Module Process Optimization and Device Efficiency Improvement for Stable, Low-Cost, Large-Area, Cadmium Telluride-Based Photovoltaic Module Production

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Summary

This is the first annual report under a three phase, 3.5 year subcontract through the National Renewable Energy Laboratory (NREL), #ZN-0-19019.

Photon Energy Inc. (PEI) has been involved with the development of CdS/CdTe devices and modules since 1984. Starting in 1987, a three(3) year subcontract under SERI contributed to progress toward the common objectives between PEI and the Department of Energy (DOE). In mid 1990, a second three(3) year subcontract was begun in order to further improve the technology base at PEI in order to better address the commercialization issues and objectives of the PEI and DOE photovoltaic goals.

The PEI objectives in Photovoltaics are covered through continuing advancement in four(4) major areas:

- * Modules efficiency
- * Module size
- * Module reliability
- * Module cost

Specific Goals For The Present Subcontract

The specific objectives of this three year program are:

- * To achieve active area efficiencies of greater than 14% on small cells,
- * To achieve aperture area efficiencies of greater than 13% on 1 ft² modules,
- * To achieve aperture area efficiencies of greater than 12.5% on 4 ft² modules,
- * To achieve greater than 20-year module life (based on life testing extrapolations) with no greater than 10% efficiency degradation.

Experimental

In order to meet the goals and milestones within this project at least six(6) basic tasks have been specified. They include:

TASK I: Windows, Contacts and Substrates (external device optimization)

TASK II: Absorber Material (Internal device optimization)

TASK III: Optimization of Device Structure

TASK IV: Encapsulation

TASK V: Process Optimization

TASK VI: Employee Safety: Evaluation and Improvement

Results and Projections

Following are a review of the most important achievements during the first phase of this subcontract.

Small Device Efficiency

A device with an area of 0.302 cm^2 was delivered to SERI and was measured in May of 1991 as 12.7% efficiency. The open circuit voltage (V_{oc}) was measured as 799 mV and the short circuit current density (J_{sc}) was measured as 26.21 mA/cm^2 for this device. These high currents (and the associated high quantum efficiencies at higher than CdS bandgap energies) have become the norm at PEI. The fill factor was low at 60.5%. If the fill factor can be raised to 70%, the corresponding efficiency will be ~14.7%. Efforts in this direction continue.

Dr. T.L.Chu and his group at the University of South Florida are on a lower-tier subcontract under our subcontract through SERI. Part of his efforts were to help develop solution-grown CdS for use at PEI as an alternate thin CdS layer. One of the iterations resulted in devices which produced up to 842 mV as measured at SERI. Combining the high voltages and fill factors on his devices with the high quantum efficiencies and short circuit currents on PEI devices should result in 15-17% efficient devices in future developments.

One Square Foot and Four Square Foot Module Efficiencies

Two 1 ft^2 modules were sent to NREL in September 1991 each with aperture areas of 825 cm^2 . The results of tests at both NREL and at PEI, show that PEI has attained aperture area efficiencies on modules between 7.6% and 8.3% on 1 ft^2 modules. The active area efficiency (~9.5-10) was abnormally high on these modules due to non-optimized division losses. Reduction of these interconnection losses, improvement of uniformity across the modules, and improvement of the fill factor (through improvement of the diode ideality factor) should result in significant improvements in the reasonably near future.

A 4 ft^2 module was tested at NREL in early November. The uncorrected outdoor value was 23.06 W., with aperture efficiency of 6.3%. The corrected output (to 1000 watts/ m^2 using a pyranometer reading) was 21.3 W.

Reliability Testing

The life testing data from NREL forms a significant part in the achievement of the reliability objective under this program. In order to be able to extrapolate life testing data accurately, one must start with very narrow measurement error bars. As will be discussed in Sec. 3.0, the difficulties associated with the accurate measurement of large-area CdS/CdTe modules have resulted in a considerable amount of effort being expended at PEI and at NREL in order to accomplish this error minimization goal.

Due to a combination of sample variations and measurement error bars, the life testing results have not been homogeneous. Some have failed (due to encapsulation quality-control insufficiencies); A few may have degraded slightly; Several have shown no signs of degradation.

The fact that several modules have shown no significant degradation indicates that there is probably no inherent degradation problem associated with CdTe modules. As further improvements to the encapsulation system and module measurement techniques are made, reliable module lifetimes are expected to become

more homogeneous and are expected to confirm excellent reliability through both real time and accelerated life testing.

Summary of Results

The efficiency and stability objectives at PEI on CdS/CdTe modules are being addressed. To summarize:

- Efficiencies of 12.7% have been achieved on small area devices.
- * One square foot modules have achieved over 8% aperture area efficiency (active area efficiency up to ~10%)
- * Four square foot modules have been tested at NREL at 23.1 watts (21.3) watts, normalized (6.3% efficiency).
- * Life testing at NREL (and PEI) shows no inherent stability problems with the CdTe technology.

Progress has been made and advancement is expected to continue in a steady fashion in Phase 2 and Phase 3 of this subcontract. The results should approach or exceed the proposed objectives.

A national award was jointly granted to PEI and SERI during this past year. This R&D 100 award is given to the 100 most important breakthroughs in the world on a yearly basis. PEI is proud to share this honor with NREL for the continuing developments on CdS/CdTe-based photovoltaic modules.

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1.0 INTRODUCTION AND OBJECTIVES

Background

Photon Energy, Inc. (PEI) has been involved in the development of CdS/CdTe photovoltaic modules since 1984. In 1987 a 3 phase, 3 year subcontract through the Solar Energy Research Institute (SERI) was undertaken. The objectives under this earlier subcontract were primarily directed toward the further development of an improved materials technology and fabrication processes for limited volume production of 1 ft² and 4 ft² CdS/CdTe photovoltaic modules, with stability and efficiency goals being the most significant milestones. The research and development efforts included improvement and further development in the areas of electroding, encapsulation, doping, small cell as well as 1 ft² and 4 ft² module performance optimization, and accelerated as well as real time life testing.

