1996 the team performed 2474 cell and module I-V measurements (I-V under standard reporting conditions). I-V cell and module calibrations were performed for the following groups:

U.S. Industry—Advanced Systems Manufacturing (a-Si), Alpha Solerco (mono-Si), APS (a-Si), ASEC (GaAs, GaInP/GaAs), ASE Americas (web Si), AstroPower (Si film), Ebara Solare (web Si), ECD/Solvonics/USSC (multi-junction a-Si), Energy PV (CIS), Iowa Thin Films (a-Si), ENTECH (mono-Si), Golden Photon (CdTe), Green Development Corp. (a-Si), ISET (CIS, CIGS), Photon Technologies (mono-Si), MicroFab Technologies (multi-Si), Materials Research Group (mono-Si), Photocomm/Solavolt (multi-Si), Siemens (mono-Si, CIGS), Solarex (CIS, a-Si tandems, multi-Si), Solar Cells Inc. (CdTe), Solar Solutions Inc. (Koncar a-Si module), Solec Int. (mono-Si), Spectrolab (GaAs, GaInP), Spire (Si reference cells and modules), Suncorp (Si ribbon), Sunwize (mono-Si), Titan Energy Systems (mono-Si), Utility Power Group (a-Si).

Universities and other groups in United States—Burdick Technologies Unlimited (Si and filtered Si solar radiometers), Colorado State University (CdTe), Colorado Solar Car Racers (mono-Si), Inst. Energy Conv. (a-Si, CdTe), Junior Solar Sprint (multi-Si), PSI corp. (mono-Si), Quantum Group (vertical multijunction Ge concentrator), Research Triangle Institute (GaAs), Star Center/Arizona State (mono and multi-crystal Si cells and modules) U.S. Air Force/Phillips Labs (GaInP/GaAs space ready module, GaAs, GaInP, cells), Univ. South Florida (CIS, CdTe), Univ. Toledo (CdTe), Western Illinois Univ. (LICOR pyranometer).

NREL internal groups—(CIS, CdTe, dye sensitized nano-crystal dye, mono-Si, multi-Si, LICOR pyranometers, GaAs, GaInP, GaInP/GaAs tandems, numerous modules for exposure studies and systems evaluation).

Foreign Groups—Australia, Univ. New South Wales (mono-Si); Belgium, IMEC (mono-Si, multi-Si); Czechoslovakia, Solartec (mono-Si); England, Imperial Coll. (InP, GaInAs multiple quantum well PV); Germany, Fraunhofer Inst. (mono-Si); India, Udhaya (mono-Si); IACS (tandem a-Si), Res PV (mono-Si), CEL (mono-Si); Israel, Univ. Tel Aviv (mono-Si, GaAs); Italy, ENEA (mono-Si); Japan, Japan Energy Co. (GaInP/GaAs record

tandem 30% at 1 sun); Netherlands, Univ. Nymegen (GaAs); Spain, IES-UPM (mono-Si); Switzerland Univ., Neuchatel, (a-Si, a-Si tandem); EPFL (nano-crystal dye-sensitized cell, submodule); Taiwan, I.T.R.I. (mono-Si).

Approximately 45 papers acknowledged the support of this group during FY 1996. This team has assisted nearly all module manufacturers with their QA/QC programs by providing telephone consultations on measurement strategy and procedures, and a calibration tractability path for their cells and modules. The technology of PV I-V and spectral response measurements was transferred to a variety of university and manufacturing groups through phone conversations and visits. The group also supported work in spectral irradiance modeling and energy rating methods resulting in several co-authorships. In support of international programs, 2-week trips to India and China were made to transfer efficiency measurement technology.

The move of the primary reference cell calibration facility from SRRL to OTF was completed with improved capabilities. The large-area continuous solar simulator was installed and preliminary characterization was completed. A custom data acquisition system was designed so that modules with voltages of as much as 400 V can be measured. The move and installation of the Spectrolab large-area and high-intensity pulsed-solar simulators was completed. Modifications to the software were required to accommodate the range of requirements for data analysis algorithms, user interface, graphical output and database management.

The team was also extensively involved in the initial and final characterization of the samples for the international intercomparison to establish the PEP World Photovoltaic Scale and evaluate calibration problems for new technologies samples. The team also participated along with Sandia as the U.S. participants in these two important international intercomparisons.

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8. C.R. Osterwald, S. Anevsky, A.K. Barua, J. Dubard, K. Emery, D. King, J. Metzdorf, F. Nagamine, R. Shimokawa, N. Udayakumar, Y.X. Wang, W. Zaiman, A. Zastrow, J. Zhang, Results of the PEP '93 Intercomparison of Reference Cell Calibrations and Newer Technology Performance Measurements, *Proc. 25th IEEE Photovoltaic Specialists Conf.*, Washington, D.C., May 13-17, 1996, pp. 1263-1266, IEEE, New York, 1996.
9. B. Kroposki, D. Myers, K. Emery, L. Mrig, C. Whitaker, and J. Newmiller, Photovoltaic Module Energy Rating Methodology Development, *Proc. 25th IEEE Photovoltaic Specialists Conf.*, Washington, D.C., May 13-17, 1996, pp. 1311-1314, IEEE, New York, 1996.
10. K. Emery, Uncertainties in Photovoltaic Performance Indicators for Service Life Prediction, *Proc. Photovoltaic Performance and Reliability Workshop*, Sept. 4-6, 1996, Lakewood, CO, NREL/TP-411-21760, October 1996.

Title: PV Module Exploratory Qualification Testing

Organization: Center for Performance Engineering and Reliability, Engineering, and Technology Validation Team
National Renewable Energy Laboratory

Contributors: C.R. Osterwald, T. Basso, B. Kroposki, and J. Pruet

Objectives

Module exploratory qualification testing involves both accelerated and environmental stress testing. The objective of module stress testing is to obtain information about the ability of module designs to withstand failure and degradation mechanisms that occur when modules are deployed outdoors for long periods of time. Accelerated stress testing attempts to increase the rate of degradation so that results are obtained in shorter time periods, and environmental stress testing is intended to simulate outdoor conditions within the laboratory. Although some of these tests are commonly referred to as qualification tests, it is not the intent for NREL to qualify designs through a formal testing program. (For an example of a qualification test sequence, see reference [1].)

Technical Approach

The goal of stress testing within the Engineering and Technology Validation Team is to discover potential problems with module designs that may not be commercially available yet such as prototypes and subcontract deliverables. To accomplish this goal, the stress testing is closely tied to failure analysis capabilities within the team. A second goal is the development and validation of new or more effective test methods. These goals are intended help improve the reliability and lifetime of PV modules.

Specific tests available include accelerated outdoor and indoor UV weathering, temperature and humidity cycling, high-voltage stress, and electrical and mechanical integrity tests. Although primarily intended for modules, these tests are also applied to balance-of-systems components that must survive outdoor conditions, such as inverters for AC modules. Facilities that are used for accelerated and environmental stress testing at the Outdoor Test Facility include several environmental chambers, both with and without light exposure, wet and dry electrical insulation tests, static and dynamic mechanical loading equipment, and ice ball impact testing. Facilities that are currently being developed are accelerated UV weathering using the Outdoor Accelerated-weathering Tracking System and an outdoor test bed for high-voltage stress testing.

Results

Results of exploratory qualification testing are typically used as preliminary information about the ability of new or prototype module designs to survive outdoor conditions. These results are normally given only to the module manufacturers that request the testing. Another primary use of the testing

capabilities at NREL is to provide information to PV standards committees about new or existing module test methods.

A major task that was completed during FY 1996 was the relocation of existing facilities into the new Outdoor Test Facility (OTF). One new environmental chamber was installed and four existing chambers were made operational. The ice ball impact test, the static and dynamic mechanical load tests, and the insulation resistance tests are now in a single location and available for use.

Testing was completed during FY 1996 on CuInSe_2 coupon ($1' \times 1'$) modules from Siemens Solar. These were glass-glass modules with an extra-wide edge seal. The goal of the testing was to study water ingress through the seals. Humidity-freeze, damp heat, and thermal cycling were performed both in the dark (the normal way) and under 1 sun illumination. The ability to perform these tests on full-size modules while illuminated is a unique capability of the facilities at NREL.

A subset of the Institute of Electrical and Electronics Engineers (IEEE) 1262 qualification sequence was performed on several United Solar Systems Corporation (USSC) roofing-shingle module prototypes. This was the first independent stress testing performed on this new type of module. The test provided new durability information for USSC.

Static and dynamic loading tests were performed on a new Golden Photon CdTe module design, and a partial-IEEE 1262 sequence of stress tests was initiated under a cooperative research and development agreement with Energy Conversion Devices (ECD) and Sovlux on a number of triple-junction a-Si modules manufactured in Russia.

Although not part of the PV program, a test sequence was begun using the new Atlas XR260 weathering chamber ($4' \times 6'$ with Xe exposure) for durability of large-size electrochromic windows. The test, which involves holding the windows at 50°C and 1 sun illumination while cycling the windows between the opaque and transparent states, is the first accelerated testing of this nature performed on electrochromic windows.

Conclusions

Following the relocation of the accelerated and environmental stress testing equipment to the new Outdoor Test Facility, stress testing has been restarted and several sequences have been completed. These test sequences have involved interactions with Siemens Solar, Golden Photon, USSC, ECD, and Sovlux.

References

1. IEEE standard 1262-1995, "IEEE Recommended Practice for Qualification of Photovoltaic (PV) Modules," IEEE, New York, NY, April 12, 1996.

Title: Photovoltaic Module and System Engineering and Performance

Organization: Center for Performance Engineering and Reliability

Contributors: L. Mrig, T. Strand, B. Kroposki, R. Hansen,, and E. van Dyk

Objectives

The objective of this research activity was to test, monitor, evaluate, and analyze state-of-the-art and advanced PV technologies at the module and system levels. The team assisted in the development and validation of PV technologies by analyzing the performance and reliability of PV modules and systems in support of the DOE National PV Program goal of a 30-year lifetime for PV modules. The results of this activity were then disseminated to the PV community in the form of publications, test reports and presentations. In addition, this team interacted with PV manufacturers (through cooperative research agreements) and other test facilities to exchange information, results, and experience. The team also provided engineering support to other in-house PV projects (e.g., Photovoltaic Manufacturing Technology [PVMaT], international projects, and thin-film partnerships), and assisted in the development of PV standards and codes for use by the PV community.

Technical Approach

Module and System Testing for Performance, Reliability, and Stability

The team maintained a database of flat-plate PV technologies performance and reliability, at both the module and system level, and continued to perform module and system stability testing on all thin-film and advanced PV technologies. Long-term outdoor exposure tests and indoor controlled light-soaking experiments were conducted to address the issue of module stability. Module performance was measured periodically during the tests. The team monitored and evaluated the outdoor performance of PV modules and small systems (approximately 1 kWp each) at NREL's PV Outdoor Test Site. This activity focused on emerging PV module technology evaluation/validation, flat-plate module and system development, and failure analysis. The team also designed and deployed small (~100W) stand-alone systems. These small systems demonstrate the feasibility of thin-film PV technologies for remote or stand-alone applications (e.g. telecommunication, lighting, etc.).

This testing was conducted at NREL to assist PV manufacturers and system integrators in evaluating array/system performance and identifying technical issues, if any, by fielding the modules and PV systems under actual operating conditions. This research furnished independently tested data to the PV community on module and system performance and reliability. The PV array and system performance data collected form the basis of technical publications and reports. A major aspect of this cooperative array/system research activity at NREL was the technical exchange of results obtained from these evaluations with manufacturers and industry.

Module and System Performance Evaluation Studies

The team researched and developed performance evaluation methodologies for modules and systems. These studies include seasonal performance, spectral measurements, and techniques for evaluating instantaneous power output and energy production of the modules and systems.

Standards and Codes

Team members participated and worked on Institute of Electrical and Electronics Engineers (IEEE) SCC21, National Electrical Code (NEC) Article 690 TRC, and International Electrotechnical Commission TC/82 committees, to help in the development of standards and codes, through consensus, for the PV industry.

Support for Internal Projects

The team provided technical support for PVMaT, Photovoltaics Building Opportunities in the United States, Photovoltaics for Utility-Scale Applications, the Federal Energy Management Program (FEMP), and international projects (e.g., India and South Africa).

Results

One of the major focus points for the team in FY 1996 was the relocation of operations from Field Experiment Test Area trailers 6305 and 6505 to the Outdoor Test Facility (OTF). This move included installing module test racks on the OTF roof, setting up the electronics test lab, reinstalling data acquisition systems into the OTF, and the design and construction of three new test pads.

Outdoor Module Stability and Performance Testing

The team has over 100 modules under study at the PV Outdoor Test Site. These modules include single-, dual-, and triple-junction a-Si, CdTe, CIS, single crystalline Si, multicrystalline Si, and thin-film Si modules. Long-term outdoor performance data are collected by periodically taking I-V curves. From these data temperature coefficients are determined. To study the module's stability over time the data are normalized to 1000 W/m² and corrected to 25°C. An example of this data is given in Figure 1. This figure shows the performance of a CIS module from Siemens Solar. The module has been exposed for over 2 years and shows good stability over time.

Indoor Controlled Light Soak Testing

Amorphous Silicon: Light Soak 4 was started in FY 1995. This test exposed 8 sets of multi-junction a-Si modules from different manufactures to simulated solar irradiance at 1000 W/m² and 50°C for 800 hours. The modules have reached the stability criteria and will continue to be tested at 35°C. This will allow for comparisons of stabilized performance with modules from the same sets that are being exposed outdoors. Status reports have been provided to the manufacturers and program managers.

Copper Indium Diselenide: Light Soak C2 was conducted on a set of mini-modules from Siemens Solar (CIS). This test exposed the modules to Damp Heat, Thermal-Cycle, and Humidity Freeze Test. Test reports were distributed to the manufacturers.

Module Performance Evaluation Methodology Development

A paper detailing the development of a module energy rating methodology was presented at the 25th Institute of Electrical and Electronics Engineers (IEEE) PV Specialist conference.

System Evaluation Results

In-situ testing of advanced thin-film PV systems has been in progress since December 1992. PV systems currently under evaluation include advanced thin-film PV technologies of a-Si, CIS, and CdTe as well as EFG x-Si and Cz x-Si. The effects of weather, temperature, solar spectrum, soiling, and age on array/system performance were studied. Work included in-depth studies of performance versus temperature and spectrum, system energy ratings, and determination of temperature coefficients. Figure 2 shows some results on research conducted on array energy production. The figure shows the normalized energy production by season for four different types of PV technologies.

Figure 2. Normalized Energy Production by Season

System Installations

The team designed, installed, and began monitoring one new system in FY 1996 at the PV Outdoor Test Site. This is the 1.8 kWdc a-Si APS Delta tracker system.

Standards and Codes

Members of this team were on several IEEE SCC 21 committees working on field testing (PAR 1373), system safety (PAR 1374), and energy ratings (PAR 1479) draft standards. The team completed work on the 1999 NEC code cycle for Article 690.

Support for Internal/DOE Projects

The team supported PVMaT as Technical Monitoring Team Members for the following Phase 4A1 subcontracts: Utility Power Group, Solar Design Associates, Omnion, Ascension Technologies, Solar Electric Specialties, Advanced Energy Systems, Inc., and Trace Engineering. Engineering support was provided to the Sustainable Rural Economic Development Ramakrishna Mission Initiative, West Bengal, India. The team coordinated, conducted tests, and provided results to the CdTe PV Partnership Team.

Dr. Ernest Van Dyk, a visiting research associate from South Africa, worked with the team in analyzing the performance of the two 6kW_{ac} grid-connected PV systems located on the roof of the SERF building.

Results of this work have shown, in addition to expected seasonal trends, that system monitoring is a valuable tool in assessing performance and detecting faulty equipment. The systems were both found to be operating at approximately 7% to 8% below their estimated rating, which was based on PVUSA test conditions. This may be attributed to the design inverter efficiency being estimated at 95% compared to measured values of approximately 87%. The continuous monitoring also revealed faulty peak-power point tracking equipment. Furthermore, methods applied for this analysis may be used to evaluate and compare systems employing different PV technologies.

This team supported FEMP by designing and installing four PV systems for the 1995 Pageant of Peace in Washington, D.C., and reviewing designs for an Earth Day Park PV system. The team also conducted studies on three different charge controllers for an international project with China.

PV Performance and Reliability Workshop

The ninth PV Performance and Reliability Workshop was held from September 4-6, 1996. There were over 100 attendees, including people from PV manufacturing, research, and consumers, and utilities. The workshop included presentations from 25 speakers covering the following areas: cell, module, and system performance, cell/module reliability, system reliability, and PV applications and field experience. This workshop provided a forum for the participants to exchange technical information on PV performance and reliability issues. During the workshop there was time for lengthy open discussions between the presenters and the audience.

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3. Kroposki, B., T. Strand, R. Hansen, R. Powel, and R. Sasala (May 1996). "Technical Evaluation of Solar Cells, Inc. CdTe Module and Array at NREL, 25th IEEE PV Specialists Conference, Washington, D.C.
4. Van Dyk, E., T. Strand, and R. Hansen (May 1996). "Technical Evaluation of Two 6-kW Mono-Si PV Systems at NREL", 25th IEEE PV Specialists Conference, Washington, D.C.
5. Emery, K., H. Field, B. Kroposki, T. Strand, and M. Wanlass (May 1996). "Temperature Dependence of Photovoltaic Cells, Modules, and Systems", 25th IEEE PV Specialists Conference, Washington, D.C.
6. Strand, T. and R. Hansen (September 1996). "Comparison of Array Performance at NREL" In proceedings *Photovoltaic Performance and Reliability Workshop*, B. Kroposki, ed., NREL/TP-411-21760
7. Kroposki, B. Chairman (October 1996). "Photovoltaic Performance and Reliability Workshop", NREL/TP-411-21760, National Renewable Energy Laboratory, Golden, CO

Title: Photovoltaic Solar Radiometric Measurements and Evaluation

Organization: NREL PV Module and Systems Performance and Engineering Project

Contributors: D.R. Myers, T.W. Cannon, and D. Trudell

Objectives

The Photovoltaic (PV) Solar Radiometric Measurements and Evaluation Team supported the PV Module and System Performance and Engineering Project with broadband (300 nanometers [nm] to 2400 nm) and spectral (wavelength-dependent) engineering measurements and expert scientific evaluation of optical radiation used to characterize performance of PV cells, modules, and systems. We acquire and transfer technical information to industry and NREL PV engineers and researchers concerning radiometric measurements, instrumentation, analysis, and indoor and outdoor solar radiation data and measurements. The team also provides optical radiometer calibrations in support of the DOE/NREL PV program and other program activities and areas at NREL.

Technical Approach

The team performs broadband radiometric calibrations at the Solar Radiation Research Laboratory and spectral and narrow-band instrument calibrations in the Optical Metrology Laboratory, shared with NREL's Metrology Laboratory. We maintain spectral and total irradiance reference standard sources, obtained directly from the National Institute of Standards and Technology (NIST), absolute-cavity radiometers compared with and traceable to the World Radiometric Reference (WRR), and quality electronic equipment which supports radiometric calibrations, measurements, and research to improve radiometry applied to photovoltaic performance evaluation. Measurement needs of NREL internal and external PV program participants are addressed as requested. Measurement systems such as the PV Reference Meteorological and Irradiance System (RMIS), two absolute-cavity radiometer pyrheliometers, eight spectroradiometer systems, and an array of broadband radiometers for measuring natural and artificial optical radiation sources, are maintained. Technical interaction with the Optical Technology Division of NIST, instrument manufacturers, and the optical radiation community provides the basis for continuous improvement in optical radiation measurements for PV applications.