In June of 1990, a second, three-phase subcontract (ZN-0-19019) through SERI (now The National Renewable Energy Laboratory (NREL)) was undertaken at PEI. The objectives are to continue the further development of an improved materials technology and fabrication processes for limited volume production of 1 ft² and 4 ft² CdS/CdTe photovoltaic modules. The specific milestones relate to small device and module efficiency improvements, to module area enlargement, to module reliability assessment and improvement, and to module cost reduction.

A lower-tier subcontract, through the University of South Florida (USF), has been utilized for a large part of the device developments under the first phase of this subcontract. Dr. T.L.Chu and his group at USF have been instrumental in the development of PEI-USF devices based on "solution-grown" Cds.

Under the 3-year subcontract through SERI (now NREL) starting in 1987, PEI succeeded in producing and delivering to NREL a number of significant deliverables. A 1 ft² module was measured at NREL with 7.3% aperture area efficiency with a corresponding output of 6.11 watts. During this subcontract the aperture area efficiency on 1 ft² modules went from 5.4% to 7.3%. Small devices (0.302 cm²), cut from 1 ft² substrates, were produced and delivered to NREL during this earlier subcontract as well. The best of these devices measured 12.3% efficiency, 0.78 volts in open circuit voltage (V_{oc}), 25.0 mA/cm² in short circuit current density (J_{sc}) and 62.7% in fill factor. Regarding stability and life testing, an encapsulation system was developed and patented under this subcontract. An early version of this encapsulation system resulted in stable life tests of over 9+ months (the duration of the test at that time) in NREL outdoor life tests.[1]

Specific Goals For The Present Subcontract

In June of 1990, a second, three-phase subcontract (ZN-0-19019) was undertaken at PEI. The specific objectives of this three year program are:

- * To achieve active area efficiencies of greater than 14% on small cells,
- * To achieve aperture area efficiencies of greater than 13% on 1 ft² modules,
- * To achieve aperture area efficiencies of greater than 12.5% on 4 ft² modules, and
- * To achieve greater than 20-year module life (based on life testing extrapolations) with no greater than 10% efficiency degradation.

In order to accomplish the above objectives, the program has been designed to include the following task areas:

TASK I: Windows, Contacts, and Substrates (External device optimization)

- * Improved CdS window layers using various methods of deposition, including chemical deposition from solution (via Dr. Chu at USF),
- * The tin oxide window layer-electrode resistivity and uniformity,
- * Improved electroding techniques,
- * Reduction of optical losses due to module division.

TASK II: Absorber Material (Internal device optimization)

- * The deposition, characterization and evaluation of CdTe alloys,
- * The characterization, evaluation, and improvement of morphology effects of the CdTe,

TASK III: Optimization of Device Structure

- * Electronic characterization and modeling of the device,
- * The development of improved device structures where applicable.

TASK IV: Encapsulation

- * Analysis and optimization of present methods,
- * Hermetic sealing techniques,
- * Isolation of and concentration on long term corrosion issues.

TASK V: Process Optimization

- * Understanding the diffusion and reaction kinetic issues of the process,
- * Exploration and improvement of heat transfer issues.

TASK VI: Employee Safety Evaluation and Improvement

- Evaluation and improvement (where necessary) of monitoring program for Cd in the workplace,
- * Evaluation and improvement (where necessary) of policies and practices affecting worker safety in the workplace,

The major results of each task are reviewed within the following general criteria:

- 1) Increasing Cell and Module Efficiencies (Sec.2.0, Small Device Results)
- 2) Increasing Module Areas (Sec. 3.0, 1 ft² and 4 ft² Module Results)
- 3) Improving Module Reliability (Sec. 4.0, Reliability Testing)

2.0 SMALL DEVICE RESULTS

Device Structure

As reported previously [2], a 0.6-0.9 μm film of tin oxide is deposited onto commercial 3 mm float glass by spray pyrolysis, at a deposition temperature of approximately 480°C. A typical resistivity for the tin oxide film is $4\text{--}5 \times 10^{-4}$ ohm-cm, and typical extinction coefficients are 900-1100 cm^{-1} . The tin oxide films generally measure 5-9 ohms per square in sheet resistance and 90%-95% transmission relative to the glass substrate over the wavelength range from 520 nm to 850 nm, with a variation of 10%-40% in sheet resistance across a 4 ft^2 substrate.

A thin layer of CdS is then deposited on top of the tin oxide. Voltage-biased capacitance measurements, using Schottky diodes deposited on this CdS, indicates a carrier concentration on the order of $1 \times 10^{18}/\text{cm}^3$. Approximately 6 μm of CdTe is then deposited on top of the CdS; the measured hole concentration of the CdTe is on the order of $1 \times 10^{15}/\text{cm}^3$. To complete the device a graphite electrode is deposited on top of the CdTe to a thickness of approximately 10 μm . The top electrode is completed by the evaporation of a tin-based metal contact of approximately 1 μm thickness.

Performance Optimization

Utilizing this structure, a device with an area of 0.302 cm^2 was delivered to NREL and was measured in May of 1991 as 12.7% efficiency.[3] The open circuit voltage (V_{oc}) was measured as 799 mV and the short circuit current density (J_{sc}) was measured as 26.21 mA/cm^2 for this device. The fill factor was low at 60.5%. When the fill factor is raised to 70%, the corresponding efficiency will be ~14.7%. Efforts in this direction continues.

Several devices from PEI were measured at NREL with over 26 mA/cm^2 for J_{sc} . The highest measured J_{sc} in that set was 26.23 mA/cm^2 [4]. These high currents, and the associated high quantum efficiencies at higher than CdS bandgap energies, have become the norm at PEI. A typical quantum efficiency spectrum is shown in Fig. 2-1. This graph has been normalized to 100% of scale. Relative quantum efficiencies in the 85-95% range at wavelengths of 400nm are achieved at present on small devices and it is expected that similar quantum efficiencies will be the norm on larger area modules as well.

Tin Oxide Resistivity Improvement

Specific resistivities of tin oxide produced on large-area substrates have been observed as low as 2.4×10^{-4} ohm-cm at PEI. This occurred on very thick layers of tin oxide (in the range of 1.8 to 2.7 microns). It has not yet proven possible to achieve these values on films with thicknesses in the useful range of 0.2 to 0.8 microns. The typical specific resistivity values which are presently utilized in the interim period are between 4.0 and 4.5 $\times 10^{-4}$ ohm-cm.

Window Material and Junction Material Optimization

Dr. T.L.Chu and his group at the University of South Florida (USF) were on a lower-tier subcontract under the first phase of our subcontract through NREL. Part of his efforts under this subcontract were to help develop solution-grown CdS for use as our thin CdS layer. Appendix A of this annual report is a revision of his Final Report to us under this Lower-Tier Subcontract. Utilizing solution-growth CdS and CdTe applied by close-spaced sublimation

QUANTUM EFFICIENCY

Sample #719C-22C#4

(Normalized to 100%)

Aquired 1/4/92

Fig. 2-1

techniques, Dr. Chu and his group have been able to supply a device to SERI that measures 14.6% efficiency and utilized an anti-reflection coating.[5]

The major conclusions of the collaborative efforts between PEI and USF are reviewed here. Under global AM 1.5 conditions (measured at NREL), the best cell had a V_{oc} of 0.8384 V, J_{sc} of 23.08 mA/cm², and FF of 57.8%, corresponding to a conversion efficiency of 11.2%. [6] Further work to improve the reproducibility of the properties of CdS films will continue to be carried out to determine the feasibility of using solution-grown CdS for the manufacture of modules.

One of the experimental iterations resulted in devices which produced over 840mV. It was measured at NREL as 842mV [7]. Dr. Chu has been able to achieve V_{oc} values that were typically higher than the best results at PEI. Combining the high V_{oc} and fill factor values on his devices with the high quantum efficiency and J_{sc} values on PEI devices should result in 14-15% efficient devices without an anti-reflection coating.

Typical standard-type devices at PEI have efficiencies in the range of 10-12%, J_{sc} values of 24-26 mA/cm², V_{oc} values of 770-800 mV and correspondingly low fill factors (54-58%). The diode ideality factor is typically measured as 2.5-4.5, via method of Sites [8]. Improvement of the diode factor is the obvious direction of effort in order to increase the fill factors on typical PEI devices. Improvement of the fill factor to 67-69% would result in efficiencies of 12.4-14.3% using the same values for the other parameters.

In recent experiments at PEI, V_{oc} values of 846 mV have been observed on devices made by PEI processing. The indications observed through the solution-grown CdS provided by Dr.Chu at USF were instrumental in helping to direct the activities within the PEI program toward this high voltage milestone. The early attempts at this device type results in a somewhat different set of parameters from the typical PEI device discussed above:

Eff = 10.4%
 V_{oc} = 838 mV
 J_{sc} = 18.1 mA/cm²
Fill Factor = 69%
Diode Ideality Factor = 2.5-4.5

Combining these parameters with a typical J_{sc} value at PEI of 24-26 mA/cm² results in efficiencies of 13.8 - 14.9%.

Thus, improvement of current on low current, high voltage, high fill factor devices such as these, or improvement of fill factor on low fill factor, high current, average voltage standard PEI devices results in the same range of device efficiencies. Issues regarding advancements on both types of devices and approaches continue to be addressed.

Exploration of solution-grown CdS is to continue under the direction of Dr.T.L.Chu since questions relating to manufacturability have yet to be fully addressed. The laboratory results appear promising, and the simplicity of such a low-temperature deposition method provides great incentive for continued developmental effort.

3.0 ONE SQUARE FOOT MODULE AND FOUR SQUARE FOOT MODULE RESULTS

One Square Foot Module Results

Two 1 ft² module were sent to NREL in September 1991. They represent the present best effort at a high-efficiency CdS/CdTe module at PEI. The following table presents a comparison of the test results at NREL on 9/17/91 and at PEI on the same modules. As will be discussed in the next subsection, there remain some issues regarding the accurate testing of larger area modules. Aperture area on both of these modules is 825 cm². The active area for AAB885B is 719 cm² and for AAC024B is 724 cm². [9]

	PEI	NREL
AAB885B		
P _{max} (un-normalized)	6.4W	6.80W
P _{max} (normalized)	6.4W	6.54W
V _{oc}	21.1V	21.1V
I _{sc} (normalized)	0.590A	0.601A
FF	52%	51.6%
Aperture Area Efficiency	7.8%	7.9%
Active Area Efficiency	8.9%	9.1%
AAC024B		
P _{max} (un-normalized)	6.87W	6.59W
P _{max} (normalized)	6.84W	6.30W
V _{oc}	21.5V	21.3V
I _{sc} (normalized)	0.605A	0.597A
FF	52%	49.5%
Aperture Area Efficiency	8.3%	7.6%
Active Area Efficiency	9.4%	8.7%

It is concluded that PEI has attained aperture area efficiencies on modules between 7.6% and 8.3% on 1 ft² modules. Active area efficiencies are rather high, due to poor utilization of module area (non-optimized interconnection losses). Active area efficiencies on modules have also been observed at PEI in the range of 9.4-9.9% (See Fig. 3-1). Interconnection optimization, uniformity across the modules and improvement of the fill factor (through improvement of the diode ideality factor) should result in significant improvements in module output for the near term. As these issues are further resolved, the originally projected milestone goal for aperture area efficiencies of 10% should be realized and exceeded.