The team contributes to the PV optical radiometry field by working with photovoltaic manufacturers, researchers in the NREL/DOE PV program, the American Society for Testing and Materials (ASTM), Institute of Electrical and Electronics Engineers (IEEE), the Council for Optical Radiation Measurements (CORM), and the NIST Radiometric Physics Division. T. Cannon is a member of the CORM board of directors, and Myers and Cannon are members of ASTM Committee E-44 on Solar, Thermal, and Alternative Energy Sources.

Results

Team accomplishments in fiscal year (FY) 1996 include the following:

- We drafted a Photovoltaic Radiometric Measurements Guide [1].

At the PV Solar Radiometric Measurements Workshop held on July 24-25, 1995, the highest priority action item requested was the development of a radiometric measurements guide addressing the needs of the PV testing community. An 80-page draft document addressing spectral and broadband radiometric techniques and

applications was developed; it is presently undergoing peer review and revision. Publication should occur in early 1997.

- We evaluated the accuracy of PV system radiometric instrumentation as a function of seasons and cloudiness at the NREL Outdoor Test Facility (OTF) [2].

Figures 1 and 2 contrast the performance of three system performance monitoring radiometers under clear and cloudy conditions. They depict variations in the ratio of irradiance at three locations at the NREL OTF to a single reference radiometer (part of the RMIS).

- With the NREL Metrology Laboratory, we calibrated over 150 different radiometers and sources for NREL PV research and industrial partners, as well as several other NREL/DOE programs.

Two PV cavity radiometers were calibrated to the WRR through the NREL Working Group of cavity radiometers, which participated in International Pyrheliometric Comparisons in Davos, Switzerland [3]. Four spectral and eleven broadband radiometers and three accelerated testing and cell performance solar simulators were also calibrated. Pulse Analysis Spectroradiometer System (PASS) spectra data were collected before and after installation of a new lamp in the Spire 240A, showing a definite red shift in the older lamp (see Figure 3). High-resolution PASS data were collected for the Large Area Pulse Solar Simulator (LAPSS) as well. Arizona State University radiometers were also calibrated by the team.

We tested and evaluated a charge couple device array spectroradiometer for flash solar simulator measurements [2] in cooperation with the Spire Corporation, as shown in Figure 4. We also provided extended wavelength spectral measurements for two different Thermal Photovoltaic Program high-intensity sources.

- We contributed to Standards and Codes, technical publications and conferences.

We provided technical comments on measurement and uncertainty aspects of IEEE, ASTM, and International Standards Organization (ISO) draft documents [4,5] for PV accelerated weathering testing at the 1996 PV Standards and Codes Forum, June 24-27, 1996, at Winter Park, CO. Cannon and Myers are members of CORM. Myers is a member of ASTM Committee E-44, and Cannon is a member of the IEEE.

Cannon was organizer and program chairman of the 24th annual meeting of the Council for Optical Radiation Measurements, in conjunction with the Optical Technology Division of the National Institute of Standards and Technology at Gaithersburg, MD, May 18-22, 1996. Cannon and Myers presented papers on the application of integrating spheres to spectroradiometric measurements of PV performance and accelerated environmental testing at the meeting [6,7]. Myers was co-author of a paper on PV module energy ratings for the 25th IEEE Conference [8] and presented results of the PV system radiometer evaluation and diode array spectroradiometer measurement issues at the 14th Annual NREL Photovoltaic Program Review meeting November 18-22, 1996, at Lakewood, CO [2].

Major industry and research technical interactions during FY 1996 included:

American Sunco: Coordinate training on Outdoor Accelerated Testing System.

Collins Radio, General Aviation Division: Uncertainty analysis and standards for optical radiometry.

Corporation for Solar Technologies and Renewable Resources (CSTRR): Technical descriptions of radiometric testing and calibration.

Dryden and LaRue (Fairbanks, Alaska): Diurnal profiles of ultraviolet radiation.

Florida Solar Energy Center: Dr. Gobind Atmaram; spectroradiometer calibrations.

Fraunhofer Institute for Solar Energy (Freiburg, Germany): Spectroradiometric instrumentation.

Jacob Blaustein Desert Research Institute (Ben Gurion University, Israel): UV spectral data

National Institute of Standards and Technology: Drs. Al Parr, Ambler Thompson. Optical Technology Division. PV Radiometric standards and needs for spectral and broadband radiometry.

Spire Corporation. In-house spectral measurements of SPIRE model 460 and 240 simulators, recommendations on applications of array spectroradiometer.

University of Hong Kong (School of Architecture): Dr. J. Close. Broadband radiometer calibration and installation issues for evaluating building-integrated PV.

Conclusions

PV system performance and stability monitoring activities at the NREL PV outdoor test site compared plane of array (POA) radiometric data with high-quality data from the RMIS, quantifying radiometer performance as a function of season and cloudiness. Calibrations of POA sensors provide traceability and known uncertainty for POA measurements. Technical contributions provided on draft standards for PV performance, qualification, and durability testing were made at the 1996 Standards and Codes Forum. Team members presented papers and made technical contributions at the following workshops and conferences:

- **Workshop on Advanced Radiometry for Joint U.S.-Saudi Arabia Renewable Energy Program, Annex II**, March 18-29, 1996, Golden, CO.
- **1996 Annual Meeting and Workshop on Flux Integrating Devices, Council for Optical Radiation Measurements**, May 18-24, 1996, Gaithersburg, MD.
- **1996 Photovoltaic Standards and Codes Forum**, June 24-27, 1996, Winter Park, CO.
- **14th NREL Photovoltaic Program Review**, November 18-22, 1996, Denver, CO.

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6. Cannon, T.W. "Design of Integrating Spheres for Outdoor Solar Radiometric Applications." Presented at 1996 Annual Meeting and Workshop on Flux Integrating Devices, Council for Optical Radiation Measurements, May 18-24, 1996, Gaithersburg, MD.
7. Myers, D.R. and Cannon, T.W. "Ganged Integrating Spheres for High-Intensity Ultraviolet Spectroradiometry." Presented at 1996 Annual Meeting and Workshop on Flux Integrating Devices, Council for Optical Radiation Measurements, May 18-24, 1996, Gaithersburg, MD.

8. Kroposki, B., Myers, D.R, Emery, K., Mrig, L., "PV Module Rating Methodology." In Proceedings 25th IEEE Photovoltaic Specialists Conference, May 13-17, 1996, Washington, D.C., p. 1311.

Figure 1. Clear-sky ratios of 3 PV system irradiance to reference irradiance for four seasons.

Figure 2. Cloudy-sky ratios of 3 system PV irradiances to reference irradiance for four seasons.

Figure 3. Comparison of NREL PASS and diode array spectral data for Spire 240A illustrating "enhanced IR" due to lack of order-sorting filters.

Figure 4. PASS versus diode array spectral data for Spire 240A simulator illustrating false IR enhancement due to lack of order sorting.

Title: **PV Standards and Codes Development**

Organization: Center for Performance Engineering and Reliability

Contributors: C.R. Osterwald, R. DeBlasio

Objectives

The objective of this work was to provide coordination for the development of PV standards, codes, and criteria for test and evaluation procedures that are consistent with the Department of Energy's national photovoltaics five-year plan.

Technical Approach

Technical approaches used for this objective included participation with the Institute of Electrical and Electronics Engineers (IEEE) Standards Coordination Committee 21 (SCC21) and the U.S. Technical Advisory Group (TAG) for International Electrotechnical Commission (IEC) Technical Committee 82 (TC-82), and chairing American Society for Testing and Materials (ASTM) subcommittee E44.09. These three groups are the principal committees currently involved in standards development for photovoltaics. By the nature of standards development, these efforts have been ongoing for many years. To facilitate these activities, a fourth NREL PV Standards and Codes Forum was held to provide individual and joint meetings of these groups at the same location and establish coordination of efforts and flow of information between committees on PV standards issues.

Other efforts included coordination of the Photovoltaic Energy Project (PEP'93) Intercomparison of reference cell calibrations and cell performance measurements. This international round-robin measurement involved national PV measurement laboratories from eight different countries and was intended to provide vital information about PV measurements for standards organizations.

Results

Coordination of the PEP'93 Intercomparison continued through FY1995, and circulation of the two sample sets was completed in August 1996. A final meeting of the participating laboratories was held at NREL on March 4-8, 1996, and a preliminary summary of the results was presented at the 25th IEEE Photovoltaic Specialists Conference in May 1996. (The final report on the PEP'93 will be published as an NREL technical report in 1997 [1].) The most significant result of the PEP'93 was the establishment of the World PV Scale (WPVS), which is a group of primary reference cells that were calibrated by national laboratories during the intercomparison. A qualified average calibration constant was obtained for each cell, and the overall 2-sigma standard deviation was 1.9%. Figure 1 shows the normalized short-circuit currents of the 20 reference cells that form the WPVS.

PV standards activities within ASTM during FY1995 dealt with several issues of importance to the PV industry. Two revisions of standards were approved and published that affect PV performance

measurements. E 973M provides spectral mismatch calculations when using reference cells, and E 1036M is a major revision of the module and array performance test method that includes new temperature and irradiance corrections developed by J. Anderson under subcontract to NREL. Three new standards were published that are intended for module reliability testing. These are E 1799, which provides a method for module visual inspections during qualification testing; E 1802, a test method for module insulation integrity when wet; and E 1839M, a test method for module mechanical integrity [2].

The 1996 PV Standards and Codes Forum was held on June 24-26 in Winter Park, Colorado. Twenty-four representatives from manufacturers, test laboratories, end users, and the national laboratories attended meetings of SCC21, E44.09, and the U.S. TAG for TC-82. Highlights of the SCC 21 meetings included initiation of work on two new draft projects. The first is a method of calculating energy production of modules for a series of reference days, and the second is a grid intertie document to help utilities standardize interfaces to grid-connected PV systems. Existing draft documents discussed were a recommended practice for field-test methods for grid-connected PV systems, and a suitability test for batteries in PV systems.

During the ASTM E44.09 meeting, revisions of existing standards for solar simulation and spectral response measurements of solar cells were discussed. Possibilities for future new standards include module hot-spot endurance testing, and a field insulation resistance test for arrays.

Following reports of the activities of the working groups of IEC TC82, the TAG reviewed several draft standards, including a PV terminology document, a UV exposure test for modules, and a method for linearity measurement.

The IEEE SCC21 PV systems development committee completed the development of a PV module qualification test that included thick- and thin-film module technologies. The IEEE Standards Board approved IEEE 1262 "IEEE Recommended Practice for Qualification of (PV) Photovoltaic Modules" in December 1995, and published the standards on April 12, 1996 [3]. This effort took four years to complete and included more than 50 representatives from the PV community. The results of this effort also meet the DOE five-year goal—ahead of schedule (1997)—to complete the development of a comprehensive module qualification test.

Conclusions

Ongoing work in PV standards development, both domestic and international, continued. For the first time, a group of worldwide national laboratories agreed on a single scale for PV reference cell calibrations.

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Fig. 1. Normalized reference cell calibration results for the World PV Scale group. The overall 2σ standard deviation is 1.9%. The point marked with a vertical arrow was removed as an outlier, and cells indicated with a (*) had defects that may affect the calibration uncertainty. Laboratory designations indicate the order in which the cells were circulated and the calibration methods used.

Title: Reliability Science of Encapsulated PV Cells and Modules

Organization: Center for Performance Engineering and Reliability

Contributors: A.W. Czanderna, Leader; F. J. Pern, S. H. Glick

Objectives:

The task goals are to develop and demonstrate innovative flat-plate PV module encapsulation materials that will provide optimum module performance and protection from the environment for a 30-year operational life in the field. The long-term objectives of this research are (1) to identify, understand, and then *mitigate* the causes of changes in PV cell and module materials that alter crucial component materials properties and reduce the performance and/or limit the *service life* of encapsulated cells and modules and (2) to identify or develop new or improved materials, incorporate them into minimodules with different encapsulation schemes, and determine if greater promise is offered for a module service lifetime of 30 years or more.

The objectives for FY1996 were to identify (a) test and screen new or improved materials that offer greater promise for a module life expectancy of over 30 years and meet low-cost goals; (b) optimal durability testing procedures and protocols; (c) PV technology specific compatibility/durability problems at material interfaces in cells/modules; (d) the causes of PV module failure or change in module materials that limit the service life or reduce the performance of the module; (e) new or improved encapsulation system designs or processing, fabrication, and construction methods that will extend the module lifetime; (f) degradation and failure mechanisms that can be used for analytical evaluation of module service life; (g) identify and test various superstrate materials (polymers and glass) for improving the photostability of ethylene vinyl acetate (EVA); and (h) test commercially available adhesive films for simplifying the PV module encapsulation process.

Technical Approach:

The eight objectives were addressed primarily for contemporary crystalline silicon flat-plate PV module technologies with the expectation that the same *general* approaches will be applicable to thin film PV modules when service life becomes an important issue for them. The technical approach consisted of establishing test methods, conducting experimental work, interpreting the results, and seeking solutions to module reliability and materials durability problems. The background and problems associated with EVA degradation in PV modules have been summarized.¹⁻⁴ A critical review of using EVA as a pottant in PV modules⁵ and factors that affect the EVA pottant discoloration rate upon accelerated exposure have been published.⁶

The generic module materials durability studies were performed primarily on polymeric pottant materials of EVA. Efforts to modify the present commercially available formulations of EVA with improved UV and thermal stabilizers have been completed and the modified materials are being validated by using accelerated life testing (ALT) and will be ranked against the existing formulations (A9918, 15295, and 15295P). The modified formulations that rank the best versus A9918 and/or 15295 and equivalents are being prepared in sufficient quantity for more quantitative ALT and deployment for real-time testing (RTT) in minimodules. All samples are being studied as separate materials, materials in contact with other module components, and in complete minimodules. The materials are being subjected to ALT using DSET Suntest units, Oriel solar simulators, and other existing light sources for test-size specimens; for ALT in FY 1997, we will be using two

to separate mechanisms thought to include UV, T, humidity, and possibly metal ion catalyzed effects.

The degradation is monitored from characterization measurements made before, during, and after testing, as described.¹⁻⁸ Nondestructive measurements of degradation that can be used in the field will be sought. Degradation mechanisms will be identified to assist in selecting new or modified materials options. The mechanisms will eventually be necessary for projecting module service lifetime. If our personnel resources are increased in the future, characterization measurements will be made on field-degraded EVA secured from the Israel National Solar Energy Center, SWDTI, and our industrial partners requesting assistance.

Efforts are being continued to identify an appropriate low-cost cover glass or polymer (e.g., Tefzel and/or modified PMMA) that will serve as an effective UV screen for EVA or remove the discoloration via photobleaching reactions, respectively. UV-vis measurements are made for the candidate materials, which will be laminated with EVA and added to our ALT matrix of experiments. The most recent of these efforts will be published in FY1997, and the potential for using self-assembled monolayers in surface modification schemes to inhibit degradative reactions will be assessed, particularly at metallization/polymer interfaces.

Results: EVA and Alternative Polymer Pottants in Crystalline Silicon Modules

EVA as a Pottant: Our critical review about EVA as a PV pottant, which consumed 82 journal pages and reviewed the literature on EVA dating to the 1950s, was finally published.⁵ The three principal foci of the review are on the development of the encapsulant by JPL and Springborn, their accelerated life testing of it and comparisons with deployment in the field, and the extensive and more complete studies of EVA degradation at NREL since 1990. With our task work now focusing on advanced encapsulants that are either improved EVA or new polymers, this chapter provides the worldwide PV community with the benefit of the NREL work. The review also places in context the reasons for the erroneous projections of service lifetime for EVA (one author projected 750 years!) within the framework of the fundamental limitations of EVA photothermal degradation in an encapsulated system without any UV filtering. It further addresses the issue of the completeness of R&D that needs to be done to permit valid projections for service lifetime of an encapsulated PV system. We concluded that the present alternative pottant polymers must be validated and additional polymers sought for assuring that a ">30-year pottant" will be available to the PV industry after the year 2000.

Degradation Mechanisms: Summaries of the known degradation mechanisms are available.^{2,5,7} Although 15295 EVA discolours and degrades by the same mechanism as A9918 EVA,⁷ it does so at a slower rate, as our studies have shown.⁸

EVA Discoloration Rate: Most of the factors that affect the discoloration rate of EVA copolymer encapsulants used in c-Si PV modules upon accelerated exposure have been investigated by employing UV-visible spectrophotometry, spectrocolorimetry, and fluorescence analysis measurements. The results indicate that the extent of EVA discoloration can be affected by both chemical and physical factors. Five chemical factors and five physical factors were studied and reported.^{3,6,8}

Effects of Thermal Processing and Formulation Additive on Degradation. An increased number of UV-excitable chromophores can be formed during the lamination and curing cycles when processing EVA. The antioxidant Naugard P additive greatly enhances the formation of UV-

excitable chromophores during curing, but other antioxidants do not.⁹ Increased concentration of UV-excitable chromophores absorb radiation and initiate the processes that result in degradation of EVA.

Which EVA and Superstrate to Use? We made an unequivocal recommendation to the PV industry in 1994 *that if they continue using EVA*, the formulation 15295 or 15295P (fast-cured with Lupersol TBEC) be used in place of A9918 for a slower discoloration rate. This recommendation followed slightly over 3 years of work in which field-degraded specimens were analyzed, the mechanisms of degradation of EVA were elucidated, and laboratory investigations were used to understand the causes of yellowing and how the processes are retarded. Mobil Solar began work in the summer of 1991 to change to a different polymer, which was a direct result of interactions with NREL, and announced the change in November 1993. Solarex began using 15295 EVA exclusively in late 1987 by laminating and curing in vacuum; their modules are widely thought to discolor at the slowest rate of the known EVA-encapsulated modules. The reasons for the slower discoloration rate are summarized in recent reviews.^{5,6} The discoloration of both A9918 and 15295 EVA is slowed further by the use of a cerium-containing glass,^{5,6} which was recommended for consideration by industry in 1991 by NREL. Although our recommendation was not accepted at the time, some PV manufacturers have used it unintentionally since 1990.

New EVA Formulations: We have identified several combinations of stabilizers other than Tinuvin 770 and Naugard P that show a large improvement for stabilizing Cyasorb UV 531 or other UV absorbers against discoloration.⁵ The modified Elvax 150 formulations are currently being tested as laminated films and in minimodules; a patent application will be filed in FY1997.

Efficiency Losses: We have continued to collaborate on projects in which the efficiency losses from yellowed EVA in modules or minimodules are being monitored. Details are available in reports from the literature,^{10a} SWDTI,^{10b} and NREL.^{1,5}

Equipment Installation and Acquisitions: We have been using a custom-made laminator for making "2 x 2" up to 4" x 4" minimodules. In addition, we installed three major pieces of capital equipment necessary for the preparation, ALT, and characterization of encapsulated PV cells and minimodules, i.e., a regular WeatherOmeter (UV, T, and RH control), a custom-made, prototype WeatherOmeter (WOM) that with modification will permit in situ I-V measurements **during** the ALT, and a custom-made miniextruder. We also subcontracted work to build a custom-made, prototype, portable degradation monitor. With the monitor, the transmittance or absorbance, reflectance, color indices (yellowness), fluorescence of EVA or other polymers and their I-V response can be measured for encapsulated PV cells or encapsulated PV cells/modules in field-deployed specimens.

With the equipment, NREL can now prepare high-quality, compounded polymer films on a laboratory scale, laminate PV cells into an encapsulated system of contemporary or advanced design, subject them to extended ALT in the WOMs, and use (mostly) existing characterization capabilities before, during, and after the ALT to establish causes of degradation. From the latter, revised formulations/designs will be devised until the further ALT, diagnostic, and mechanistic work will permit *valid* service lifetime projections.^{11,12}

Industrial Interactions: We have interacted extensively with over 50 personnel from the PV and chemical industries to exchange information and/or secure samples of various polymer encapsulant candidates and glass superstrate materials for improving EVA photostability.

Other Activities: (1) A patent application and an invention disclosure were filed for modified EVA formulations. (2) A. Czanderna served as guest editor for a special issue of *Solar Energy Materials and Solar Cells (SEM/SC)* containing expanded versions of the most significant papers presented at the WCPEC. Fifty-three peer-reviewed manuscripts are included in the special issue.¹³ (3) We also developed new characterization techniques to study EVA browning,¹⁴ summarized the current status of reliability issues in PV modules,¹⁵ led a small group that summarized the challenges and opportunities in photochemistry research in an OER/BES/DCS-sponsored workshop,¹⁶ and made a minor contribution to a chapter on PV performance and reliability.¹⁷ (4) In two articles, J. Pern summarized general aspects of (a) PV development and applications and (b) PV encapsulation techniques and EVA browning issues for Chinese journals.

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PV Module and System Performance and Engineering Subcontracts

Title: Photovoltaic Module Certification/Laboratory Accreditation Criteria Development

Organization: Arizona State University
Tempe, Arizona

National Renewable Energy Laboratory
Golden, Colorado

Contributors: R.L. Hammond, B.D. Wood, C.E. Backus, R.L. Sears, Principle Investigators, ASU
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Objectives

The objectives of this subcontracted work were to perform much of the development and groundwork that would be needed prior to the actual initiation of a certification/accreditation program, using the continuity and momentum from the first phase of this project [1]. Specific tasks that were to be accomplished included:

- Developing the pro forma corporation bylaws and draft articles of incorporation needed to form a certification body, using the criteria in documents PV-1, PV-2, and PV-3 (developed in the first phase [1]).
- Developing the pro forma budget for a certification body
- Developing recommendations for obtaining seed money to implement a certification program
- Recommending either the American Association for Laboratory Accreditation or the National Voluntary Accreditation Program as the laboratory accreditation body for the program
- Identifying possible refinements to the performance testing procedures contained in PV-3
- Motivating senior-level managers of PV manufacturers to endorse and participate in the potential certification program
- Developing a measurement traceability hierarchy to either the National Institute for Standards and Technology or the World Radiometric Reference for all measurements needed for certification.

Technical Approach

The approach used to develop the required documents in this phase was similar to that used in the first phase. ASU wrote the initial drafts of the documents by drawing heavily on domestic and international standards for certification and labeling programs. The drafts were then distributed to a 30-member criteria development committee representing PV manufacturers, end users, standards and codes organizations, and testing laboratories. Comments and objections received from committee members via fax and telephone were then incorporated into the draft documents. This approach minimized the need for committee meetings; in fact, only a single meeting at the outset was held.

Results

Most of the documents developed under this phase were not controversial. This was probably due to the fact that most were administrative or legal in nature. As such, only the initial drafts of the documents were sent to the committee for comments. The first of all documents received a majority consensus. The second and final draft of each document therefore represented a total consensus of the committee. ASU assembled the documents into a final subcontract report which was then edited and published as an NREL technical report [2].

In order to make the report complete and standalone, the criteria documents from the first phase, PV-1, PV-2, and PV-3, were included. Additional criteria documents developed for this phase were PV-4 and

PV-5, an addendum to PV-1, and the proposed legal structure of the certification body. These documents are named below.

PV-1 Criteria for a Model Quality System for Laboratories Engaged in Testing Photovoltaic Modules

PV-1.1 Calibration, Traceability, and Statistical Requirements of Accredited Laboratories Supporting the Photovoltaic Module Certification Program

PV-2 Model for a Third-Party Certification and Labeling Program for Photovoltaic Modules

PV-3 Testing Requirements for a Certification and Labeling Program for Photovoltaic Modules

PV-4 Operational Procedures Manual for the Certification Body of the Photovoltaic Module Certification Program

PV-5 Application and Certification Procedures for the Photovoltaic Module Certification Program

Legal Structure:

Articles of incorporation

Bylaws

General rules of procedure for standing committees

Specific rules of procedure for standing committees

Following the completion of the subcontract by ASU and the publication of the technical report, efforts were made to initiate a PV certification program using these materials. These efforts resulted in the formation of PowerMark Corporation (PMC), a non-profit corporation. Manufacturers that have joined the program and currently are represented on the PMC Board of Directors includes Solarex Corporation, AstroPower, and ASE Americas. PMC has formed most of the needed committees and is preparing to begin certification testing by the spring of 1997.

Conclusions

A subcontract with Arizona State University has resulted in a technical report that contains all of the draft documents and information needed to initiate a third-party certification and labeling program specifically for PV modules. These criteria were used to form PowerMark Corporation, a PV module certification body that is currently working toward initiation of testing to certify module designs.

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Title: NREL Module Energy Rating Methodology

Organization: Endecon Engineering, San Ramon, CA

Contributors: C. Whitaker, Principal Investigator; J. Newmiller, W. Howard; L. Mrig
B. Kroposki, D. Myers, K. Emery, and J. Anderson

Objectives

Develop a simple measure of PV performance that will provide a realistic estimate of how one or more modules will perform in a user's specific application.

Technical Approach

A strawman approach to a module energy rating was developed. Then an industry Technical Review Committee (TRC) to provide feedback and guidance on the strawman and subsequent documents convened. Finally a PV performance model of sufficient accuracy was developed and validated. Along with the model, weather data profiles were defined that describe a range of operating conditions in the U. S. These conditions emphasize performance differences between various module types.

Results

Some general characteristics of a module energy rating were decided. These were:

- Target audience is primarily the end user
- Ratings should provide stabilized single-module energy values in Watt-hours
- Energy values should be provided for both peak-power and fixed voltage operation
- Flat-plate modules should be modeled with fixed latitude-tilt orientation
- Concentrator modules should be modeled with two-axis tracking orientation
- Energy values should be based on four extreme conditions days and one average day

Model validation and sample calculations were performed between August and December 1995, at which point the draft final report was sent out to the TRC [1]. A paper was also presented at the 25th IEEE conference that detailed the methodology [2].

Conclusions

A general method for describing a PV module energy rating was developed and agreed upon by an industry-representative Technical Review Committee. Specific reference day conditions were developed and defined. There are still issues to resolve regarding the validation of the energy rating methodology. Among the issues is how to accurately define the power output of modules under various conditions. Also defining a characterization method that accurately predicts outdoor performance is critical.

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Abstract

Under the DOE sponsored PV:BONUS Program, Energy Conversion Devices, Inc. (ECD) and United Solar Systems Corp. (United Solar) have developed and are now demonstrating and commercializing two new lightweight flexible BIPV modules specifically designed as replacements for conventional asphalt shingles and standing seam metal roofing. These modules can be economically and aesthetically integrated into new residential and commercial buildings, and used to address the even larger roofing-replacement market. An important design feature of these modules, which minimizes the installation and balance of system costs, is their ability to be installed by conventional roofing contractors without special training. The modules will be fabricated from high-efficiency, triple-junction spectrum-splitting a-Si alloy solar cells developed by ECD and United Solar. These cells are produced on a thin, flexible, approximately half-mile long stainless steel substrate in roll-to-roll deposition machines fabricated by ECD, and encapsulated with polymer materials.

In this report we summarize the principal features of these two new BIPV modules and highlight the demonstration programs which are showcasing these modules. United Solar will begin marketing these new BIPV products in 1997.

Shingle Module

United Solar has developed a photovoltaic shingle module[1] that emulates a conventional asphalt shingle in form, structural function and installation. The module can be easily and aesthetically incorporated into any building that would ordinarily use asphalt shingles. The module requires no special mounting hardware and is fastened to the roof sheathing with a conventional roofing nail. Experienced roofing tradesmen, with no previous PV experience, can be trained to install these module in about 2 hours; through an iterative optimization of the module design and of installation techniques, the installation time for these modules has been reduced to about 1.5 times that of conventional shingles. An important feature of this design is that the mechanical and electrical installations are performed separately and independently by roofers and electricians respectively.

To install the modules, the workmen first drill a series of holes in the roof using chalk lines and a hole-template. The workmen then remove the release paper covering a small piece of adhesive sealing membrane on the module where the leads exit, insert the leads through the hole in the roof, position the module, and fasten the module with roofing nails. The modules are lightweight (about 7 oz/ft²) and are consequently easily handled. At a later time, an electrician working under the roof connects the modules leads together using epoxy sealing wire nuts. The wires are run through conduits and wire raceways to the combiner boxes.

In June a 2 kW array of prototype shingle modules was installed on the Southface Ecology House in the Atlanta Olympic Village. This installation, shown in Fig. 2, has since been receiving very favorable reviews from architects, builders, and visitors to the center. In November this new product received Popular Science's 1996 "Best of What's New" Grand Award.

Standing Seam Metal Roofing Module

ECD has developed a PV metal roofing panel that is an exact replacement for a standard metal roofing "pan" manufactured by the ATAS International Corp. in Allentown PA. It requires no electrical feedthroughs or additional fasteners, and uses standard metal roofing materials and installation techniques already in use by the metal roofing industry. The modules are fabricated from triple-junction spectrum-splitting a-Si alloy solar cells produced on a thin, flexible stainless steel substrate. The polymer-encapsulated modules are large-area (typically up to 22 ft long and 1.5 ft wide), lightweight, and flexible. The metal roofing pan is made from galvanized-aluminum substrate finished with a fluoropolymer paint.

Figure 2. United Solar's Shingle Modules on the Southface Ecology House at Olympic Village in Atlanta, Georgia, July 1996.

Figure 3. ECD's PV Metal Roofing Modules on the NAHB Research Center 21st Century Townhouse Project.

An important feature of the module, which minimizes the total system's costs, is that the module can be installed by conventional roofing contractors and electricians without any special training. ECD's metal roofing has been showcased on the National Association of Home Builders Research Center's 21st Century Townhouse Project in their research park outside Washington, D.C. (see Fig. 3). The installation for the 18 panels took approximately 5 minutes per panel. Most of the roofer's time was spent on the detail trim work. After the installation, the roofers reported that (1) installing the PV was no different or time-consuming than installing a conventional roof; (2) the PV panels were a bit easier to manage than conventional metal pans due to the increased stiffness from the lamination. Since May the array has been in operation charging a set of sealed lead-acid batteries and feeding excess power to the grid.

ECD and United Solar are in the process of refining the product design for widespread commercialization. While the prototype PV metal roofing modules were designed to be interchangeable with a specific metal roofing panel (ATAS International's standing-seam panel) new products are being designed to be compatible with any type of structural or architectural standing seam metal roofing system.

Conclusions

ECD and United Solar have developed two new PV roofing products that take advantage of the lightweight, flexible PV material manufactured by United Solar. The products are being refined to minimize cost and installation time, the latter being a new constraint on module design. Both products are being qualified to IEEE par 1262 standard and will have U.L. approval. Commercial production will begin in 1997.

Acknowledgments

We would like to acknowledge the help of our colleagues at the following organization who have helped make this project a success: Kurt Kaminer at Arizona Public Service Company, Bob Pratt at Detroit Edison, Kip Serota at Minoru Yamasaki Associates, and Steven Strong at Solar Design Associates.

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Title: PV Module Degradation--EVA Pore Volume

Organization: Polymer Science Dept., Penn State Univ., University Park, PA

Contributors: D. L. Allara, principal investigator

Objective:

The objectives of this effort were (i) to conduct a methodical evaluation of the feasibility of using spectroscopic ellipsometry (SE) as a non-destructive means of detecting the pore or void volume changes in ethylene vinyl acetate (EVA) as a result of increased curing of the polymer, and (ii) to use data from objective (i) to evaluate the potential of using SE for correlating the extent of degradation in field-degraded samples with the expected increase in gel content from prior NREL studies of clear, light yellow, yellow, yellow brown, and brown EVA.

Technical Approach:

As background, the long term degradation of modules fabricated with ethylene vinyl acetate (EVA) copolymer has been an ongoing concern to the DOE PV Program and to PV manufacturers. Evidence indicates that the EVA degradation is related to the formulation of EVA as well as the EVA copolymer itself (See the report on Reliability Science of Encapsulated PV Cells/Modules elsewhere in this volume). A need exists for measuring the extent of degradation of EVA for field deployed modules as well as for laboratory test specimens. One measure of the degradation is the gel content of the EVA, and how this changes with time. The increase in gel content will of necessity cause a change in the pore volume in the polymer from cross linking. The latter alters the physical properties of the polymer that may cause the EVA to lose important components of their physical properties.

EVA was prepared with varying gel content as specimens that are suitable for making state-of-the-art, SE measurements of the pore or void volume. The gel content has been varied from 50% to at least 100% and determined by an extraction procedure. If a suitable correlation can be established for the EVA thickness that is optimal for SE measurements, the thickness will be varied to approach commercial reality and to determine the feasibility of SE measurements for determining pore sizes in EVA of increasing thicknesses.

SE will then be used to establish the feasibility of obtaining a correlation between the pore size and distribution in EVA prepared by NREL staff. The EVA, which has been degraded in various stages from criteria already known to NREL staff, was prepared on substrates and in the configuration to provide optimum results from the SE measurements. Ultimately, the samples will be prepared at several thicknesses that approach reality to establish how well the SE measurements still correlate with the extent of degradation.

Results and Discussion:

Curing of EVA thin films. Thin films of EVA copolymer were prepared in the thickness range 20 nm to 200 nm, and then cured under vacuum at $145^{\circ}\text{C} \pm 2^{\circ}\text{C}$ for 1 h. The samples were placed in

a vacuum oven equipped with a Varian direct drive vacuum pump that was used to maintain continually the oven pressure at 50 mTorr. Before use, the oven was thoroughly cleaned with ethanol and kept under vacuum at 100°C for 12 h. After the 1 h cure, the samples were kept under vacuum and returned to room temperature over the course of 12 h.

Single wavelength ellipsometry data taken on the samples before and after the curing process were virtually identical for the entire thickness range of the films. However, the beam from the helium-neon laser (632.8 nm) in the ellipsometer was observed to scatter on some parts of the cured wafers indicated the existence of a roughness above $\sim 1 \mu\text{m}$. Further, the film surfaces were inhomogeneous by visual inspection. It appeared that the film surfaces roughened during the cure in localized regions. This same phenomenon was observed during spectroscopic ellipsometry (SE) measurements and will be discussed below.

Infrared (IR) Spectra. Polarized IR spectra of a 91.8 nm EVA film have been obtained and analyzed as difference spectra by subtracting the IR spectrum taken for an uncured sample from the corresponding cured one. Using a kinematic sample holder, the exact same portion of the film was analyzed in obtaining both spectra. The difference spectrum shows that the curing process results in a slight reduction in the methyl C-H and the carbonyl stretching intensities ($\sim 5\%$) but does not reveal the presence of any new absorptions nor any significant peak frequency shifts. In the case of a 53.2 nm film, the observed changes were even smaller. For all film thicknesses, the small decreases in the IR peak intensities are consistent with small changes in the film density possibly arising from evaporation of residual solvent and/or physisorbed organic impurities (the cure temperature is over 200°C above T_g). A polarization difference spectrum was obtained by placing the cured sample at two orthogonal orientations relative to the polarizer transmission axes (while maintaining normal incidence) and then subtracting the two spectra obtained. The spectrum shows that the films are completely amorphous with no net orientation of the IR-active functional groups in the copolymer.

Spectroscopic Ellipsometry (SE). In the spectroscopic ellipsometer used in these studies, a broadband output of a xenon arc lamp is directed along a set of optical rails mounted on a goniometer. For the present measurements, a fixed angle of incidence of 69.5° was used. To maximize the source intensity at the sample, the source is collimated by focusing the light to a point, using a short focal length lens placed adjacent to the Xe lamp, adjusting the size of the point with an iris and then passing the diverging beam from the point into another lens, which is placed at a distance equal to its focal length away from the iris, to generate a final collimated output beam. The latter is then sent through a calcite polarizer, which is rotating at a fixed frequency and in this case is about 55 Hz. The speed of rotation need not be constant, and may be set to any speed that the encoder circuit and feedback electronics can accept. The effect of the rotating polarizer is to create rotating, linearly polarized light, which then reflects off the sample. The sample has x,y,z, and q degrees of freedom. After reflection from the sample, the light is directed through a calcite polarizer (analyzer) for which the polarization direction is held fixed at 30° with respect to the optical bench. The linearly polarized output light is then directed into a Czerny-Turner double monochromator with a resolution of 0.5 nm. The detector is a 5 amp Hamamatsu PMT. The output signal, modulated by the rotation frequency of the polarizer, is transformed by Hadamard analysis to the desired quantities ψ and Δ . These variables completely describe the change in the polarization state of the light upon reflection from the sample (e.g., see R.M.A. Azzam and N.M. Bashara, *Ellipsometry and Polarized Light*, North Holland, Amsterdam, 1977, Chapter 3).

The SE instrument was calibrated using a 200 nm gold film evaporated on a silicon wafer. Gold was chosen for its high reflectivity and extreme sensitivity to the angle incidence. Therefore, it is a good test to verify that the optical alignment has not significantly drifted over time. The simulation is for the simple 2-layer air-gold model, and shows a very good fit to the experimental spectrum.

The SE data for three EVA films of thicknesses 21.5 nm, 52.3 nm, and 91.8 nm were plotted as an overlay of difference spectra for the uncured film at various locations on the wafer. This provides information about the spot to spot thickness gradients of the film. These spectra were then compared to simulated spectra of SiO₂ films of the same thicknesses on Si(111). The SiO₂ spectra are similar to the EVA ones and showed the same peaks and overall curve shape; however, the peak locations were shifted in energy to higher and/or lower values. These simulations verify that the peaks observed in the EVA spectra are caused by film thickness interference effects, and not to electronic features in the films.

A second spectrum, which was obtained for an average of 2 to 5 spots on the sample, included for each thickness an overlay plot of the cured and uncured samples. The standard deviation of the two data sets are similar in each case; however, the analysis time was longer for the cured films because diffuse scattering of the light beam reduces the intensity at the detector with a consequent decrease in signal to noise. It appears that the changes observed are about twice the magnitude of the sample spot-to-spot variation. A thorough error analysis of this effect is in progress. In contrast to the uncured samples, the source beam spot was visible on the cured films (it was approximately a 1 mm x 3 mm ellipse). A third plot was taken as a difference spectrum of the data found for the cured and uncured EVA. In all cases, the observed changes are located near peaks in the y and Δ spectra. This is reasonable since these are the wavelength regions that are most sensitive to the particular wafer thickness.

Work at NREL in FY1996. Five analyzed thin-film A9918P EVA layers of varying thickness that had been spun-coated onto silicon-[111] substrates were sent to NREL for exposure to degradative treatments. The exposure was accomplished in a DSET Suntest CPS unit with flowing N₂ at a BPT of 58°C to 60°C for about 5 months. The samples were exposed along with controls. Further details about the exposure will be part of the final report due in FY1997. Results from fluorescence analysis at NREL show that photobleaching of chromophores occurred due to the presence of trace O₂ in the flowing N₂. Under the same conditions, A9918 EVA degrades and turns a light yellow. After the exposures, the thicker EVA layers are no longer uniform. A full analysis of IR and SE data taken in FY1995 of the cured films and the degraded films will be completed when the complete data sets, including those from the fully degraded films, are in hand. The samples were returned to the PI in September, 1996; the final report is due in December, 1996.