Performance Measurement Issues

PEI modules have proven to be difficult to measure accurately. For modules, that due to their size cannot be tested on the continuous Xenon artificial sunlight source at NREL, there has been considerable question regarding accurate measurement of PEI module output. The pulse simulator (LAPSS) typically utilized for large-area module testing does not appear to be a satisfactory means of testing modules such as ours which have a testing sensitivity related to the prior-biasing condition of the module. On the above modules, comparisons of tests were carried out on both the LAPSS source and a corrected outdoor test. The LAPSS test varied between 14.7% low to 20.7% low [10]. This large variation itself precludes the use of the LAPSS for testing or life testing use at the present time.

Even on the continuous Xenon artificial sun source at NREL, one has to insure that pre-biasing of the device at other than the maximum power point is

IV PERFORMANCE CURVE FOR AAB887A

Tested At PEI

Using Standard Calibrated at NREL

8/19/91

Normalized to 1000 W/m²

Fig. 3-1

minimized or avoided. As an example of this sensitivity to pre-biased condition, Fig. 3-2 shows a device test (0.30 cm^2) with 10 seconds under illumination at 2.0 V forward bias prior to acquiring the current-voltage (I-V) performance curve. Fig. 3-3 shows the same device tested after pre-biasing at 0 V (short circuit) for 30 seconds prior to testing without a maximum power point soak before measuring the I-V curve of the device. Fig. 3-4 shows a repeat test of Fig. 3-2 to indicate the reversibility of the effect. Fig. 3-5 shows the proper testing sequence utilizing a 10 second maximum power point soak prior to running the I-V curve for the device. Fig. 3-6 is the same device tested 15 minutes later, after the sample has re-equilibrated to room temperature. A positive-temperature coefficient for the fill factor is readily observed here. The rate of ramping through the voltages during acquisition for these devices was approximately 40mS per point, points taken in steps of ~ 10 mV. The V_{oc} is affected by temperature to the extent of ~ 2 mV per degree Celsius and the temperature rise of the substrate is estimated to be less than ~ 10 degrees Celsius.

It becomes apparent that these devices do not immediately adjust to their instantaneous bias condition. Since this is the case, it is necessary to incorporate a maximum power point tracking algorithm into the testing sequence in order to obtain accurate, repeatable, and realistic device efficiencies.

The J_{sc} values appear from these curves to be independent of the pre-biasing sensitivity condition. The V_{oc} , and therefore the calculated parameter of fill factor, appears to be quite dependent on the pre-biasing condition. The only parameters that can then be properly determined from a standard I-V curve on this type of device are the J_{sc} and the maximum power point (assuming a maximum power point tracking algorithm is utilized). In order to attain accurate V_{oc} and fill factor values, the V_{oc} of the device (or module) must be taken after relatively long term equilibration (at a constant temperature) using a standard intensity (with a standard spectral content) light source with a fixed-value high-impedance meter. An accurate V_{oc} will then be measurable and an accurate fill factor can then be properly determined.

In a study of this effect conducted at Colorado State University [11], the major conclusions were:

The voltage effect is real and reversible.

The voltage effect is dependent on voltage history, not illumination history.

Physically, the effect is almost certainly the result of changing the occupation of traps at the junction.

This voltage effect is expected to be significantly reduced as the junction quality is improved (lower diode ideality factor).

An attempt was made to measure the decay constants of the maximum power point output under various biasing conditions. A part of the results of this experimental work by K.Emery are shown in Fig. 3-7.[12] Notice the slowness of the response re-equilibration after each change in pre-biasing condition. Also notice the reversibility of this effect.

A significant amount of measurement difficulty and uncertainty has arisen on the PEI modules due to the above described testing issues. For module sizes larger than $\sim 4" \times 6"$, there has been considerable question regarding accurate

TESTING VARIATIONS TO DEMONSTRATE

Effects of Pre-Bias Conditions (10 secs at forward bias of 2.0V)

1/19/92

Device #719A-22C#2; Area = 0.302 cm²

Fig. 3-2

TESTING VARIATIONS TO DEMONSTRATE

Effects of Pre-Bias Conditions

(30 secs shorted and illuminated)

1/19/92

Device #719A-22C#2; Area = 0.302 cm²

Fig. 3-3

TESTING VARIATIONS TO DEMONSTRATE

Effects of Pre-Bias Conditions

(10 secs at forward bias of 2.0V)

1/19/92

Device #719A-22C#2; Area = 0.302 cm²

Fig. 3-4

TESTING VARIATIONS TO DEMONSTRATE

Effects of Pre-Bias Conditions

(10 secs max power point soak)

1/19/92

Device #719A-22C#2; Area 0.302 cm²

Fig. 3-5

TESTING VARIATIONS TO DEMONSTRATE

Effects of Pre-Bias Conditions

(10 secs mpp soak, After 15 min)

1/19/92

Device #719A-22C#2; Area = 0.302 cm²

Fig. 3-6

PHOTON ENERGY SAMPLE

"Upper"

8/19/91

Relaxation Curves
Fig. 3-7

measurement of PEI module outputs. The pulse simulator typically utilized for large area module testing does not appear to be a satisfactory means of testing modules such as ours which have a testing sensitivity to the prior-biasing condition of the module. (See also the 4 ft² module results in next section).

It is believed that the methodology planned to be implemented at NREL will be quite satisfactory. This methodology involves outdoor testing utilizing a proper standard (and/or very accurate spectral measurements of the insolation). It includes maximum power point tracking to determine the maximum power point directly, thereby avoiding any significant pre-bias effects. In addition, it includes testing the device or module prior to any significant module temperature rise. In the interim, there remains some disagreement over the actual measurements on 1 ft² and 4 ft² modules between NREL and PEI, but the difference is slowly being reduced in magnitude. The effort provided by the NREL testing facilities and J. Sites of Colorado State for helping to determine these testing problems and the direction for the proper solutions is appreciated.

The testing sequence presently utilized at PEI keeps the module out of the sunlight until just prior to testing in order to avoid temperature effects. A 4" x 6" standard calibrated at NREL (with similar spectral response characteristics to the module being tested) is utilized for normalization of the module current to a standard insolation of 1000 W/m² just prior to the module measurement. At least a 10 second maximum power point pre-soak is utilized prior to accepting the maximum power point value and continuing the acquisition of the I-V curve itself. The V_{oc} and fill factor values obtained from the curve are never taken too seriously due to the issues discussed above. The power output and I_{sc} are believed to be accurate within an error of approximately 3-4% of the value obtained.

Four Square Foot Module Results

A 4 ft² module (AAC027) was tested at NREL on November 6, 1991. The uncorrected outdoor value was 23.06 W. [13] The corrected output (normalized to 1000 watts/m² using a pyranometer reading, and not correcting for spectral differences) was 21.3 W. The indoor test on the LAPSS (Pulsed Simulator) resulted in a significantly low result of 18.2 watts. In light of the testing issues discussed above, it can be well understood why the LAPSS tests are inappropriate. Tests at PEI were in close agreement with the NREL outdoor test (21.6 Watts). The aperture area efficiency measured at NREL was 6.4% (aperture area 3323 cm²). The active area efficiency was 7.3% (active area 2909 cm²). As the optimization of the process and technology advances, increases in 4 ft² module output should result. Fig. 3-8 shows the normalized I-V curve measured outdoors at NREL on this 4 ft² module. Test temperature was estimated as 29 Celsius.

IV PERFORMANCE CURVE FOR AAC027

4 Square Foot Module
Measured Outdoors at NREL

11/3/91

Normalized to 1000 W/m² via Pyranometer

Fig. 3-8

4.0 RELIABILITY TESTING

The life testing data from NREL is meant to form an integral part in the achievement of the reliability objective under this program. That is, the ability to extrapolate life testing data to determine what amount of degradation (if any) will occur after 20 years exposure in the outdoor environment. In order to be able to extrapolate life testing data accurately, one must start with very narrow error bars on their measurement. As mentioned above, the difficulties associated with this accurate measurement of large-area CdS/CdTe modules has resulted in a considerable amount of effort being expended at PEI and at NREL in order to accomplish the necessary reduction in magnitude of these measurement error bars. The design of the methodology of testing and life testing at NREL is central to the ability of PEI (and other module manufacturers) to be able to determine the long-term reliability of their product without having to wait for 15-20 years.

The module deliverables under this subcontract are designed to keep close tabs on the improvements in design and efficiency that follow the development of superior modules. All the module deliverables are intended for initial measurement and subsequent life testing. With this in mind it was agreed that PEI should deliver sets of modules to NREL on a regular basis for testing and life testing.

Life-Testing Results

There have therefore been a number of sets of modules in a variety of stages of development delivered to SERI and NREL by PEI in the past several years. A number of the early sets were meant to serve as "proof-of-concept" indications that no initial degradation occurs and that CdTe is inherently stable if properly encapsulated.

Fig. 4-1, Fig. 4-2, and Fig. 4-3 show life testing data for three groups of submodules and modules delivered to NREL and life tested. [14] Each set has included in the data presentation for one of the modules in each set, an associated band indicating the estimated measurement error bars due to measurement issues. An estimate for the error of plus-or-minus 4-7% of the value is based on 2-3% for the pyranometer mis-calibration, 1-2% for not correcting for the spectral content of these outdoor measurements, and 1-2% for not correcting for the module temperature, (Some temperatures were as high as 43 Celsius measured on the module, not the film itself.) The error bands on these life testing data utilized plus-or-minus 5% of the value and are only representative of a nominal measurement error and do not include seasonal or marginally overcast test days that affect spectral content.

The values in these figures were determined from the actual outdoor measured output of the modules corrected to 1000 Watts per square meter utilizing a standard pyranometer. No corrections for spectral content were made. Future life tests on these type CdS/CdTe modules will likely be made utilizing a standard reference cell with similar spectral response to the modules being tested (in addition to the pyranometer reading) so that the error bar size can be determined for each measurement. Temperature rise of the modules can be minimized (or at least standardized) so that the error due to temperature can be reduced to insignificance as well. Both temperature and spectral variations, if significant, should show up as a seasonal variation. It may be possible to discern a slight seasonal variation from the data here with an active imagination. Longer life tests with a more statistical number of modules will be able to better deduce the extent of these issues.

LIFE TESTING DATA

Taken at NREL

Deployed Jul. '89
4" x 6" Submodules

Fig. 4-1

LIFE TESTING DATA

Taken at NREL

Deployed Oct. '90
1 Square foot Modules

Fig. 4-2

LIFE TESTING DATA

Taken at NREL

Deployed Apr. '91
1 Square Foot Modules

Fig. 4-3

A number of the earliest attempts were presented for life testing without sufficient weatherproofing. The result has been that after several years the encapsulation system on a number of these modules has failed. As the encapsulation system and weatherproofing has advanced, these types of failures have been reduced as well. As progress continues these types of field failures are expected to be reduced to insignificance.

Discussion and Conclusions on Life Testing Results

It has been difficult to tell the difference between a significant degradation of the module and error involved in the measurement of the module. As was discussed above, it is expected that as the error bars relating to the module output measurement are further reduced, proper extrapolations of life tests can be made. Until this occurs to a sufficient extent, extrapolation of life testing cannot be properly done and conclusions relating to reliability cannot be confidently drawn.

Due to some sample variations and the size of the measurement error bars, the life testing results have not been homogeneous. Some have failed somewhat dramatically (primarily due to insufficient quality control during the encapsulation process); some have appeared to degrade slightly; some have shown no signs of degradation.

Quality control issues related to encapsulation have been determined to be responsible for most if not all of the dramatic failures in the field. It was earlier concluded that 1 ft² modules had water vapor permeabilities of 2mg to 50mg per year per linear foot of module edge.[15] Thus, as long as the assembly of these encapsulated modules proceeds properly, the performance of the encapsulation system is quite good. Testing of the encapsulation quality is not trivial, and development of acceptable methodology for this quality control step has somewhat lagged. As this quality control improves, however, it is expected that such failures will be reduced to insignificance.