Conclusions:

As a potential non-intrusive test for polymer degradation in field-degraded modules, the investigators are using IR and SE as tools in which SE has the potential of being used for measuring changes in the pore volume in the polymer. Their initial characterization with both SE and IR show that A9918 EVA films suffer no obvious chemical or orientational changes after exposure to the standard thermal curing conditions, although visual inspection shows that the surfaces have become inhomogeneous and rougher. The IR data show that the films remain amorphous with no evidence for forming crosslinking or conjugated double bonds at the sensitivity of the IR probe. Small

changes in thickness develop based on the SE data. After degradation in UV and T for about five months to induce changes that are known to cause gel content changes, the samples were returned to Penn State for SE and IR evaluation in early FY1997.

Title: Long Term Effects on Roof-Mounted Photovoltaic Modules

Organization: Southwest Technology Development Institute (SWTDI)

Contributors: A. Rosenthal and S. Durand

Objectives

The objectives of this effort were (i) to conduct a methodical monitoring of roof-mounted, PV module performance degradation, and (ii) to document module operating temperatures as a function of roof-mount design.

Technical Approach

The essential content below was reported in 1995 [1a]. The long term degradation of modules fabricated with EVA is an ongoing concern to the DOE PV Program and to PV manufacturers. The rate of EVA degradation is related to module operating temperature, which raises concerns about roof-mounted modules since they operate hotter than ground- or rack-mounted modules.

In coordination with NREL staff, SWTDI selected 12 modules of a specific design from each of 4 manufacturers that had been dedicated to a long term evaluation effort. Modules with a significant exposure history (installed prior to 1985) were selected. Both crystalline and thin film modules were chosen for evaluation. All of the modules available for this project had already been mounted on the rooftops of prototype buildings at the SWTDI. Selected modules on each prototype building were rewired so that each module is electrically terminated at a terminal strip to facilitate taking individual module I-V curves. Each of these modules has a thermocouple bonded to its back surface and terminated at the terminal strip. For the modules selected, SWTDI records were reviewed to retrieve available data on the "as delivered" module efficiencies. Manufacturers were also contacted to determine if records of individual module I-V curves were available and if they would be able to retrieve I-V curve data for the selected modules. When individual module efficiencies could not be obtained, measured array efficiencies were used to estimate individual module efficiencies.

For the selected modules, SWTDI measured the individual module efficiencies at the beginning of the contract, and obtained I-V curves (light only) at a measured module temperature. SWTDI developed a detailed measurement protocol that was reviewed by NREL prior to beginning the measurements. SWTDI then made the measurements according to their planned protocol at intervals from Feb. 1992 through April, 1994; the project was again funded from November, 1994 through February, 1996 with the same technical approach, except dark I-V curves were also requested by NREL. SWTDI provided NREL with a copy of the data as well as with a summary report after data collection. Following the initial efficiency measurements, one module of each type was packaged and shipped to NREL for destructive analysis. The remaining modules remained mounted at SWTDI for continued, real-time, exposure testing in the Las Cruces, NM solar environment.

For objective (ii), SWTDI prepared a summary report documenting all module mounting designs installed at SWTDI along with an evaluation of the module operating temperatures. The summary report included a commentary on the various mounting methods that discusses the design tradeoffs such as ease of installation, ease of maintenance, water tightness, and the design impact on module operating temperature. Results of a 1985 SWRES study of module temperature vs. module spacing above the roof were also included. This summary report was delivered in 1992, three months after the contract was initiated. For objective (i), the final report was delivered to NREL in May, 1994, for the period 2/1992-4/1994; a report covering 11/94 through 2/96 was received in 12/96.

Hardware Limitations in the Long-Term Evaluation of Modules

The project test plan required I-V curves to be taken on 48 PV modules every two weeks for several years. Prior to the implementation of testing, dedicated hardware was developed for this purpose. The hardware, which was designed by engineers on the staff of SWTDI, was also reviewed by a professor of power electronics at New Mexico State University.

The I-V curve tracer that was developed uses the following instruments to measure the necessary parameters:

Table 1. Sensor Hardware

<u>Parameter</u>	<u>Sensor</u>	<u>Accuracy</u>	<u>Repeatability</u>
DC Current	Current Shunt	$\pm 0.1\%$	$\pm 0.1\%$
DC Voltage	Voltage Divider	$\pm 0.1\%$	$\pm 0.1\%$
Irradiance	LiCor Pyranometer	$\pm 3\%$ (typ)	$\pm 1\%$
Temperature	Type T Thermocouple	$\pm 1^\circ\text{C}$	$\pm 0.2\%$
	Total	$\leq 5\%$	$\leq 2\%$

In addition to the sensors, the I-V curve tracer uses a 14 bit analog to digital converter (A/D) with an accuracy of ± 1 LSB. This represents a possible error of only 1 part in about 16,000.

For this project, the absolute accuracy of a given module I-V curve was not as important as the ability to resolve changes recorded in successive I-V curves for each module, so the repeatability figure is extremely important. The repeatability figure of $\pm 2\%$ (Table 1) indicates that changes in module performance can only be unambiguously resolved when they exceed 2%.

Unfortunately, raw I-V curves cannot be compared directly. Since module performance is a function of both irradiance and module temperature, I-V curves acquired under various conditions must be normalized (translated) to a set of standard conditions for comparisons to be meaningful. Normalization was performed according to the procedure given in ASTM 1036-85 in which a set of standard algorithms was used in conjunction with module specific coefficients to translate an I-V curve acquired under one set of conditions to its analog under another (standard) set of conditions. There are limits to the accuracy and repeatability associated with using these normalizing equations. These limits are a function of how accurately the normalizing coefficients have been derived and how large the difference is between the actual and standard conditions. In general use, normalization according to the ASTM standard is probably accurate to only $\pm 5\%$ for any given I-V curve. With careful practice, $\pm 2\%$ is a reasonable estimate of the accuracy of the normalization.

Results and Discussion:

The criteria for selecting the four arrays/module types used in this study were as follows. All candidate modules had to have been encapsulated with EVA (ethylene vinyl acetate) and passed JPL Block V specifications. Preference was given to the arrays and modules that had achieved the longest cumulative exposure to sunlight and for which early performance documentation was available.

The four arrays/module types selected for the study were (a) Solarex model MIT#1002967 polycrystalline silicon modules installed in July 1981, (b) Mobil Solar model Ra-180 single crystal silicon modules installed in October 1983, (c) Solarex model SA-20 amorphous silicon modules installed in May 1988, and (d) Sovonics model P-101 amorphous silicon modules installed in January 1989. All performance reports presented mean ratings (normalized to conditions of 1000 W/m² and 45°C module temperature) for the modules in each of the four arrays. Normalization was achieved using coefficients derived according to the ASTM standard E1036-85. That method utilizes I-V data obtained over a range of temperatures. The coefficients for each module type are

listed for each module in the final report. The mean module rating is presented in Table 1 for each array under test since the project was begun in 1992.

Table 1. Normalized Mean Module Ratings In Watts (W)

Array	(7/92) (W)	(1/93) (W)	(7/93) (W)	4/94 (W)	(3/95) (W)	(11/95) (W)	Loss %
Solarex MIT	49.05	49.60	48.19	47.62	47.4	47.8*	3.5%
Mobil Ra-180	129.45	128.45	131.10	127.63	130.2	123.0	4.6%
Solarex SA-20	12.21	11.31	12.5	11.61	11.16	11.25	**-
Sovonics P-101	10.07***	7.50	8.72	7.61	7.59	7.82	----

*One module was removed for destructive analysis in April, 1994, with a rating of 43.3 W and 9.9% decline from its output in 11/1992. It was projected to be 40.5 W (4%/year) for the purposes of this Table [1b].

**A 10% decline occurred in one year for one of the eight modules; five of the ten failed by 11/95.

***Inaccurate first rating reflects improper normalization.

After three years of study, some of the modules demonstrate an unambiguous decline in performance, as can be seen by the loss in percent over the 3.5-year period. For example, the Solarex MIT modules exhibit a **collective** loss of 3.5% per module. However, a detailed analysis on a **module by module** basis for the ten Solarex modules deployed in 1981 show declines of 3% to 10% for 5 modules, but 1.5% or less for the other 5. While the average of all ten modules is 3.5% or 1.0% per year, three of the modules exhibited declines in excess of 2.3 %/year. The EVA in all of the modules has a yellow-brown color. The widening variances in the module power output can be a source of mismatch losses in large arrays, but the only possible mismatch losses in the present study is for differences in the output of each individual cell in series with each other. Additional comments on the four module types were reported for the period 2/1992 through 4/1994 [1b].

Future:

The initial SWTDI subcontract expired in April, 1994, but a new subcontract was placed to cover an additional 15 months of monitoring from November, 1994 through February, 1996. The work reported by SWTDI and NREL analysis of the data demonstrate that monitoring individual modules is essential to identify which modules undergo accelerated degradation. The modules that degrade the most can be more gainfully subjected to post mortem analyses to learn more about the **causes** of the degradation.

The only other published systematic monitoring of performance losses of individual modules in an array was reported recently by D. Faiman and coworkers of Ben Gurion U. (BGU), Israel [2]. Both the SWTDI and BGU studies would be better if I-V data had been gathered on each individual module at the time of deployment and periodically thereafter, and if dark I-V data were also collected during the present and ongoing monitoring. The latter was specified in the SWTDI contract extension. The failed and badly degraded modules will be sent to NREL in 1997 for post mortem analyses.

1. a. NREL Photovoltaic Program FY 1995 Annual Report, S. Smoller, Coordinator, NREL/TP-410-21101, June, 1996, pp. 377-379; b. Ibid, FY1994 report, K.A. Summers, Coordinator, NREL/TP-410-7993, June, 1995, pp. 349-352.
2. D. Berman, S. Biryukov, and D. Faiman, Solar Energy Materials and Solar Cells, **36**, 421 (1995); another paper in the same journal by the same authors is in press for late 1996.

Title: **PV Translations Equations and PV Module Energy Ratings Concept**

Organization: Sunset Technology Corporation
Highlands Ranch, Colorado

Contributors: J. Anderson, Principal Investigator

Objectives

Develop new photovoltaic translation equations for translating photovoltaic I-V performance characteristics from one temperature and irradiance conditions to another such condition. A second task was to develop a concept for an energy rating system for PV modules.

Technical Approach

Translation Equations

New translation equations were developed and extensively checked against actual test data. Compared to the currently-used translation equations, the new equations more accurately translate I_{sc} and V_{oc} , I-V curve data points, and maximum power. The new equations also utilized dimensionless coefficients.

Energy Ratings

The energy rating concept developed has 4 basic parts:

- Universal Map of Performance: This is a matrix of I-V performance characteristics versus irradiance and module temperatures
- Reference Environmental Functions: This is a group of five reference days. Four of these days represent generic extreme days and the fifth reference day represents a nominal type of day.
- Wattage Influence Factor Effects: This segment consists of modifiers which take into account module temperature factors
- Coefficients of Performance: This is the way the energy rating information is displayed.

Results

Translation Equations

New equations have been developed for the purpose of evaluating the performance of photovoltaic cells, modules, panels, and arrays. These equations enable the performance values determined at one temperature and irradiance condition to be translated to any other condition of temperature and irradiance. This method is detailed in reference 1.

Energy Ratings

An approach has been defined for evaluating module energy output in a simple manner. The concept consists of evaluating a module on a solar simulator to derive a matrix of performance characteristics as a function of irradiance and temperature, and then using that data to determine energy output for 5 reference days. This method is detailed in reference 2.

References

1. Anderson, A.J., (January 1996) "Photovoltaic Translation Equations: A New Approach" Final Subcontract report NREL/TP-411-20279
2. Anderson, A.J., (March 1995) "An Energy Rating Concept for Photovoltaic Modules"

Title: **A Prototype Portable Custom-Made PV Encapsulant and Solar Cell Degradation Monitor (A Spectrophotometric Analyzer)**

Organization: University of Colorado at Denver (UCD)

Contributors: J. Boon (PI), L. Anderson, and J. Lanning

Objective

The specific objective of this subcontract project is to use existing knowledge and techniques to fabricate, test, and deliver to NREL a custom-made prototype portable PV encapsulant and solar cell degradation monitor. The prototype portable degradation monitor will reduce to practice an NREL invention disclosure (#IR 95-10). The project is to be completed at the end of 18 months (Sept., 1997). The six (6) main tasks and schedule of deliverables are described in the Statement of Work (SOW).

Technical Approach

Two basic requirements for this project are (1) to complete the architectural design and fabricate a portable degradation monitor and (2) to develop and complete a software module or package that will execute the desired measurements, perform data analysis, and estimate the extent of EVA degradation.

The monitor will be equipped with specially designed or assembled optical, mechanical, electrical, and electronic components and/or features that will perform the desired or required measurement feature(s) by using either a stationary mode or scanning mode. In the optical (spectroscopic) mode measurements of absorption/transmission, fluorescence, and reflectance (for color indices) will be made for the polymer encapsulant by using fiber optics. In the electrical mode measurements, current-voltage (I-V) curves will be acquired for the encapsulated solar cells. Either one or both of the two measurement modes should be selectable by the user.

Developing the software and demonstrating it will accomplish all required functions are the most critical parts for the success of this project. Function control, data acquisition (optical and electrical measurements), display, transfer, storage, processing, manipulations, and analysis will be made with a laptop personal computer (PC) using commercial software and custom programs developed for the project. The custom-developed programs will carry out the functions and demonstrate the capability to automatically manipulate, analyze, and correlate the data files and results acquired from the spectrophotometric and I-V measurements, produce graphical results, and estimate the changes in materials. Programs for estimating the extent of EVA degradation will be developed on the basis of modeling equations and parameters/variables to be established in NREL's PV Module Encapsulation Research Laboratory. Complete documentation and source codes of the programming structure and functions are required and will be provided by UCD.

The project is being closely supervised by the NREL technical monitor, who also provides the necessary guidance and/or directions on the details regarding software development required for the system. Monthly progress reports by UCD are being routinely received, and meetings and discussion regarding the progress and problems, if any, are conducted regularly.

Progress to Date

The UCD group has acquired the parts needed for the hardware (including a laptop PC), completed the system architectural design, fabricated filter wheels and compartment (for absorption/transmission measurement), and completed the part of software architecture for basic system control and data acquisition. A summary titled "Photovoltaic Cell Degradation Monitor Construction Plans" was received on 12/6/96.

For the essential software development and documentation, the basic functions for system control, data acquisitions, and graphic display were demonstrated (12/6) for a *stationary*-mode absorption measurement using an optical fiber and a diode array minispectrometer. The measurement and data display were activated with an icon-control menu in Windows on a laptop PC. These measurement and display functions can be applied to the fluorescence and reflectance measurements with appropriate hardware components installed. The PI is presently trying to resolve some programming hurdles for the control of stepper motors, which is the most pivotal component for the *scanning* mode measurements.

Technical details for the fluorescence, reflectance (for color indices), and I-V measurements are currently being addressed by UCD coinvestigators, Profs. L. Anderson and J. Lanning, who also participated in the design for spectroscopic (L.A.) and I-V (J.L.) measurement functions and hardware respectively. The UCD group was advised to consult K. Emery of NREL on the details of hardware and software design for I-V measurements.

Due to reprioritization of work by the PI, some of the software development and hardware construction are behind schedule, but present expectations are that the project will still be completed by 9/97. This is because the PI is confident that the complete hardware construction and installation for all specific functions can be completed within two to three weeks after major software programming tasks on the I-V, fluorescence, and reflectance measurements are completed.

By mid-January, the PI will deliver the source codes and documentation of completed program parts for review. NREL staff will deliver to UCD some unaged and discolored EVA laminates. The UCD group will use the samples to validate the performance of all three spectroscopic (UV-vis, fluorescence, and reflectance) measurements and compare their results with those acquired at NREL.

Future Work

After completing the complete system hardware installation and performance validation, which is projected to be in mid-March or earlier, no additional hardware construction should be needed. The entire project will then focus on developing the advanced custom software. This will follow discussions about the custom software that will have the functions and capabilities to automatically (1) manipulate, analyze, and correlate the data files and results acquired from the spectrophotometric and I-V measurements, (2) produce graphical results, and (3) estimate the changes in materials. The basic modeling requirements for estimating the extent of EVA degradation will be also discussed and the programming structures established. The last three months of the work are available for further hardware fine-tuning and software modification and finalization, which will include programming effort for modeling the service life prediction.

6.0 PV MARKETS AND APPLICATIONS—Introduction

John Thornton

To help the nation achieve its goals for sustainable energy use and development, the PV Markets and Applications Team supports the analytical, applications, and market development activities of the U.S. Department of Energy's (DOE) National Photovoltaics Program. As we support both DOE Headquarters in Washington, D.C., and the DOE Golden Field Office (GO) in Colorado, we provide a focal point for DOE activities through project development, subcontract management, and technical assistance. Our work is carried out both in-house at the National Renewable Energy Laboratory (NREL) and through subcontracts with other research and development (R&D) groups.

We work closely with other R&D centers at NREL, as well as with staff at Sandia National Laboratories and in the private sector, to achieve our objectives. In FY 1996, the team was also involved in other activities and programs in the DOE Office of Energy Efficiency and Renewable Energy, such as the Federal Energy Management Program (FEMP). In this report, we describe our activities for FY 1996 in two categories: domestic markets and applications and international markets and applications.

Domestic Markets and Applications

Training, Education, and Technical Assistance

Training. Under NREL's direction, the Interstate Renewable Energy Council developed a training program for state parks officials. Called "Workshop in a Box," the program provides a videotape and other tools to help parks officials conduct training sessions within their own agencies. This approach vastly increased the number of people trained each year.

Consumer workshops were a new activity this year. We conducted two at NREL that supplied hands-on training to members of the public interested in installing PV on their residence, farm, or ranch. More than 200 members of the public attended.

Education. During FY 1996, we conducted major educational activities that introduced PV technologies and applications to as many as 1 million people. Our activities included:

- Exhibits and hands-on workshops at the National Western Stock Show in Denver, Colorado
- Operation of a 10-kW PV system at the 1996 Christmas Pageant of Peace in Washington, D.C., which was exposed to more than 200,000 visitors in 3 weeks
- Exhibits shown during Earth Day Week in Washington, D.C.
- Workshops specially tailored for more than 100 state energy officials who visited NREL
- Cost-sharing of a traveling "PV for the Farm" exhibit by the University of Illinois, with potential exposure to 300,000 of the public.

Technical Assistance. We designed and fabricated a 4-kW PV system for a park near DOE Headquarters in Washington, D.C., to demonstrate how well a PV system can be integrated into urban areas. The system will be mounted on the south portal of a highway tunnel that runs under the Mall near the Smithsonian Institution. We are awaiting final permits from the District of Columbia before installing the system.

To help PV become more competitive, NREL also funded analytical support to the National Association of Regulatory Utility Commissioners (NARUC). This support helps to develop policy that will allow PV and other renewables to compete on an equitable basis in a restructured utility environment.