The fact that a number of modules have shown no significant degradation indicates that there is probably no inherent degradation problem associated with CdTe modules. As further improvements to the encapsulation system and module measurement techniques are made, reliable module lifetimes are expected to become more homogeneous and are expected to show excellent continuing reliability on both real time and accelerated life tests.

A milestone for the third phase of this subcontract is: "To achieve indications of less than 10% degradation of modules extrapolated to 20 years." Given the life testing results already in hand, it should be possible with reduced measurement error bars and improved encapsulation weatherability to meet or exceed this milestone.

5.0 CONCLUSIONS AND FUTURE PLANS

In all areas under this subcontract, significant advancement toward the milestones has been achieved. In many cases the milestones have been exceeded.

The efficiency results on 1 ft² and 4 ft² modules are not quite as expected by this time. However, progress has been made and advancement is expected to continue in a steady fashion in Phase 2 and Phase 3 of this subcontract. The results should approach or exceed the proposed milestones.

The most important areas under the next phases of this subcontract are:

- * Continued development of efficiencies on small devices.
- * Continued efficiency improvements (both active area and aperture area) on 1 ft² and 4 ft² modules.
- * Continued efforts in encapsulation design and the quality control steps of the encapsulation assembly sequence.
- * Continued and expanded life testing at both NREL and PEI to insure quality and longevity.

6.0 ACKNOWLEDGEMENTS

We at PEI would like to acknowledge the efforts of the NREL administrators, monitors, and technical support teams as well as the other NREL subcontractors who have contributed to the efforts and advancement at PEI under this Subcontract.

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Awards

A national award was jointly granted to PEI and NREL during this past year. This R&D 100 award is given to each of the 100 most important breakthroughs in the world on a yearly basis by R&D magazine. PEI is proud to share this honor with NREL for the continuing developments on CdS/CdTe-based photovoltaic modules and technology.

APPENDIX A

LOWER-TIER SUBCONTRACT

through

THE UNIVERSITY OF SOUTH FLORIDA

CADMIUM SULFIDE FILMS

Transparent conducting semiconductors (TCS) have major applications in optoelectronic devices, such as the heterojunction partner (or window) in thin film solar cells. The high optical transmission in the visible region and high electrical conductivity occur in many non-stoichiometric or doped oxides and sulfides, such as fluorine-doped tin-oxide ($\text{SnO}_2\text{:F}$), tin-doped indium oxide (ITO), oxygen-deficient or aluminum doped zinc oxide (ZnO:Al), cadmium sulfide (CdS), etc. The electron affinity, lattice parameter, and thermal expansion coefficient of the TCS should be compatible with those of the absorber. CdS is the most commonly used window material for efficient thin film cadmium telluride (CdTe) heterojunction solar cells. However, the bandgap energy of CdS , 2.42 e V, is relatively small for CdS/CdTe solar cells, since $0.1\mu\text{m}$ of a CdS film absorbs 36% of the incident radiation with energy greater than the bandgap energy. Thus, a very thin CdS film, a few hundred angstroms in thickness, must be used in order that the solar cell shows good response in the blue region. Alternatively, a solid solution of CdS and ZnS (bandgap energy = 3.66 e V), $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ may be used as the window material. However, the compatibility of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ with CdTe has not been established. The deposition of CdS and $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ films from an aqueous solution has been investigated in this program.

1. Overview of CdS Deposition

The commonly used techniques for the deposition of CdS films include vacuum evaporation, chemical vapor deposition, chemical

spraying, and solution growth. Evaporation from a CdS source in a conventional bell jar system is the standard deposition technique in the fabrication of $\text{Cu}_2\text{S}/\text{CdS}$ solar cells. The carrier concentration in deposited CdS film, usually 10^{15} to 10^{16}cm^{-3} , is determined by the parameters of the evaporation process, such as substrate temperature. Highly conductive films (carrier concentration of 10^{18} to 10^{19}cm^{-3}) can be deposited by the coevaporation of In. Chemical vapor deposition technique using the reaction between elemental Cd or a volatile Cd compound with hydrogen sulfide in a gas flow has been used extensively for the growth of CdS films and crystals. The solution spray technique is better suited for larger scale applications. Typically, an aqueous solution containing equimolar CdCl_2 and thiourea of 0.01 M to 0.1 M concentration is used. The chemical reaction takes place when the solution is sprayed onto a heated substrate, deposition CdS. The properties of the deposited films depend on the substrate temperature, spraying rate, and post-spray heat treatment. The heating of CdS in a hydrogen-containing atmosphere lowers its resistivity due to the generation of S vacancies.

The deposition of CdS films on glass and coated glass substrates from aqueous solutions has been reported by several authors during the past few years [1-5] and is briefly reviewed here. The solution growth technique utilizes the reaction between a cadmium complex (ammonia, cyanide, or triethanolamine) and an organic sulfidizing agent [thiourea, $\text{CS}(\text{NH}_2)_2$, or thioacetamide, $\text{CH}_3(\text{CSNH}_2)_2$] on the substrate surface. The cadmium complex and

organosulfur compounds provide very low concentrations of Cd^{++} and $\text{S}^{=}$ in solution. When the product of the ion concentrations in solution exceeds the solubility product of CdS (1.4×10^{-29} at 25°C), a chemical reaction takes place, producing CdS . The chemical reaction may take place on the substrate surface to yield an adherent film and may take place in the solution precipitating CdS . The homogeneous reaction in solution is highly undesirable, since the absorption of CdS particulates on the substrate surface yields powdery and non-adherent films. Thus, the deposition parameters, such as temperature and composition of the solution, must be optimized to promote the surface reaction.