Sunrayce 97

We established Sunrayce 97 headquarters at NREL early in FY 1996. Along with the Sunrayce Board of Governors, headquarters then began planning Sunrayce 97. NREL awarded grants of \$2,000 each to 30 universities that submitted high-quality proposals describing their plans for participation in this popular solar-powered race. In summer 1996, NREL assisted in transferring Sunrayce headquarters to Detroit, Michigan. At the end of FY 1996, we negotiated a subcontract with New Resources Group for all Sunrayce 97 event management.

PV Demand-Side Management Analysis

Developing intermediate markets for photovoltaics is vital to the growth of the PV industry. The building sector is receiving increasing attention for intermediate applications: PV can be used in this key market as a dispatchable peak-shaving tool. The Center for Energy and Environmental Policy (CEEP) at the University of Delaware continues to research the technical and economic viability of dispatchable peak-shaving photovoltaics (DPS-PV) for electric utilities and their customers. CEEP uses its menu-driven *PV Planner* software package to do this.

The FY 1996 objectives of this research were to (1) analyze the value of PV to utilities and their customers as a targeted peak-shaving option in specific areas at specific times, and (2) provide an economic analysis of two complementary applications with significant market potential for integrated PV building systems in the domestic U.S. utility market. These applications are emergency lighting and uninterrupted supplies of power.

CEEP extended the DPS-PV system to incorporate the distributed utility concept. Research shows that the economic value of PV to a utility and its customers is increased by targeting dispatchable PV applications in areas where, and at times when, the utility's avoided costs are high. Many utilities have overlooked the considerable cost of transmission and distribution (T&D) in their resource planning. DPS-PV applications that increase utilities' use of their assets offer significant economic benefits when investment costs rise for local T&D. When the DPS-PV system is sited in an area with a particularly high cost of service, the utility can take advantage of such "nontraditional" benefits.

Utility Support

We continued to provide analytical and technical support to the emerging energy industry. Currently, the influence of deregulation/reregulation and competitive market transformation on utilities' planning and decision making varies from state to state. The situation for individual utilities is evolving and is highly dependent on changes in the regulatory, legislative, and financial sectors. This chaotic situation requires our presence and support not just at the national level but also at the state and community levels.

Support at the National Level. We coordinate work with the Utility PhotoVoltaic Group (UPVG), Photovoltaics for Utilities (PV4U), Interstate Renewable Energy Council (IREC), NARUC, National Association of Utility Consumer Advocates (NASUCA), National Conference of State Legislatures (NCSL), Solar Energy Industries Association (SEIA), and the Energy Information Administration (EIA) at DOE.

Support at the State and Community Level. We direct analytical and technical support provided to state legislatures, energy offices, regulatory commissions, utilities, and municipalities.

Support to Utilities. During FY 1996, this support included the following:

- Developing and testing PV distributed resource software, in coordination with Sandia. Individual utility support included both direct technical support to the UPVG TEAM-UP projects and direct analysis.
- Completing a series of workshops, coordinated with PV4U, attended by an average of 50 utility, regulatory, and policy representatives
- Developing and publishing a new load-matching brochure that identifies the capacity credit for PV across the nation
- Completing the initial analysis of the financial risk mitigation potential of various attributes of PV technologies; we also laid the groundwork for a determination of the influence and opportunity for PV as financial criteria evolve in both the credit-rating agencies and the investment community.

We also developed valuation results for utility financial analysis work. This work will eventually incorporate the influence of financial and political factors related to transitional deregulation policies emerging around the nation. We plan to do case studies in FY 1997, and this work will directly to support individual utilities developing PV-related business plans.

Support to the States. Our support to states included the following:

- Conducting the FY 1996 series of workshops
- Initiating policy valuation support
- Continuing to work on the multistate facility value analysis project
- Through the state of Colorado, beginning to test the performance of PV lighting systems used in state park facilities
- In a multistate valuation project, identifying more than 200 on-grid and off-grid cost-effective PV applications; two states have been analyzed, and we are still collecting data on 12 others
- Completing a state-by-state analysis that identified cost-effective markets in five states for customer-sited PV; our initial analysis used data that was average or typical.

In the future, we will incorporate policy value and utility risk value into our analysis. The policy valuation support is individually targeted, because each state has different approaches to deregulation and reregulation policies. Our plans for future support will provide a policy value analysis on state revenue impacts (including economic development), utility financials, the PV industry, and customer value; thus, we will be able to provide a good overview of PV market potential from these policies.

International Markets and Applications

Brazilian Rural Electrification Pilot Project

Through NREL, the U.S. Department of Energy, Office of Solar Electric Conversion, is undertaking a cooperative joint pilot project in the Federal Republic of Brazil with eight Brazilian states and the Centro de Pesquisas de Energia Eletrica (CEPEL).

Our goal is to establish and assess the efficiency, operability, and reliability of rural electrification based on solar energy. During 1996, we completed most of Phase 2 of the program. The completion of the two 50-kW hybrid power systems is scheduled to continue into 1997. Delays in commissioning and starting up the hybrid systems were due mostly to delays in in-country purchases of battery systems. Still, we were able to complete the procurement and delivery of two battery systems in late FY 1996. Most of the installations of the Phase 2 stand-alone systems were completed during the year; the solar home systems installed as part of Phase 1 continue to provide reliable power to the consumers.

China

During 1996, we assisted DOE in establishing project opportunities in China. This work included developing four annexes to the DOE/Chinese State Science and Technology Commission protocol agreement.

We launched an initial project in the province of Gansu and laid plans for additional cooperative efforts. This work expands the work previously done in China by the Solar Electric Light Fund (SELF). SELF established a system of credit financing for home PV systems in the Gansu Province, working with a nonprofit entity that managed the revolving credit accounts used to finance systems and to procure equipment and services from local vendors.

The project with DOE and NREL will expand the SELF project in Gansu, in which at least 600 home PV systems have been scheduled for installation during an 18-month period. This should help to create a critical mass for market and infrastructure development, reduce the amount of subsidies used in financing systems, and increase the use of rural energy offices to provide marketing support for deploying PV systems. We also supported a World Bank mission that focused on developing a renewable energy project in China.

India

During 1996, we assisted DOE in establishing project opportunities in India, and we launched an initial project with the Ramakrishna Mission.

Through a competitive procurement, we implemented a contract with Applied Power Corporation, including Remote Power as the training partner. A primary goal of this initiative is to create a sustainable infrastructure in West Bengal to expand the program beyond what DOE and NREL supply. The Ramakrishna Mission, a well-respected humanitarian organization in India, arranged to be the banker-revenue collector to implement partial cost recovery from the 300 villagers who will be furnished home lighting systems. After accounting for in-country subsidies, the villagers will purchase the rest of the system on a time repayment plan; they will provide a 44% down payment with the remainder to be financed over 10 years at low interest and repaid in monthly installments. The down-payment funds will be put into a revolving capital fund to finance the purchase of systems in the future. The monthly installments, plus a per-month charge, will fund the maintenance of the systems.

Future purchases may provide an opportunity for entrepreneurs to establish businesses that can rent home lighting at an affordable rate to villagers who want such systems but are unable to make the initial down payment. Other applications, such as battery charging, solar lantern charging, spice grinding, and water pumping, will be installed in seven other villages and could also produce revenue for many of the villagers. Additional applications such as street lights, community lights, TV, hospital vaccine refrigerators, and water pumping will be furnished to the villages to improve their quality of life.

South Africa

During 1996, we worked with DOE and Sandia on a multitiered program that included building manufacturing capability, market development, technical interchange for R&D, and pilot testing of a variety of technologies.

Manufacturing. Suncorp Manufacturing Corporation was developed in partnership with South African universities and investment organizations. It is the first majority-owned PV manufacturing plant in the country and is testing new production techniques. We have provided technical assistance and continue to support the technical capacity building of Suncorp as it expands from modules to complete systems. This plant is now

operational with products meeting ISPPRA certification standards. Ten new jobs were created, and jobs should reach about 12-15 when full, single-shift production capacity is reached.

Market Development. REFSA (Renewable Energy for South Africa, formerly known as SAFIRE, the South African Financing and Implementation Agency for Renewable Energy) was formed to create a sustainable environment for rural off-grid electrification of homes and businesses. DOE has strongly supported this program by working on sustainable financial mechanisms to support the projected installation of 200,000 systems annually, technical specifications, and detailed planning and process definition of the National Rural Electrical Cooperative (NRECA).

Technical Guidance. DOE also provides technical guidance in developing training programs, both for educators and potential business persons. Initial training of educators was implemented through Renewable Energy for African Development (REFAD) as a planned 5-year program. REFAD is assisting REFSA in administering a \$1.1 million grant from the U.S. Agency for International Development to implement the pilot phase.

Village Power and Hybrid System Analysis

During 1996, we continued to work with NREL's National Wind Technology Center to develop and release the *Hybrid 2* computer simulation code. This code is now being used to help design systems for the NREL PV programs in China and Ghana, as well as wind activities in several other countries. We will use data received from two hybrid power systems in Brazil to verify the code in FY 1997.

Published Papers

Thornton, J.P. "The Economics of Photovoltaics in Municipalities." *SOLAR 96, Proceedings of the 1996 Annual Conference, The American Solar Energy Society, Asheville, NC, April 1996.*

Thornton, J.P. "Photovoltaic Market Trends." *Proceedings of the RENEW 96 Conference, Northeast Sustainable Energy Association, Boston, MA, March 1996.*

Thornton, J.P. "Cost-Effective Applications of Photovoltaics." *Vision 2001, Energy and Environmental Engineering, Proceedings of the 18th World Energy Engineering Congress, Atlanta, GA, November 1995.*

Thornton, J.P. "PV Opportunities in the Federal Sector." *AIP Conference Proceedings, 13th NREL Photovoltaics Program Review, American Institute of Physics, NY, 1996.*

Wallace, W., and Y. Simon Tsuo. "Sino/American Cooperation for PV Development in the People's Republic of China." *Proceedings of the 25th IEEE Photovoltaics Specialists Conference, Washington, D.C., May 1996.*

Domestic Applications and Market Development Subcontracts

Title: Analysis of Building Integrated Photovoltaic Systems and the Implications for a Long-Term Market Development Program.

Organization: McNeil Technologies, Inc. Springfield ,VA

Contributors: K. DeGroat, S. Tanner, Principal Investigators; M. Brown, H. Jones

Objectives

The purpose of this study is to assist the Department of Energy's Photovoltaics Division in promoting Building Integrated Photovoltaic (BIPV) systems to consumers and to identify strategic markets for the technology in the near and mid-term. The results of the study will be used to help the Department design appropriate programs to promote BIPV technology to communities, the building industry and local citizens through the proposed Million Roofs Solar Power Initiative (MRI).

The MRI is a proposed partnership between Federal agencies and communities to install one million building applications of Photovoltaics, active solar systems and energy efficient design. The Initiative will be led by DOE, but will also include other agencies whose programs affect building technologies and finance. The goal of the program is to remove institutional and financial obstacles to the use of solar technologies and help encourage widespread deployment among homeowners and businesses throughout the United States.

One of the major barriers to widespread BIPV deployment is the high first cost of PV systems. The purpose of this study is to better determine the total economic impact of these systems. This will aid communities in defining the specific benefits of these systems so that consumers may make objective and informed decisions about the technology and its impact in the local economy. In addition, it will help to identify specific mechanisms that Federal, state and local governments can institute to encourage the increased deployment of this emerging technology.

Approach

This analysis builds upon previous studies that have identified favorable markets for grid-connected BIPV systems. [1] [2] As a first step, McNeil developed a simple spreadsheet that attempted to reproduce the basic results of these studies and to include some additional features. The results from this preliminary analysis are shown in the summary of the "President's Million Roofs Solar Power Initiative" [3]. Although these studies showed that BIPV systems are currently economic for a limited number of states, it was determined that a more detailed analysis was needed to accurately model the many variables that affect PV system operation and economics.

The performance and benefits of BIPV systems are dependent upon many factors including climate, building energy use, utility electricity rates and financing terms. To generate credible cost comparisons, all of these factors must be considered. To accomplish this a model was needed which synthesizes these elements and incorporates the following:

- ◆ Accuracy- the model should utilize available data resources and simulation programs to recreate as closely as possible real-life building performance.

- ◆ Flexibility- the model should remain flexible with its inputs such that it can accommodate comparisons among a wide range of buildings and locations.
- ◆ Adaptability- the model should be able to readily incorporate change and additional levels of analyses.

After a thorough search no one existing model was discovered that met all the requirements for the study. Therefore, an integrated model was developed that incorporates a number of existing models as modules. The integrated model will be used to:

1. perform BIPV system cost-comparisons for the same types of buildings in different locations and different types of buildings in the same location.
2. analyze the relative impact on the cost-effectiveness of BIPV systems of different input factors (e.g. climate, and utility electricity rates).
3. compare BIPV system costs to traditional architectural material costs.

Preliminary analyses will be conducted for typical residential buildings in Boston, MA and Phoenix, AZ. The locations were chosen because of the large variation in climate and because they fell within the boundaries of previously identified niche markets. In the future, commercial building types will be modeled as they possess substantially different energy consumption patterns, which should affect the economics of the BIPV systems involved. At this point, the model has not been run for commercial buildings, but information has been collected and a preliminary configuration developed.

A substantial amount of data was collected from the residential and commercial building energy surveys conducted by the Energy Information Administration on the energy consumption and number of different sizes and types of buildings. Data was also collected on the average energy use, basic design, and occupancy of these buildings. Based on this data, the buildings that were chosen to be modeled are:

1. a 2,280 square foot single detached home of two stories and 1,950 square feet of heated floor space. The HVAC system chosen was gas heat/hot water and electric air conditioning. The home incorporates a 4.3 kW integrated photovoltaic roof.
2. a 10,000 square foot office building of three stories. The HVAC system chosen was gas heat/hot water and electric air conditioning. The building incorporates a photovoltaic curtain wall and/or photovoltaic roof array.

Integrated Computer Model Overview

The constructed model integrates a building energy simulation program, a photovoltaic array simulation program, and life-cycle costing analysis. For each simulation, the model generates as a final result, the cost at which the specific BIPV system becomes cost-effective. Cost-effective, for purposes of this analysis, is defined as the life-cycle cost of the BIPV system which is equal to or less than the cost of utility supplied electricity over the lifetime of the system. An important feature of the model is that it generates an hourly load profile for a building and combines it with the hourly performance of the photovoltaic array integrated into that building, and matches the resulting electric

load profile with the electricity rates of the local utility on an hourly basis.

Model Components

The following components are brought together as shown in Figure 1:

Energy-10 is a building simulation program that is primarily used by architects and engineers to design low-energy buildings. The model uses *Energy-10* to generate a full year's hourly load profile for a low energy building. *Energy-10* has built in defaults describing typical energy usage profiles for a variety of commercial buildings and residential buildings. These defaults are based on the

Figure 1 Integrated BIPV Input/Output Model Diagram

residential and commercial building surveys conducted by the Energy Information Administration. As well, *Energy-10* applies default passive solar design strategies to produce reference case low-energy buildings.

PVFORM is used to simulate the physical performance of a specified PV array. For the purposes of this study, *PVFORM* requires the hourly load data generated by *Energy-10* for simulation and data from the same climate data files used by *Energy-10*. The *PVFORM* climate data files are extracted from the TMY2 (typical meteorological year) data set, and include hourly values for direct radiation, global radiation, ambient temperature, and wind speed. Studies have shown that *PVFORM* can predict PV array performance to within 5% of actual experience.

maketmy2 and *pvconvert* were generated with a standard C compiler. They are used to transform *Energy-10* output and typical meteorological year data into a format suitable for *PVFORM* input.

ERATES is a program that allows the input of electric utility rate schedules. It will match an hourly electricity load profile with the utility rates and calculate the annual electricity costs of the building.

Microsoft Excel spreadsheets are used in conjunction with the other model components to facilitate data format translation and to perform the life-cycle costing analysis. The life-cycle costing analysis spreadsheet sets the BIPV system life cycle cost (LCC) equal to the LCC of the non-PV system. The maximum cost-effective cost for the BIPV system is found by solving the LCC equation (i.e. $LCC = \text{the present-value of the installed system} + \text{the present-value capital replacement cost} + \text{the present value energy cost} + \text{the present-value of operating, maintenance, and repair costs}$) for the present value of the installed system cost.

Preliminary Results and Future Research

During FY96 the effort was focused on developing and testing the model structure. Now, more detailed testing is needed to determine the accuracy of the output.

Future Effort

Ultimately, the residential model will be run for a variety of cities using different BIPV products and array specifications. Weather and utility data has already been collected and formatted to run the residential model in seven other cities. Essential simulations to be run include the commercial building curtain wall and rooftop models. The results can be used to compare the cost-effective potentials between the different BIPV applications, as well as the gaps between actual and simulated break-even prices of PV products. In addition, the model can be used to demonstrate cost comparisons between BIPV and high cost architectural materials.

Effort for FY97 will focus on reviewing the initial assumptions for the existing modules and further refining the LCC module. The final LCC module will incorporate a tax analysis and more detailed financial analysis to show the effects of tax incentives and mortgage and financing terms on the actual and perceived costs of the BIPV system. The final results will be incorporated into the program plan for the Million Roofs Initiative, as well as into material used to explain the program to communities and other stakeholders.

References

1. Wenger, H et al., "Niche Markets for Grid-Connected Photovoltaics," U.S. DOE.
2. Frantzis, L et al., "Building Integrated Photovoltaics: Analysis and U.S. Market Potential" Arthur D. Little, Inc. Ref No. 44513. Feb 1995
3. Rannels, J et al., "The President's Million Roofs Solar Power Initiative," U.S. DOE. Jan 1997

Title: Renewable Energy Applications and Economic Analysis for Electric Power

Organization: Pacific Energy Group, Walnut Creek, California

Contributors: Howard Wenger and Tom Hoff (Pacific Energy Group); Christy Herig (NREL Technical Monitor), Brian Parsons, and Roger Taylor (NREL), Patrina Eiffert-Taylor (FutureSpecs), Richard Perez (State University of New York)

The "Renewable Energy Applications and Economic Analysis for Electric Power" research program accomplished four tasks:

- Task 1. Developed a risk management approach to integrate renewables in the electric industry
- Task 2. Identified niche markets for grid-connected photovoltaics
- Task 3. Conducted surveys to understand architects' perspectives on the use of PV in buildings
- Task 4. Enhanced a distributed PV resource evaluation tool called QuickScreen

Task 1:	Integrating Renewable Energy Technologies in the Electric Utility Industry: A Risk Management Approach
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Contributors:	Tom Hoff (Pacific Energy Group); Christy Herig and Brian Parsons (NREL); Jack Cadogan (DOE Headquarters)
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Background and Approach

The bulk of this research focuses on evaluating the risk-mitigating attributes of renewable energy technologies. It identifies risks that are of concern to utilities and other power producers, including fuel prices, demand, environmental regulations, capital cost, supply, and industry structure. The research qualitatively discusses and quantitatively determines how the risk-mitigating attributes of renewable energy technologies are of value to various types of plant owners. Explicit consideration is given to the attributes of fuel costs, environmental costs, lead time, modularity, availability, initial capital costs, and investment reversibility.

A second focus of this research is to illustrate how to capture some of the risk-mitigating attributes of renewable technologies identified above through the use of hypothetical case studies. The case studies include: delay of T&D upgrades in grid-connected applications using distributed photovoltaic (PV) generation; expansion of the utility grid to non-grid-connected areas using customer-owned PV within a "solar home" development; a municipal utility's investment in a wind plant versus its investment in a natural gas-based plant; and a renewable aggregator's investment in a wind plant. The case studies demonstrate that investment decisions can be altered when uncertainties and the risk-mitigating attributes of renewable energy technologies are considered.

Conclusions

The general conclusion of this research is that renewable energy technologies, especially modular technologies such as wind and PV, can provide decision makers with physical risk-management

investments. The research specifically: provides an overview of project evaluation methods as background information; qualitatively describes how renewable energy technology attributes can be used to manage risks faced by various types of plant owners in the electric supply industry with consideration given to the effect of market structure; derives analytical methods to numerically compute the risk-mitigating value of the various attributes; uses simple examples to illustrate how renewable energy technology investments can be used by decision makers to manage risks.

References

1. Hoff, T. E., and Herig C. "Managing Risk Using Renewable Energy Technologies." *THE VIRTUAL UTILITY: Accounting, Technology & Competitive Aspects of the Emerging Industry*. S. Awerbuch and A. Preston, eds., KLUWER Academic Publishers, Norwell, MA, forthcoming.
2. Hoff, T. E., and Herig C. "Strategic Planning in Electric Utilities: Using Renewable Energy Technologies as Risk Management Tools." Annual American Power Conference, Chicago, Illinois, April 1996.
3. Hoff, T. E., and B. Parsons. "Strategic Planning in Electric Utilities: Using wind Technologies as Risk Management Tools." American Wind Energy Association Annual Conference, July 1996.

Task 2:	Niche Markets for Grid-Connected Photovoltaics
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Contributors:	Howard Wenger (Pacific Energy Group); Christy Herig and Roger Taylor (NREL), Patrina Eiffert (FutureSpecs), and Richard Perez (State University of NY)
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Background and Approach

This research identifies target market niches for Customer-Sited Photovoltaics (CSPV) in the United States.¹ The intent is to demonstrate markets that are cost-effective *today* and identify those showing the most near-term promise. Exploitation of niche markets is one strategy that could help speed the commercialization of grid-connected photovoltaics. This research also develops quantitative methods to evaluate local, state, and federal policies that effect commercialization of renewables.

A two-step analysis approach is used to identify target CSPV markets in the United States. The first step is to identify attributes such as PV electricity production, utility electric rates, solar tax incentives, and net metering availability on a state-by-state basis.

The second step is to conduct financial cash-flow analyses for each state for a base case CSPV application. The cash-flow analysis determines the break-even PV system price, the price at which the net present value goes to zero.

Selected Results

The states are ranked by break-even PV system price. Three market tiers are identified, with the best markets in the southwest and northeast. The top 5 CSPV niche markets are Hawaii, California, Arizona, New York, and Massachusetts with break-even PV prices between \$4.30/W and \$7.50/W. A 4% low interest loan would boost this range by 40% to \$6.20/W-\$10.30/W. In either case, *PV is cost-effective at today's prices* of about \$6/W-7/W.

¹ CSPV is broadly defined to include all grid-connected PV applications that reside on residential and commercial customer sites. Sample applications include architectural PV as a dual-use building material, building rooftop additions, and parking lot structures.

Utility rates and PV capacity factor are a good first-order screen for targeting markets. An added incentive, such as a tax credit, can catapult a market contender. Compare for example North and South Carolina. Each state has almost identical utility rates and PV capacity factor, but North Carolina's solar tax credit moves its market ranking to 6 while South Carolina ranks 26, in the middle of the pack.

Conclusions

Some of the research conclusions include: (1) The research developed a two-step analysis approach which proved useful for finding grid-connected PV markets; (2) There are cost-effective grid-connected PV applications *today*, notably in Hawaii; (3) Policy instruments, such as buy-downs of loan interest and capital cost (e.g., U.S. DOE-funded TEAM-UP program) are effective mechanisms for reaching cost-effectiveness in the top U.S. markets; (4) The research results are good approximations for commercial customers.

References

1. Wenger, H., Herig, C., Taylor, R., Eiffert, P., and R. Perez, *Niche Markets For Grid-Connected Photovoltaics*, IEEE Photovoltaic Specialists Conference, Washington, D.C., May, 1996.

Task 3: **The Architect's Perspective on the Use of PV in Buildings**

Contributors: Howard Wenger (Pacific Energy Group); Christy Herig (NREL); Patrina Eiffert-Taylor (FutureSpecs)

Background

NREL and the American Institute of Architects, sponsored six one-day regional workshops on the application of PV in the built environment. These workshops, conducted by Solar Design Associates, were targeted at practicing architects and design professionals who are recognized to be in a key position for facilitating the acceptance of PV in the building sector.

Two workshops held in Phoenix, AZ on October 4, 1995 and Los Angeles, CA on November 17, 1995 were selected for the population sample of this research. After attending the day long workshop, 76 participants completed a questionnaire aimed at establishing the architect's decision making criteria and identifying perceptions about product design, costs, early market niches and barriers. Selected questionnaire results follow.

Selected Results

- Participants' Backgrounds: More than 90% of the workshop participants are licensed architects. Half work in small firms of one to three employees, and 36% in firms with more than 10 people. Most (70%) did not know much about PV before attending this workshop.
- Decision Making Criteria: According to the results, the *most important* decision criteria for architects to select PV are "the client wants PV", it "produces clean power", and "promotes sustainability". The cost of PV per squarefoot and per kilowatt, lowering of electricity bills, and the multi-functional properties of Building Integrated PV (BIPV) are also *important*.
- Financial Criteria: Participants ranked a "utility electricity buyback plan or net metering" number 1 as the most appealing financial incentive to integrate PV into buildings. "Federal tax

incentives" and "state tax incentives" ranked 2 and 3 with "mortgage financing plans" and "PV manufacturer financing plans" ranking lower.

Participants were asked what financial measures they and their clients would use to justify using PV. "Simple payback" received the highest score -- 75% require payback periods of 5-10 years. 23% of the participants would utilize "return on investment" as a financial measurement, ranging between 5% to 15% rate of return.

- **Product Cost.** Architects perceive the fair market price of most products to be less than \$45/sf. The fair market price of roofing and awning products are generally perceived to be lower than facade systems. PV asphalt-like roofing shingles are perceived to have the lowest fair market price of any product, with 80% of the responses noting they should cost less than \$20/sf. The PV skylight system has the highest perceived fair market price, with 30% of the responses checking a range greater than \$45/sf.

References

1. *The Architect's Perspective on the Use of PV in Buildings*, Wenger, H. J., *Photovoltaics in Buildings Questionnaire Results*, AIA Research Workshop, October, 1995.

Task 4: QuickScreen Software for Distributed PV Evaluation (Beta Version 1.0)

Contributors: Howard Wenger, Tom Hoff, Dale Furseth (Pacific Energy Group)

The QuickScreen software package is a planning tool to quickly find the best distributed resource sites within a given electric service area and determine economic feasibility. It is targeted for electric service personnel who make resource and distribution planning decisions. Regulators and analysts may also find it useful to make informed policy decisions.

QuickScreen Beta Version 1.0 evaluates the cost-effectiveness of distributed PV generation. The software is intended to provide a simple-to-use tool that requires minimal data inputs. It runs on all PC-compatible Windows® platforms, featuring a point-and-click user interface and online context-sensitive help. Several sample utility projects and results are provided to quickly get the user up and running. Users should be able to complete an evaluation in less than an hour.

The development of QuickScreen was accomplished in two phases. The first phase, sponsored by Sandia National Laboratories (John Stevens, Technical Monitor) developed the analytic tools that form the basis of QuickScreen calculations. The second phase, sponsored by NREL (Christy Herig, Technical Monitor) and accomplished in this Task 4, converted the analytic tools into the QuickScreen software package. To obtain QuickScreen software, contact Christy Herig at 303-384-6546.

References

1. Wenger, H., Hoff, T. and D. Furseth, *QuickScreen User's Guide*, Beta Version 1.0, National Renewable Energy Laboratory, Golden, CO, August 1996.
2. Wenger, H., Hoff, T. Furseth, D., Herig, C. and J. Stevens, *QuickScreen Software for Distributed PV Evaluation*, Utility PhotoVoltaic Group PV Experience Conference, Denver, CO, October 1996.

Title: Solar Resource Utility Load Matching Assessment

Organization: Atmospheric Sciences Research Center, The University at Albany, Albany, New York

Contributors: Richard Perez, principal investigator, and Robert Seals

OBJECTIVES

The project was initiated in 1991. Its initial objective was to estimate the effective capacity of photovoltaics (PV) for a sample of US utilities. This investigation required time coincident hourly electric load and local PV output data obtained via simulation from satellite remote sensing. Hence a secondary, but fundamental, objective of this work was to demonstrate the accuracy of satellite remote sensing for the considered application. The project continued with a larger sample of US utilities as well as "sub-utilities" – buildings and substations. The rationale was to confirm and refine the relationships observed between load shapes and the effective capacity of PV– i.e., knowing load shape parameters would be sufficient to estimate PV's effective capacity. Once verified, these relationships were applied to the mapping of PV's effective capacity in the US.

The current and future objectives this projects are:

- (1) To continue increasing the utility load sample with the objective of both providing a service to utilities and further validating load shape-capacity relationships.
- (2) To investigate the year-to-year variability and long term trends of US effective capacity maps
- (3) To investigate the seasonal variability of PV effective capacity distribution in the US
- (4) To investigate customer load data in order to characterize possible end-use type/load match relationship
- (5) To apply the results and capabilities developed throughout this project to specific case studies with relevance to PV valuation

RESULTS AND DISCUSSION OF ACTIVITIES COMPLETED IN FY 95

Recap on past findings

The following results have been documented during past phases of this study:

- Satellite-based solar resource data can be used to adequately address PV-utility interaction issues in the US.
- PV's effective capacity, quantified by the Effective Load Carrying Capability (ELCC) parameter, is substantially larger than PV's capacity factor for most US utilities.
- Effective capacity is not well correlated with the solar resource. However, a well defined relationship exists between effective capacity and simple load shape parameters.
- An initial map showing the distribution of PV' effective capacity in the US was produced. This map shows that regions of highest capacities do not always overlap with "traditional" high solar resource regions – the differences are strongest in the great plains, the mid-Atlantic seaboard, the extreme southeastern US and the great basin regions – see Fig., below. Regions of highest ELCCs are associated with the following factors (1) existence of marked summer heat waves, (2) summer electric loads driven by commercial consumption and (3) small proportion of electric heating.

Update on current investigations

A substantial fraction of our effort this year was spent on producing a detailed report documenting the above findings [1] and on helping NREL design a brochure to disseminate these results in a simple but explicit format [2].

Upon completion of these reporting tasks, we initiated work on:

- investigating the year-to-year variability and long term trends of US effective capacity maps

- investigating the seasonal variations of these maps.
- investigating PV's effective capacity with respect to end-use loads
- addressing relevant utility issues

Year-to-year variability US effective capacity maps: We acquired peak load data for 176 major US utilities from the Utility Data Institute [3] spanning six years from 1990 to 1995. As for the initial map (see [1,2]), the 1990-1995 maps were drawn, by gridding utility service territories and applying the peak load-ELCC relationship that we had previously developed. Maps for 1987 and 1988 are also being prepared, based on load information from 42 major utilities assembled in previous phases of this study.

We hereby present a preview of this analysis. Maps for 1990 and 1995 are compared in Figs. 1 and 2, as an illustration the yearly variability of PV ELCC in the US. These findings are summarized in Fig. 3, where 1987-95 average ELCCs and their standard deviations are compared for 13 US regions.

Florida and the southeastern US exhibit the highest variability. The mid-Atlantic seaboard, the central Great Plains and the south-west coast exhibit consistently high ELCCs. The long term (1987-1995) average ELCC distribution in the US is mapped in Fig. 4. This map confirms and strengthen the features of our the initial map [1,2].

Figure 1: US Distribution of PV's effective load carrying capability in 1990
(2-axis trk. PV, low utility penetration)

Figure 2: US Distribution of PV's effective load carrying capability in 1990
(2-axis trk. PV, low utility penetration)

We are currently investigating regional ELCC trends and their causes. We note a slight underlying increase over time, particularly in the Western US, on which strong variations, apparently linked to weather extremes (both hot and cold) are superimposed. Weather impact on PV's ELCC, particularly extreme cold winters, appear to be strongest in regions with notable electric heating loads, e.g., Florida.

Figure 3: Average ELCC by region, and observed 1987-1995 variability
(2-axis trk. PV, low utility penetration)

Figure 4: US Distribution of PV's effective load carrying capability -- 1987-1995 average
(2-axis trk. PV, low utility penetration)

Investigating the seasonal variations of ELCC: Although the yearly ELCC discussed above represents a physically sound measure of PV capacity credit, the rationale for this seasonal investigation is to prepare information directly usable for PV valuation. Indeed, user-sited capacity is valued in terms of demand reduction, which is generally billed on a monthly basis.

This investigation is currently in its initial stage. As a preview of our initial results, we show an example of monthly ELCCs experimentally derived for two utilities, one with a high yearly ELCC (ConEdison) and one with a lower yearly ELCC, (Niagara Mohawk) -- see Fig. 5. The similarity between the two curves is quite remarkable. In fact, most US utilities exhibit summer ELCCs approaching or exceeding 70%. Monthly ELCC values appear to be closely linked to monthly maximum temperatures, while the highest summer value appears to be primarily related to load shape parameters such as the

Fig 5: Monthly ELCC for a summer peaking (CONED) and a winter peaking utility (NMPC)

time of peak load, the extent of evening load shoulder and the daily load excursion.

Investigating end-use customer load data: Our objective is to attempt identifying PV load management opportunities as a function of building type and service territory. Our approach consists of determining ELCC for a sample of buildings, from time coincident (satellite-derived) solar-radiation data and experimental building load data.

At this time, our sample – 17 building load years – is not nearly large enough to provide definitive results. However, fragmentary building type trends do seem to emerge. In the table below, we present the average and standard deviation of two effective capacity parameters (2 axis trk. ELCC at 2% penetration and MBES at 10% penetration) for four building categories where we had at least 2 data points.

	Average ELCC (%)	Standard Deviation (%)	Average MBES (hours)	Standard Deviation (hours)
Hospitals	63%	11%	2.3	1.2
Offices (no electric heat)	67%	10%	0.8	0.5
Airports	33%	13%	4.3	1.2
Residences	65%	39%	0.6	0.2

Office/commercial air-conditioned, non-electrically heated buildings: These have the highest effective capacity averaging 67% ELCC. The MBES benchmark shows that less than an hour of storage would be needed in addition to a PV system to guarantee a firm 100% demand reduction for this type of building.

Hospitals: Effective capacity averages 63% ELCC, showing a good statistical agreement between the resource and the load. However, the MBES is considerably higher than for office buildings, standing at over 2 hours, is indicative of high and lasting off-peak loads for hospitals.

Airports: Both benchmarks indicate only marginal load matching for these mainly 24 hr./day operations.

Residences: This is an very low data sample. The average ELCC is probably meaningless with a 35% standard deviation. However, it is remarkable that the MBES is small in both cases. The reason may very well be that because residential loads are typically noisy, it does not take much energy reserve to effectively reduce peak loads.

-- In particular we are currently evaluating the impact of a dispersed PV resource would have had in mitigating the Western System Coordinating Council outage of August 1996.

ACKNOWLEDGMENTS

This project was undertaken as a part of NREL contract XR-1-11168-1. Christy Herig is the project manager. Thanks to Roger Taylor, William Wallace, Howard Wenger, David Renné, Dan Tarpley and the UPVG staff for their help throughout the load matching project.

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Title: **Evaluation of Peak-Shaving Opportunities for Photovoltaics**

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Objectives

The development of intermediate markets for photovoltaics (PV) is vital for near-term growth of the PV industry. One key market sector receiving increasing attention for intermediate applications is the use of PV in the building sector as a dispatchable peak-shaving tool. CEEP is continuing to conduct research on the technical and economic viability of dispatchable peak-shaving photovoltaics (DPS-PV) for electric utilities and their customers using its menu-driven *PV Planner*, a software package developed by CEEP. The objectives of this research during FY 1996 were:

- To analyze the value of PV to utilities and their customers as an area- and time-specific targeted peak-shaving option;
- To provide an economic analysis of two complementary applications with significant market potential for integrated PV-building systems in the domestic U.S. utility market—emergency lighting and uninterrupted power supply;
- To provide assistance in the development of economic and policy models for the use of PV as a remote-area power technology in developing countries; and
- To offer a training program of sustainable energy development for private and public mid-career decision-makers from developing countries.

Tasks and Research Results

Task A: **Targeted DPS-PV Applications**

CEEP extended the development of the DPS-PV system to incorporate the distributed utility (DU) concept. Research has shown that economic value to a utility and its customers is increased by targeting dispatchable PV applications in the areas where, and time periods when, the utility's avoided costs are high. Many utilities previously overlooked transmission and distribution (T&D) costs in their resource planning. As investment costs for local T&D become significant, DPS-PV applications to increase its asset utilization offer significant economic benefits. When the DPS-PV

system is sited in an area with a particularly high cost of service, the utility receives "non-traditional" benefits.

Regulators have embraced non-bypassable line charges and portfolio standards as the preferred strategies for continued investment in end-use efficiency and renewable energy in a competitive electricity market. A DU analysis that encourages the evaluation of localized benefits can assist utilities and regulators in their efforts to identify high-value applications for energy efficiency and renewables. A DU approach involves a set of mechanisms that explicitly acknowledge the value of distributed resources including DPS-PV. When viewed from a DU perspective, these options offer greater value to a utility and its customers by recognizing area- and time-specific marginal costs. A DU approach also represents an institutional shift in which new emerging modular technologies can play a role in a new less centralized, environmentally less polluting electric utility industry. CEEP researchers recently published a paper describing the methodology for comparing the DU approach to the conventional economic externality model in evaluating the economics of PV in a deregulated electricity market (see Letendre et al., 1996).

CEEP has also conducted economic analyses of DPS-PV for specific building types located in the service territories of eleven different U.S. utilities. The analyses identified those building types with load characteristics most suitable for cost-effective DPS-PV applications and those regions of the country where these systems are closest to being cost-effective. The results indicate that dispatchable peak-shaving PV systems are well suited for large office buildings and fast food restaurants located in the northeastern part of the U.S. and North Carolina (Table 1). The northeastern region has relatively high electric rates, and North Carolina offers a 35% renewable energy investment tax credit. Table 1 lists the combinations of building types and regions with benefit-cost ratios greater than or equal to 1.00, indicating cost-effectiveness at current installed PV systems prices (excluding storage) of \$8.70 per Wp.

Table 1
Cost-Effective DPS-PV Applications: Building Types and Regions

Building Type	Electric Utility (region)	B/C Ratio	Payback (years)
Large Office Building	Long-Island Lighting Company (NY)	1.02	10.22
Fast Food Restaurant (no electric heat)	Duke Power (NC)	1.02	9.51
Large State Office Building	Consolidated Edison (NY)	1.01	10.25
Fast Food Restaurant (with electric heat)	Duke Power (NC)	1.00	10.32
Fast Food Restaurant (with electric heat)	Crescent Electric Membership (NC)	1.00	10.70
Fast Food Restaurant (no electric heat)	Crescent Electric Membership (NC)	1.00	10.70

Source: Center for Energy and Environmental Policy

Task B: Building-Integrated Emergency Power Applications

CEEP extended the concept of DPS-PV to incorporate the complementary benefits of emergency power options. Two emergency power options which are widely used in the commercial sector were evaluated: emergency lighting and uninterruptible power supplies (UPS) for computer operations. Current markets place a premium value on in-building emergency power, far exceeding values common in utility calculations. The largest cost is for battery-based emergency lighting systems, at \$2,500-\$6,000 per kW. Cheaper generator technology is available but is valuable only for larger scale needs and when only short interruptions are permissible. The more expensive battery-based systems are required for small units (such as modular emergency lighting) and in applications requiring fast switchover time. According to the manufacturer of the AC Battery module, a DPS-PV unit could be modified to serve the functions of emergency power at little additional cost. Further research on technical and economic feasibilities of the integrated system is now underway. Fifteen manufacturers and vendors of emergency power systems have completed extensive cost and service surveys administered by telephone and on-site interviews with CEEP staff. This information is being used to modify a DPS-PV system being commercialized through the PV.BONUS Program so that it can save emergency power needs. Building operators will also be interviewed to identify their needs for emergency power in more detail and to obtain their reactions to a PV-based system.