In the work of Call et al. [2], two solution compositions were used: $\text{Cd}(\text{NO}_3)_2 + \text{KOH} + \text{NH}_4\text{NO}_3 + \text{CS}(\text{NH}_2)_2$ and $\text{Cd}(\text{NO}_3)_2 + \text{KOH} + \text{KCN} + \text{CS}(\text{NH}_2)_2$. Hexagonal CdS films with strong preferred orientation along the c-axis were obtained at $80^\circ \pm 5^\circ\text{C}$. Heat treatment in forming gas at 350°C has been found to reduce the resistivity of CdS to useful levels but produced no significant grain-enhancement. Thin film $\text{CdS}/\text{Cu}_2\text{S}$ solar cells were made by the deposition of multilayers of CdS films (maximum thickness obtainable from a single deposition is limited to a few tenths of a micrometer) on Al, Zn, and Mo substrates followed by immersion in a CuCl solution. The photovoltaic characteristics of the cells were poor; the highest open-circuit voltage, short-circuit current density, and conversion efficiency were 0.3 V, $2.7 \text{ mA}/\text{cm}^2$, and 0.13%, respectively.

The growth kinetics of CdS films from an ammonical solution of a

cadmium salt and thiourea have been reported [3]. The concentration of NH_3 and the stirring of the solution are important parameters. Vigorous stirring facilitates the replenishment of the reaction species at the substrate surface. The addition of NH_3 to the Cd-salt solution first produces a white precipitate of $\text{Cd}(\text{OH})_2$, which dissolves by the further addition of NH_3 to form $\text{Cd}(\text{NH}_3)_4^{++}$. The relative quantities of $\text{Cd}(\text{OH})_2$ and $\text{Cd}(\text{NH}_3)_4$ are determined by the concentration of NH_3 in solution. Using a solution containing 0.1 M CdAc_2 and 0.2 M $(\text{NH}_2)_2\text{CS}$ at 65°C , the rate of CdS formation was found to depend strongly on the concentration of NH_3 , or the pH of the solution; a saturation thickness of about 200 Å was reached at a pH of 10.8 after 5 min of reaction (40 Å/min), and an ultimate thickness of about 500 Å was obtained after 10 min (50 Å/min). The authors have claimed that better quality of CdS films were obtained when the concentration of NH_3 was not sufficient to dissolve the $\text{Cd}(\text{OH})_2$ precipitates. This is believed to be unlikely because of the low reaction rate between solid $\text{Cd}(\text{OH})_2$ and thiourea in solution. The small saturation thickness is due most likely to the high rate of CdS formation. The reaction rate can be significantly reduced by using lower concentrations of reaction species and by using an ammonium salt as a buffer.

The addition of an ammonium salt to the reaction mixture has indeed improved the quality of CdS films[5]. Using a solution containing 0.02 M CdCl_2 , 0.065 M NH_4Cl , 0.21 M thiourea, and 0.65 M NH_3 , adherent and reflective films of 0.2-0.3 μm thickness with grain diameter of 0.1-0.2 μm have been deposited on glass and ITO/glass substrates at 90°C . The optical bandgap energy of as-

deposited CdS has been measured to be 2.45 eV which is reduced to 2.38 eV after heating in hydrogen. Associated with the change in bandgap energy, the dark resistivity is reduced from 10^9 to 0.15 ohm-cm and the AM resistivity is reduced from 700 to 0.1 ohm-cm.

The growth of In-doped CdS films from an aqueous solutions has also been reported [6]. A measured amount of InCl_3 was added to an ammonical solution of CdSO_4 and thiourea. The thickness and electrical conductivity of deposited films were found to vary with the concentration of InCl_3 in solution. For example, the conductivity of doped CdS deposited with 0.01 wt % In is higher than that of undoped film while the use of 0.05 wt % In produced CdS films with lower conductivity than the undoped films. However, the incorporation of In into CdS is unlikely because of the facts that the solubility of $\text{In}(\text{OH})_3$ in water is only 2.2×10^{-9} moles/L at 20°C and that unlike $\text{Cd}(\text{OH})_2$ is insoluble in ammonia. In this work, the incorporation of donors into CdS was accomplished by using boron to substitute for cadmium in the crystal lattice.

2. Deposition of CdS Films Aqueous Solutions

In this program, CdS films have been deposited on glass and SnO_2 -coated glass substrates from an aqueous solution. The reagents used for the deposition process include a cadmium salt, (acetate, chloride, or sulfate), an ammonium form a complex $\text{Cd}(\text{NH}_3)_4^{++}$, with a stability constant of 3.6×10^6 at room temperature, i.e. the concentration of Cd^{++} is on the order of 3×10^{-7} M in a solution of 1 M $\text{Cd}(\text{NH}_3)_4^{++}$ and 1 M NH_3 . The rate of decomposi-

tion of thiourea increases with increasing pH and temperature of the solution. The important parameters are: the preparation of the substrate surface, the concentration and composition of the solution and its temperature, stirring rate, and post deposition cleaning. Cleanliness is essential in the entire sequence of processing.

2.1 Procedure

Substrates of different areas were used: 9 cm² (3 cm x 3 cm), 150 cm² (10 cm x 15 cm), and 900 cm² (30 cm x 30 cm). Most of the experiments were carried out using glass and SnO₂/glass substrates of 150 cm² area furnished by Photon Energy, Inc. The glass substrates were etched in diluted hydrofluoric acid (1HF(49%):10 H₂O) to remove a surface layer, followed by thorough rinsing with deionized (DI) H₂O. The SnO₂/glass substrates were cleaned successively in tetrachloroethylene, acetone, methanol, and DI H₂O with ultrasonic agitation. Eight substrates were used in each experiment. Teflon clamps were used to hold two substrates together back to back; they also served as spacers to separate the adjacent pairs of substrates by about 2 cm. Four pairs of the substrates were held vertically in a 4 liter beaker containing a stirring bar, and the bottom of the substrates was about 2.5 cm above the bottom of the beaker to allow the stirring of the solution. Approximately 3L of a solution containing CdAc₂ and MH₄Ac in DI water was introduced into the beaker. The beaker was covered with a plastic wrap, placed on a stirrer hotplate, and stirring was maximized. After the temperature was stabilized at the desired value, 70° - 90°C, NH₄OH and thiourea

were added. The reaction was allowed to proceed for the desired length of time.