C. Support for PV Applications in Developing Countries

CEEP has conducted an economic feasibility study of off-grid renewable energy applications in China's Inner Mongolia Autonomy Region (IMAR). The study is being undertaken in collaboration with the Institute of Policy and Management of the Chinese Academy of Sciences and the New Energy Office of the Inner Mongolia Government. The major finding to date, based on 41 household-scale systems operating in the IMAR, is that the complementarity of wind and solar resources makes PV-wind hybrid systems a highly attractive option to provide reliable, year-round electricity services to remote herder communities. Based on the analyses completed by CEEP and the Chinese Academy of Sciences, the U.S. DOE, the Chinese government and the Inner Mongolia Government are considering a joint project to install 300 household-scale wind and PV systems in two of the IMAR's counties, serving as an incubator for a larger application in the region.

CEEP has developed an analytical tool capable of simulating performance of off-grid wind and PV systems to identify least cost options for this project. In addition to the work on household-scale renewable applications, CEEP is assisting NREL in a feasibility study of village-level renewable power systems in the IMAR.

Task D. Sustainable Energy Development Training

CEEP completed the second year of its training initiative jointly sponsored with the Tata Energy Research Institute (India). The Program on Energy, Environment, Resources and Sustainability (PEERS) included an intensive study at CEEP from July 10 to August 2, 1996, for 13 mid-career decision-makers from India, Sri Lanka and Nepal. The U.S. phase of PEERS consisted of four major components: 1) classroom instruction; 2) guest seminars and individual meetings with experts; 3) professional excursions for meetings with officials of the U.S. government, the World

Bank and UNDP, and with representatives of energy and environmental firms; and 4) the preparation of project design reports and their presentation before the staff of CEEP and two external reviewers. (As a condition of program eligibility, a participant must be authorized by their sponsoring organization to carry out a specific project incorporating sustainability principles. CEEP staff assist participants in preparing project designs for submission to the sponsoring organization.) The 1996 PEERS participants hold positions in central and state governments, industry, media, and non-government organizations. The group included three officials from the Indian Administrative Service, and officials from the central governments of Sri Lanka and Nepal. Six representatives of industry (petrochemicals, fertilizers, finance, electric power) were in the 1996 class, which also included a member of an Indian NGO (Gram Vikas) and a member from the print media (Indian Economic Times).

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International Applications and Market Development Subcontracts

Title: **Renewable Energy Policy Development and Commercial Project Identification in China**

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Objectives

To identify renewable energy potential and the development priorities for China generally and for Inner Mongolia specifically, as a provincial case study, based on economic and technical feasibility studies.

To identify the major barriers—technical, financial, political, institutional and social—to effective development of high priority renewable technologies and strategies for China and Inner Mongolia.

To assist policy makers in China at appropriate levels to incorporate high priority renewables into the strategic planning process for China as a whole and for Inner Mongolia specifically; e.g., incorporation of recommendations into China's Ninth Five Year Plan planning process.

To recommend appropriate institutional and policy responses and implementation mechanisms for developing potential renewable energy markets in China to decision makers in key agencies (such as commissions or ministries) at the central and provincial levels.

Approach

A specific case study was performed for the Inner Mongolia Autonomous Region. The field study included 44 households, 28 institutions, 30 villages, 28 townships, 4 counties, and two regions (cities). The survey covered an area of 900 km from east to west and 500 km from north to south.

The case study involved collecting information from 5000 pages of documents and materials in the research, design, and application units of the New Energy Office and Planning Commission of Inner Mongolia, the Provincial Electricity Bureau, various, meteorological stations, etc., and leading institutions at the provincial level.

Data processing and qualitative and quantitative analyses was performed in collaboration with the Center for Energy and Environmental Policy at the University of Delaware.

Results

1. In Inner Mongolia specifically the solar and wind energy resources are as follows:
 - The solar radiation ranges from 1280 to 1860 kWh/m²y and ranks second in the country, after the Tibet Plateau. The proportion of the four seasons is 32%, 33%, 20%, and 15% respectively, in spring, summer, autumn and winter. The sun hours are in the range of 2900–3400 hours per year, increasing from east to west and from south to north. The average air temperature in a day is more than 10°C and the days with sunshine hours of more than 6 hours is in the range of 80–100.

- The total wind energy potential in Inner Mongolia is estimated at 1010 GW of which 101 GW is usable, accounting for 39% of the estimated total national wind energy resources in China. Inner Mongolia is ranked first in the country for wind potential. Rich wind resources are located in farming and animal husbandry areas with scattered populations located far away from the electricity network but in areas suitable for using wind energy. Observations in the past 30 years show that the variability of wind energy in the region is small. The variability coefficient ranges from 0.05–0.21 in the whole and from 0.05–0.10 in 65% of the region.
- The seasonal variation of wind energy matches the seasonal energy demands of agriculture and animal husbandry. Solar and wind energy is complementary in Inner Mongolia. In the winter months, wind is relatively more available than solar energy and the opposite is true in the summer months. PV/wind hybrid systems are therefore particularly suited for Inner Mongolia.

2. General information on the development of PV technology and industry in China:

- There are 10 manufacturers of solar cells in China, with an annual production capacity of 4.5 MW. Eight production lines were imported, among them six for production of monocrystalline silicon cell and two for amorphous. Up to 1995, a total of 5,180 kWp had been installed. The development of PV systems in China is based on the following three considerations: a) electrical accessibility in remote areas of agriculture and animal husbandry; b) the power supply in the future, and c) environment issues.

Market of PV Cells in China (1995)

Application	accumulated installation (KWp)	Market proportion (%)
communication	3000	60
household PV system in remote areas	1000	20
Agriculture and industry	500	10
Consumer	500	10

Development forecasting of market for PV cells

	Demand (MW/y)	Module price (USD/Wp)	System price (USD/Wp)
1995–2000	1.5–5	5–4	8.5–1.5
2001–2010	5–10	4–2.5	6–12.5
2010–	> 20	<2.5	5–10

Forecasting of solar power (MW/y):

Application	1993	1994–2000	2001–2010
Household PV system	0.6	15	60

Village PV station	0.06	3.5	30
Communication	2.64	11.5	40
Networking PV station	0	1	5
Networking solar-thermal station	0	35	100
Total	3.3	66	235

3. The development and forecasting of wind energy in China:

- There are 150,000 household wind power generators of less than 300 W, with a total capability of 17 MW, located mainly in Inner Mongolia and offshore islands and used for lighting and TV.
- There are 13 wind power stations with total capability of 15 MW. The main wind turbines used are in the 300–500 kW range, imported from abroad.
- It is planned to develop a total capability of 1 million kW of wind power by 2000 and connect wind power stations with the electrical network. The wind power generators imported will mainly be in the of 300–600 kW range.

4. The development and planning of PV and wind power in Inner Mongolia:

- There are 991,000 households of farmers and herdsman in Inner Mongolia without electricity. Among them are 506,000 households in sparsely populated, remote areas that lack electrical and electric grid. Only PV and wind power can meet their demand for electricity.
- 140,000 sets of wind generators of 100 W, 200 W, and 300 W, and PV modules of 16 Wp, 32 Wp, and 50 Wp have been installed. The total capacity and annual power generation of wind generators is 11.225 MW and 20.48 GWh respectively. The installed capacity of solar modules is 100 kW. Thanks to the preferential policy that 200 Yuan RMB would be used to subsidize a household who bought a 100-W wind generator or a 16-Wp PV module, Inner Mongolia ranks the first in developing solar and wind power generation.
- Development trends of PV and wind power in Inner Mongolia include the following:
 - 1) The power of household PV and wind generators is getting larger: growing from 50 W to 100 W, and now a household generator of 330–500 W has been developed that is a hybrid wind/PV systems design.
 - 2) A stand-alone PV-wind hybrid system for household use is developing fast. Because of the complementary characteristics of wind and solar resources, this kind of generator can achieve a high reliability as an all-weather power supply, supply power to larger appliances like refrigerators, and extend the working period of storage batteries. Such a system is cheaper than the pure PV system and easier to manage than a wind-diesel hybrid system.

- 3) Wind-PV, wind-diesel, and wind-PV-diesel hybrid systems are good solutions to power supplies in remote rural areas.
- 4) Regarding connecting large wind power stations with an electrical network, it is planned that two stations will be extended and eight will be constructed, and that the total installed capacity will reach 200 MW by 2000, 600 MW by 2010, and 2680 MW by 2020 accounting for 10% of the installed electric generating capacity in Inner Mongolia.

5. Benefit analysis of PV and wind power

Investment in capital construction (USD/kW)

thermal power	large hydroelectric	nuclear	wind	PV
500-850	850-1000	1000-1200	400-1000	2000-3300

Price of solar cell produced in China (USD/Wp)

monocrystalline	polycrystalline	noncrystalline
5.2	4.0	3.1

Price of commercial PV power stations at 10 kW level (USD/Wp)

module	system balance	power control	indirect cost	battery	total
4.0	1.2	0.9	0.7	3.0	9.8

Cost forecasting of PV power in China (US cents/kWh)

Discount rate	2000		2010		2050
	Networking	Standalone	Networking	Standalone	Networking
6.4%	12	22	8.7	17	3.8
8.2%	15	26.2	10.3	20	4.5
12%	20	32.5	13.7	25	6.1

- The average investment of 13 wind power stations in China is 1070 USD/kW, almost the same as that of large thermal or hydroelectric power stations.
- Compared with the price (7 US cents/kWh) of the Dayawan Nuclear Power Station, the networking electricity price of wind power stations in China ranges from 7.6–12 US cents/kWh. Concerning the largest wind power station under construction at Hui-teng-xi-le in Inner Mongolia, it is estimated that the electricity price will be 7.58 US cents/kWh, the cost 5.5 cents/kWh, the project rate of return 16.6% and the term of investment 7.4 years. The Nan'ao wind power station in Guangdong province also indicates the commercial feasibility of investment in wind power stations in China.

6. Investigation report on 41 household systems in Inner Mongolia:

- Location: 10 systems are located in areas with high PV and wind resources, 21 in areas with good resources and 10 in areas of usable resource.
- Generator: 22 wind power generators are used, including generators of 100 W in 14 households, 200 W in four households and 300 W in four households. The PV systems used totaled 10, including one of 22 Wp, two of 35 Wp, two of 75 Wp, one of 85 Wp and four of 100 Wp. There are six PV-wind hybrid systems: two using a wind generator of 300 W and a PV array of 120 Wp; three using a generator of 300 W and 60 Wp PV panels; one using a generator of 100 W and a PV panel of 35 Wp; and three wind-diesel hybrid power systems.
- Power: there are six systems with less power than 100 W, 17 with 100 W, six with 200 W, four with 300 W and eight with more than 300 W. The smallest one is with 22 Wp and the largest is 42 W.
- Origin: all wind power generators are produced in China. Thirteen PV cells are produced in China, two in the USA and one in Germany.
- Income of household: The lowest family annual income of the 41 households is 2500 USD and the maximum is 34,100 USD. Among the 41 households, there are six with an annual income of 2500–3500 USD, 14 with an income of 4000–6000 USD, 11 of 7000–12,000, six of 13,000–19,000, three of 20,000–25,000 and one having an annual income more than 25,000 USD. Thirty-one households have an annual income of 2500–12,000 USD, the middle level of income for Chinese herdsmen, accounting for 76% of investigated households. There are 10 rich families with an income more than 12,000 USD, accounting for 24% of investigated households.

Correspondence of income and generator used

Annual income (USD)	Generator used
1000	50 W wind power generator or 16–32 Wp PV
1000–4000	100 W wind power generator or 60 Wp PV
more than 4000	>300 W wind power generator or >400 W PV-wind hybrid system

Correspondence of load and power system

Power system	appliance	load (kWh)
100 W wind power generator or <100 Wp PV system	Lighting, black-and-white-TV, radio, and type recorder	140–390
200–300 W wind power generator	Lighting, color TV, radio, and type recorder	550–1080
300 W wind power generator 100 Wp PV system	Lighting, color TV, refrigerator, type recorder, washing machine	> 1100

- Rich herdsmen with annual incomes of more than 4000 USD are generally interested

in buying the PV-wind hybrid system of 300 W wind power generator and 100-150 Wp PV module. They are also interested in power for bigger color TV sets (21 inch), washing machines, refrigerators, and even water pumps, electrical shears, and milking machines.

- The main complaint of the 41 households studied is the quality of storage batteries that can be used for only 1-3 years.

Summary

With richer resources of solar and wind energy, China has made favorable policies for promoting the development of solar and wind energy and paid much attention to the development of PV systems and small-sized wind power generators for households, communications, etc. Inner Mongolia is one of the regions in the country where the research, development, and application of renewable energy started earlier and developed faster, especially for household wind and PV power systems. As the living standard of the herdsmen has been rising, the development (through international cooperation) has entered a new stage with large wind energy power stations and PV-wind hybrid systems for households.

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Title: Photovoltaics for Rural Energy in Gansu Province in the People's Republic of China

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Objectives

This work represents an expansion of work previously performed in China by the Solar Electric Light Fund. SELF established a system of credit financing for household PV systems in the Gansu Province within China, working with a non profit entity established to manage the revolving credit accounts used to finance systems and to procure equipment and services from local vendors. The project with the U.S. DOE and NREL will expand the SELF project in Gansu (to install at least 600 household PV systems over an 18 month period) to create a critical mass for market and infrastructure development, reduce the amount of subsidies used in financing systems, and increase the use of rural energy offices (under the Ministry of Agriculture) to provide marketing support for PV system deployment. Objectives include:

- development of a viable commercial infrastructure for deployment of PV systems for rural energy development in Gansu,
- inclusion of the U.S. renewable energy industry in application and market development for rural energy systems in China,
- further development various financing mechanisms for rural energy systems in China, and
- engage and encourage cooperation among appropriate Chinese agencies.

Tasks and Research Results

Detailed Project Plan

During the course of the first year of work, a detailed implementation plan was negotiated with the Chinese partners in the project, led by the Gansu Solar Electric Light Fund, a non profit organization established in Gansu to manage the project on the China side. The implementation plan included the involvement of the rural energy office network of the Ministry of Agriculture at the county level, which provided marketing assistance in surveying villages and locating customers for solar home systems. Rural energy office personnel also provided follow-up customer survey information and monitoring. A training program established a local technician network at the village level to install and maintain the systems. Local companies were selected to provide system integration and installation services for the equipment. These local companies

were also responsible for providing system warranties. The U.S. cost share for the project was provided mainly in the form of U.S. equipment supplied by U.S. companies, mainly PV modules, but also batteries and charge controllers. Agreements were established between the primary funding agencies, the U.S. DOE on the U.S. side, and the Ministry of Agriculture and the State Council Office for Poverty Alleviation and Rural Development on the China side.

Equipment Procurement

Chinese and U.S. equipment was procured competitively in the form of PV modules, batteries, charge controllers, and high efficiency fluorescent lights. The U.S. side was primarily responsible for PV modules and batteries. Most PV modules were crystalline silicon based, however, some amorphous silicon based solar lighting kits were supplied for testing in Gansu. Most systems are 20 Watt lighting systems, however, a number of 50 Watt systems will be deployed at schools for education purposes, and other applications will be tested.

Quality Assurance

A set of test procedures were established for testing solar home system components for the project and test team established in Gansu to provide quality assurance testing for the systems deployed in the project. A testing program will also be followed after system installation in order to monitor performance and typical use patterns for the systems. An extensive training program was also established to train village technicians and other project participants. To date, 35 village technicians have been trained for Phase I installation of systems to be conducted in November and December, 1996.

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Title: Evaluation of Intermediate Applications for Photovoltaics in Developing Countries

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Objectives

In addition to the work on photovoltaics (PV) as peak-shaving applications, CEEP is continuing to conduct research on the technical and economic viability of PV as a rural electrification technology in developing countries and develop a renewable energy and sustainable development training module for key decision makers from developing countries. More specifically, the objectives of this research during FY 1996 were:

- To provide assistance in the development of economic and policy models for the use of PV as a remote-area power technology in developing countries; and
- To offer a training program of sustainable energy development for private and public mid-career decision-makers from developing countries.

Tasks and Research Results

Support for PV Applications in Developing Countries

CEEP has conducted an economic feasibility study of off-grid renewable energy applications in China's Inner Mongolia Autonomous Region (IMAR). The study is being undertaken in collaboration with the Institute of Policy and Management of the Chinese Academy of Sciences and the New Energy Office of the Inner Mongolia Government. The major finding to date, based on 41 household-scale systems operating in the IMAR, is that the complementarity of wind and solar resources makes PV/wind hybrid systems a highly attractive option to provide reliable, year-round electricity services to remote herder communities.

Based on the analyses completed by CEEP and the Chinese Academy of Sciences, the U.S. DOE, the Chinese government and the Inner Mongolia Government are considering a joint project to install 300 household-scale wind and PV systems in two of the IMAR's counties, serving as an incubator for a larger application in the region.

CEEP has developed an analytical tool capable of simulating performance of off-grid wind and PV systems to identify least cost options for this project. In addition to the work on household-

scale renewable applications, CEEP is assisting NREL in a feasibility study of village-level renewable power systems in the IMAR.

Sustainable Energy Development Training

CEEP completed the second year of its training initiative jointly sponsored with the Tata Energy Research Institute (India). The Program on Energy, Environment, Resources and Sustainability (PEERS) included an intensive study at CEEP from July 10 to August 2, 1996, for 13 mid-career decision-makers from India, Sri Lanka and Nepal.

The U.S. phase of PEERS consisted of four major components: 1) classroom instruction; 2) guest seminars and individual meetings with experts; 3) professional excursions for meetings with officials of the U.S. government, the World Bank and UNDP, and with representatives of energy and environmental firms; and 4) the preparation of project design reports and their presentation before the staff of CEEP and two external reviews. (As a condition of program eligibility, a participant must be authorized by their sponsoring organization to carry out a specific project incorporating sustainability principles. CEEP staff assist participants in preparing project designs for submission to the sponsoring organization.

The 1996 PEERS participants hold positions in central and state governments, industry, media, and non-government organizations. The group included three officials from the Indian Administrative Service, and officials from the central governments of Sri Lanka and Nepal. Six representatives of industry (petrochemicals, fertilizers, electric power) were in the 1996 class, which also included a member of an Indian NGO (Gram Vikas) and a member from the print media (Indian Economic Times).

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7.0 LIST OF ACTIVE SUBCONTRACTS

Subcontracts for FY 1996				
Contractor, Principal Investigator, Address	Work Title (Research Activity)	Contract Number	FY 1996 Funding (\$K)	Start/End Dates
CRYSTALLINE SILICON AND ADVANCED DEVICES Crystalline Silicon				
Duke University T. Tan Durham, NC 27708	Impurity Gettering in Commercial PV Silicon	XD-2-11004-1	138.0	3/92 1/97
Georgia Institute of Technology A. Rohatgi Atlanta, GA 30332	Fundamental Research on Post-Growth Quality Enhancement Techniques in Crystalline Silicon Materials	XD-2-11004-2	123.3	4/92 12/96
Massachusetts Institute of Technology L. Kimerling Cambridge, MA 02139	Role of Point Defects and Impurities in Processing and Performance of Crystalline Silicon Solar Cells	XD-2-11004-4	158.8	7/92 1/96
North Carolina State University G. Rozgonyi Raleigh, NC 27695	Detailed Noncontact Electrical and Structural Characterization of PV Silicon Substrates	XD-2-11004-06	109.8	5/92 12/96
Texas Tech. University S. Eistreich Lubbock, TX 79409	Theoretical Analysis of Hydrogen-Vacancy-Impurity Formation and Dissociation	XAX-5-15230-01	27.0	6/95 2/97
University of California at Berkeley E. Weber Berkeley, CA 94720	Identification and Control of Lifetime-Reducing Defects in Polycrystalline Silicon Photovoltaic Materials	XD-2-11004-3	136.0	7/92 6/97
University of South Florida L. Jastrzebski Tampa, FL 33620	Optimization of Gettering Processes for PV Silicon	XD-2-11004-05	136.1	5/92 4/96

Subcontracts for FY 1996

Contractor, Principal Investigator, Address	Work Title (Research Activity)	Contract Number	FY 1996 Funding (\$K)	Start/End Dates
CRYSTALLINE SILICON AND ADVANCED DEVICES				
High-Efficiency Materials and Devices				
California Institute of Technology H. Atwater Pasadena, CA 91125	Novel Low-Temperature Substrate Technology for Compound Semiconductor Solar Cells on Low-Cost Substrates	XAL-4-13357-01	28.7	7/94 7/97
Research Triangle Institute R. Venkatasubramanian Research Triangle Park, NC 27709	High-Efficiency GaAs Solar Cells on Polycrystalline Ge Substrates	YAL-4-13357-03	206.0	8/94 10/97
University of California at Los Angeles E. Yablonovitch Los Angeles, CA 90095	Ultra-Efficient Epitaxial Liftoff Solar Cells Exploiting Optical Confinement in the Wave Limit	XAL-4-13357-02	110.0	7/94 7/97
CRYSTALLINE SILICON AND ADVANCED DEVICES				
Exploratory Materials and Devices				
Johns Hopkins University P. Searson Baltimore, MD 21218	Solar Electric Conversion at Dye-Sensitized Nanostructured Electrodes Fabricated by Sol-Gel Processing	XAD-3-12114-4	90.7	7/93 9/97
North Carolina State University S. Bedair Raleigh, NC 27695	New Approaches for High-Efficiency Cascade Solar Cells	XAD-3-12114-5	0.0	8/93 7/97
University of Illinois A. Rockett Urbana, IL 61801	Fundamental Studies of the Effect of Crystal Defects on CuInSe ₂ /CdS Heterojunction Behavior	XAD-3-12114-1	96.5	6/93 10/97
University of Utah P. Taylor Salt Lake City, UT 84112	Electronic Processes in Thin-Film PV Materials	XAD-3-12114-02	0.0	4/93 12/96

Subcontracts for FY 1996

Contractor, Principal Investigator, Address	Work Title (Research Activity)	Contract Number	FY 1996 Funding (\$K)	Start/End Dates
University of Washington B. O'Regan Seattle, WA 98105	Electrochemical Fabrication of Dye-Sensitized Heterojunctions for PV Energy Conversion	XCR-5-15234-01	21.9	6/95 6/97
CRYSTALLINE SILICON AND ADVANCED DEVICES Historically Black Colleges and Universities (HBCU)				
Central State University C.W. Fuller Wilberforce, OH 45384	HBCU PV Research Associates Program	XAX-5-15021-04	22.4	10/95 10/98
Clark Atlanta University G. Grams Atlanta, GA 30314	An Assessment of the Operation of Photovoltaics Devised for Solar Energy Applications	XCR-6-15327-01	0.0	10/95 7/97
Clark Atlanta University C. Papageorgopolous Atlanta, GA 30314	HBCU PV Research Associates Program	XAX-5-15021-02	21.3	9/95 9/98
Hampton University S. Hood Hampton, VA 23668	HBCU PV Research Associates Program	XAX-5-15021-07	49.3	10/95 10/97
Mississippi Valley State University B. Balam Itta Bena, MS 38941	HBCU PV Research Associates Program	XAX-5-15021-06	42.4	10/95 10/98
Southern University P. Bhattacharya Baton Rouge, LA 70813	HBCU PV Research Associates Program	XAX-5-15021-05	20.6	9/95 9/98
Texas Southern University J. Hill Houston, TX 77004	HBCU PV Research Associates Program	XAX-5-15021-03	22.6	10/95 10/98
Wilberforce University R. Nadella, E. Asikele, T. Habash Wilberforce, OH 45384	HBCU PV Research Associates Program	XAX-5-15021-01	62.8	9/95 9/98

Subcontracts for FY 1996

Contractor, Principal Investigator, Address	Work Title (Research Activity)	Contract Number	FY 1996 Funding (\$K)	Start/End Dates
THIN-FILM PV TECHNOLOGIES PROJECT				
Astropower, Inc. J. Rand Newark, DE 19716	Light-Trapped, Interconnected, Silicon-Film Modules	ZAF-5-14142-02	675.0	11/94 11/97
Colorado School of Mines D. Williamson Golden, CO 80401	Microstructure of a-Si-Based Solar Cell Materials by Small-Angle X-Ray Scattering	XAN-4-13318-04	84.9	4/94 4/97
Colorado School of Mines J. Trefny Golden, CO 80401	Process of Electrochemically Deposited CdTe-Based Solar Cells	XAF-5-14142-11	152.4	5/95 4/98
Colorado State University J. Sites Fort Collins, CO 80525	Device Physics of Thin-Film Polycrystalline Cells and Modules	XAX-4-14000-01	110.0	12/93 10/97
Energy Conversion Devices X. Deng Troy, MI 48084	Development of High, Stable-Efficiency Triple-Junction a:Si Alloy Solar Cells	ZAN-4-13318-11	244.0	7/94 12/97
Energy Photovoltaics A. Delahoy Princeton, NJ 08543	CIS Photovoltaic Technology	ZAF-5-14142-04	1,029.4	3/95 1/98
Florida Solar Energy Center N. Dhere Cocoa, FL 32922	CdTe Module Testing and Study of Transient and Irreversible Effects in Thin-Film Solar Cells	XCR-6-16773-01	30.0	5/96 5/98
Florida Solar Energy Center N. Dhere Cocoa, FL 32922	Polycrystalline Thin-Film CuInSe ₂ and CdTe PV Solar Cells	XG-2-11036-5	0.0	4/92 5/97
Golden Photon, Inc. S. Albright Golden, CO 80403	Improvement of Near-Term CdTe Processing and Product Capabilities and Establishment of Next Generation CdTe Technology	ZAF-5-14142-06	633.2	8/95 8/99

Subcontracts for FY 1996

Contractor, Principal Investigator, Address	Work Title (Research Activity)	Contract Number	FY 1996 Funding (\$K)	Start/End Dates
Harvard University R. Gordon Cambridge, MA 02138	Optimization of Transparent and Reflecting Electrodes for a-Si Solar Cells	XAN-4-13318-05	142.3	5/94 5/97
Iowa State University V. Dalal Ames, IA 50011	Comprehensive Research on Stability and Performance on a-Si:H and Alloys	XAN-4-13318-08	309.9	6/94 5/97
ISET V. Kapur Inglewood, CA 90301	Application of CIS to High-Efficiency PV Module Fabrication	ZAF-5-14142-07	517.8	4/95 4/98
National Institute of Standards and Technology A. Gallagher Boulder, CO 80303	Atomic-Scale Characterization of a-Si:H Films and Devices	DAD-4-14084-1	138.5	4/94 3/97
Pennsylvania State University R. Collins University Park, PA 16802	Wide-Band-Gap Solar Cells with High Stabilized Performance	XAN-4-13318-03	207.9	7/94 7/97
Purdue University J. Gray West Lafayette, IN 47907	Development and Application of a Computer Model for CdTe and CuInSe ₂	XG-2-11036-2	0.0	3/92 12/96
Siemens Solar Industries D. Tarrant Camarillo, CA 93011	CIS-Based Thin Film PV Technology	ZAF-5-14142-03	1,038.6	8/95 8/98
Solar Cells, Inc. G. Dorer Toledo, OH 43607	Technology Support for Initiation of High-Throughput Processing of Thin-Film CdTe PV Modules	ZAF-5-14142-05	986.1	3/95 3/98
Solarex Corporation R. Arya Newtown, PA 18940	Amorphous Silicon Research	ZAN-4-13318-01	257.0	9/94 9/97
Solarex Corporation R. Arya Newtown, PA 18940	Research on Thin-Film CIS-Based Solar Cells and Submodules	ZAF-6-14142-12	225.5	12/95 1/97

Subcontracts for FY 1996

Contractor, Principal Investigator, Address	Work Title (Research Activity)	Contract Number	FY 1996 Funding (\$K)	Start/End Dates
Syracuse University E. Schiff Syracuse, NY 13244	Research on High-Bandgap Materials and Amorphous-Silicon-Based Solar Cells	XAN-4-13318-06	100.8	5/94 5/97
United Solar Systems Corporation S. Guha Troy, MI 48084	Amorphous Silicon Research	ZAN-4-13318-02	310.0	7/94 7/97
United Solar Systems Corporation S. Guha Troy, MI 48084	Thin Film a-Si Alloy Research Partnership	ZAF-5-14142-01	526.0	2/95 2/98
University of California at Los Angeles R. Braunstein Los Angeles, CA 90024	Photocharge Transport and Recombination Measurements in Amorphous Silicon Films and Solar Cells by Photoconductive Frequency Mixing	XAN-4-13318-10	30.0	5/94 5/97
University of Delaware-IEC R. Birkmire Newark, DE 19716	Processing and Modeling Issues for Thin-Film Materials and Devices	XAV-3-13170-01	1,124.8	12/93 4/97
University of Florida T. Anderson Gainesville, FL 32611	Processing of CIS-Based Solar Cells: Characterization of Deposition Processes in Terms of Chemical Reaction Analyses	XAF-5-14142-10	124.2	5/95 5/98
University of North Carolina D. Han Chapel Hill, NC 27514	Experimental and Theoretical Study of the Factors Governing the Staebler-Wronski Photodegradation Effect in a-Si:H Solar Cells	XAN-4-13318-09	80.2	7/94 5/97

Subcontracts for FY 1996

Contractor, Principal Investigator, Address	Work Title (Research Activity)	Contract Number	FY 1996 Funding (\$K)	Start/End Dates
University of Oregon D. Cohen Eugene, OR 97403	Identifying Electronic Properties Relevant to Improving Stability in a-Si:H-Based Cells and Overall Performance in a-SiGe:H-Based Cells	XAN-4-13318-07	133.0	4/94 4/97
University of South Florida D. Morel Tampa, FL 33620	Advanced Processing of CdTe and Cu(InGa)Se ₂ -Based Solar Cells and Submodules	XAF-5-14142-09	167.4	4/95 4/98
University of South Florida D. Morel Tampa, FL 33620	Heterojunction Development and Optimization in Thin-Film Compound Semiconductor Cells	XAD-3-12114-03	203.6	5/93 7/97
University of Toledo A. Compaan Toledo, OH 43606	High-Efficiency Thin-Film Cadmium-Telluride-Based Solar Cells	ZAX-4-14013-01	108.9	1/94 10/97
University of Toledo A. Compaan Toledo, OH 43606	Optimization of Laser Scribing for Thin-Film PV Modules	ZAF-5-14142-08	130.0	4/95 4/97
Washington State University L. Olsen Richland, WA	Alternative Window Schemes for CuInSe ₂ -Based Solar Cells	XAF-6-15375-01	77	11/95 11/97

PHOTOVOLTAIC MANUFACTURING TECHNOLOGY (PVMaT) PROJECT

Advanced Energy Systems, Inc. R. Wills Wilton, NH	Next Generation Three-Phase Inverter	ZAF-5-14271-10	66.0	9/95 5/98
Ascension Technology, Inc. E. Kern Waltham, MA 01773	Manufacture of an AC Photovoltaic Module	ZAF-5-14271-05	189.4	7/95 2/98
ASE Americas M. Kardauskas Billerica, MA 01821	Market Driven EFG Modules	ZAF-6-14271-13	200.0	12/95 2/99

Subcontracts for FY 1996

Contractor, Principal Investigator, Address	Work Title (Research Activity)	Contract Number	FY 1996 Funding (\$K)	Start/End Dates
AstroPower, Inc. J. Rand Newark, DE 19711	Large-Area Silicon-Film™ Panels and Solar Cells	ZAF-5-14271-03	1,361.9	6/95 2/98
Evergreen Solar, Inc. J. Hanoka Waltham, MA 02154	Advanced Polymer PV System	ZAF-5-14271-09	156.0	12/95 11/97
Golden Photon, Inc. T. Brog Golden, CO 80401	Commercial Production of Thin-Film CdTe PV Modules	ZAI-3-11294-03	938.4	1/94 3/97
Iowa Thin Film Technology F. Jeffrey Ames, IA 50010	Monolithic a-Si Modules on Continuous Polymer Substrates	ZAF-5-14271-04	265.0	7/95 10/98
Omnion Power Engineer Corp. H. Meyer East Troy, WI 53120	Three-Phase Power Conversion System for Utility Interconnected PV Applications	ZAF-5-14271-02	308.2	8/95 2/98
Photovoltaics International, LLC N. Kaminar Sunnyvale, CA 94086	Manufacturing of the PVI PowerGrid	ZAF-6-14271-11	1,072.4	10/95 1/99
Siemens Solar Industries R. King Camarillo, CA 93011	Photovoltaic Cz Silicon Module Improvements	ZAF-6-14271-12	295.3	11/95 1/99
Solar Cells, Inc. D. Sandwisch Toledo, OH 43607	High-Throughput Manufacturing of Thin-Film CdTe PV Modules	ZAI-4-11294-02	500.0	11/93 11/98
Solar Design Associates S. Strong Harvard, MA 01451	Development of Standardized, Low-Cost AC PV Systems	ZAF-5-14271-01	68.0	9/95 2/98
Solar Electric Specialties Company G. Minyard Willits, CA 95450	Design, Fabrication, and Certification of Advanced Modular PV Power Systems	ZAF-5-14271-07	84.9	9/95 9/97
Solarex Corporation J. Wohlgemuth Frederick, MD 21754	Photovoltaic Manufacturing Technology Phase 2B, Process-Specific Issues	ZAI-4-11294-01	924.0	12/93 12/96

Subcontracts for FY 1996

Contractor, Principal Investigator, Address	Work Title (Research Activity)	Contract Number	FY 1996 Funding (\$K)	Start/End Dates
STR (formerly Springborn Laboratories, Inc.) W. Holley Enfield, CT 06082	Advanced Development of PV Encapsulants	ZAG-3-11219-02	0.0	12/92 5/97
Trace Engineering C. Freitas Arlington, WA 98223	2-kW DC to AC Power Inverter Module for PV Applications	ZAF-5-14271-08	109.5	9/95 9/97
Utility Power Group M. Stern Chatsworth, CA 91311	Development of a Low-Cost Integrated 20-kW AC Solar-Tracking Subarray for Grid-Connected PV Power System Applications	ZAF-5-14271-06	508.7	7/95 7/97

MODULE PERFORMANCE AND RELIABILITY

Arizona State University R.L. Hammond Tempe, AZ	Photovoltaic Module Certification/Laboratory Accreditation Criteria Development	AAF-13301-01	0.0	7/94 12/95
Endecon Engineering C. Whitaker San Ramon, CA	NREL Module Energy Rating Methodology	AAI-4-14192-01	0.0	5/94 8/95
Energy Conversion Devices, Inc. M. Izu Troy, MI	Rooftop PV Systems	AAI-5-14423-01	0.0	9/93 9/94
New Mexico State University/Southwest Technology Development Institute A. Rosenthal Las Cruces, NM 88003	Long-Term Environmental Effects on Roof-Mounted PV Modules	XAX-5-14448-01	0.0	11/94 2/96
Pennsylvania State University D.L. Allara University Park, PA	PV Module Degradation—EVA Pore Volume	XAX-4-13471-01	22.0	11/93 6/96
Sunset Technology Corporation J. Anderson Highlands Ranch, CO	PV Translations Equations and PV Module Energy Ratings Concept	TAD-4-14166-01	0.0	7/95 7/96

Subcontracts for FY 1996

Contractor, Principal Investigator, Address	Work Title (Research Activity)	Contract Number	FY 1996 Funding (\$K)	Start/End Dates
University of Colorado at Denver J. Boon Denver, CO	A Prototype Portable Custom-Made PV Encapsulant and Solar Cell Degradation Monitor (A Spectrophotometric Analyzer)	XAX-6-14454-01	117.7	3/96 9/97
PV MARKETS AND APPLICATIONS Domestic				
McNeil Technologies K. DeGroat Springfield, VA 22150	Photovoltaic Technology, Application, and Market Analysis Support	AAK-6-16784-01	198.1	6/96 8/97
Pacific Energy Group H. Wenger Walnut Creek, CA 94596	Renewable Energy Applications and Economic Analysis for Electric Power	AAX-5-15330-01	82.5	8/95 8/96
SUNY at Albany R. Perez Albany, NY 12205	Solar Resource Utility Load-Matching Assessment	XAR-1-11168-1	50.0	9/91 12/94
University of Delaware J. Byrne Newark, DE 19616	Evaluation of DSM Incentive Opportunities for Photovoltaics	XR-2-11248-1	25.0	10/91 6/96
PV MARKETS AND APPLICATIONS International				
Institute of Policy and Management L. Xiuguo Beijing, China 100080	Renewable Energy Policy Development and Commercial Project Identification in China	AAT-5-15002-01	21.8	3/95 3/96
Solar Electric Light Fund R. Freling Washington, DC 20009	Photovoltaics for Rural Energy in Gansu Province in the Peoples' Republic of China	AAX-6-15376-01	100.0	12/95 8/97
University of Delaware J. Byrne Newark, DE 19616	Evaluation of Intermediate Applications for Photovoltaics in Developing Countries	XCU-7-16806-0	125.0	2/97 12/98

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13. ABSTRACT (Maximum 200 words) This report summarizes the in-house and subcontract research and development (R&D) activities under the National Renewable Energy Laboratory (NREL) Photovoltaics (PV) Program from October 1, 1995 through September 30, 1996 (fiscal year [FY] 1996). The NREL PV Program is part of the U.S. Department of Energy's (DOE) National Photovoltaics Program, as described in the DOE Photovoltaics Program Plan, FY 1991-FY 1995. The mission of the DOE National Photovoltaics Program is to: "Work in partnership with U.S. industry to develop and deploy photovoltaic technology for generating economically competitive electric power, making photovoltaics an important contributor to the nation's and the world's energy use and environmental improvement. The two primary goals of the national program are to (1) maintain the U.S. PV industry's world leadership in research and technology development and (2) help the U.S. industry remain a major, profitable force in the world market. The NREL PV Program provides leadership and support to the national program toward achieving its mission and goals.					
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