Many experiments were performed in this system, and the concentrations of the reactants were varied over a wide range. The concentrations of CdAc_2 , thiourea, NH_4Ac , and NH_4OH were $(1-3) \times 10^{-3}$ M, $(1-6) \times 10^{-3}$ M, $(1-4.5) \times 10^{-2}$ M, and $(0.375-1.6)$ M, respectively. Various concentrations of H_3BO_3 were used for the deposition of B-doped CdS films. A Typical solution used for the deposition of CdS films has the composition of 2×10^{-3} M in CdAc_2 , 4×10^{-3} M in thiourea, 4×10^{-2} M NH_4Ac and 1.25 M in NH_4OH . From this solution, adherent and transparent CdS films of 7000 Å thickness were deposited in four hours. The solution was clear at the beginning of the deposition and remained so for about fifteen minutes when a light yellow color was observed on the substrate surfaces. After about thirty minutes, the solution was medium orange in color, and the substrates were barely visible in the beaker. Small particles of CdS could be seen in the solution after about ninety minutes.

Scaling the process to facilitate the deposition of CdS films on 30 cm x 30 cm substrates was a greater challenge than expected. An entirely different apparatus was needed because glass containers of sufficiently large dimensions were not readily available. Stainless steel and aluminum vessels were found to be unsuitable because of their reactivity towards the solution used for the deposition process. Although aluminum oxide is inert toward the CdAc_2 - NH_4Ac -thiourea- NH_4OH solution, anodized aluminum was found to be unsuitable due, probably, to pinholes in the anodic oxide.

The deposited films were nonadherent and dark in color. Since organic polymers are chemically inert, a polypropylene vessel of 45 cm x 20 cm x 40 cm in dimensions was used. This system enabled the deposition of CdS films on four substrates placed in sets of two substrates held back to back by teflon clamps on the bottom. The two pairs were separated with a teflon cross bar containing two grooves separated by 7.5 cm to hold the substrates in place, and fit tightly inside the tank. Two 1 kW vycor immersion heaters were placed in two corners. A thermocouple encased in Pyrex was connected to a temperature controller which actuated a relay to power the heaters. One stirring motor with a polypropylene stirring rod was mounted on each end of the tank. The stirring rods extended to within 2.5 cm of the bottom of the tank, and consisted of three rectangular paddles approximately 5 cm x 7.5 cm apart on a rod of 1.25 cm diameter.

Several depositions were performed in this system with CdAc_2 in the concentration range $(1.4-2) \times 10^{-3}$ M, thiourea in the concentration range $(2.8-4) \times 10^{-3}$ M, NH_4Ac in the concentration range $(1.4-3.5) \times 10^{-2}$ M, and NH_4OH in the concentration range 0.35-1.1M. The following is an example of the deposition procedure. Thoroughly cleaned substrates were placed back to back, and two teflon clamps were fixed to the bottoms of both pairs of substrates. Then the substrates were placed in the vessel, the spacer bar was mounted across the top, 28 liters of DI H_2 , 550 ml of 0.2 M thiourea were added. The solution was initially clear, a light yellow color was observed after 1 minute. After 8 minutes, the bottom of the tank obscured by the solution, which

was dark yellow. After 20 minutes, the substrates could no longer be seen, and the solution was light orange in color. After 35 minutes, the solution was dark orange and a high density of particles was observed in the solution. It appears that the polypropylene container causes the precipitation to occur rapidly compared with the depositions performed in Pyrex beakers, due predominantly to the high density of nucleation centers provided by the textured surface of polypropylene. The resultant films are much thinner, no greater than 3000 Å and nonuniform.

2.2 Effects of Solution Composition

The maximum thickness of adherent CdS films obtainable in a single deposition depends on the temperature, concentration, and composition of the solution. The growth of CdS films is completed when Cd^{2+} or S^{2-} in solution are depleted. Adherent CdS films are produced by the heterogeneous reaction on the substrate surface through the absorption of Cd^{2+} or S^{2-} ; a low rate of CdS formation usually facilitates the heterogeneous process. The homogeneous process may be suppressed by increasing the concentration of NH_4Ac , the concentration of NH_4OH , or both. Once these concentrations are optimized, it is necessary to increase the concentration of CdAc_2 and thiourea to increase film thickness. By decreasing the temperature, the rate of film formation is decreased, offering another way of suppressing the homogeneous process.

The effects of process parameters on the terminal thickness of

CdS films deposited on substrates of 10 cm x 15 cm area were studied in detail. In a series of experiments, the concentration of CdAc_2 and $(\text{NH}_2)_2\text{CS}$ were maintained at 3×10^{-3} M, and 6×10^{-5} M, respectively, while the concentrations of NH_4Ac was adjusted to yield the same pH, 9.35. As the concentration of NH_4Ac is increased, the concentration of NH_4OH must also be increased to maintain a constant pH. The results in Fig. 1 show the terminal thickness of the CdS films as a function of the concentration of CdAc_2 in solution at constant pH (9.35), temperature (90°C), $\text{CdAc}/(\text{NH}_2)_2\text{CS}$ ratio (2), and NH_4Ac concentration (0.035 M). As the concentration of CdAc_2 is increased, the terminal thickness increases up to a CdAc_2 concentration of 2.75×10^{-3} M and decreases at higher concentrations. This can be explained as the terminal thickness being source limited at low concentrations of CdAc_2 reaching an optimum value, and then being limited by the absorption of the excess homogeneous product at higher concentrations of CdAc_2 .

3. Properties of CdS films

3.1 Structural Properties

As-deposited CdS films are smooth, adherent, and specularly reflective after ultra sonic cleaning. Thickness is controllable in the range of 700 Å to 8000 Å on 10 cm x 15 cm substrates. CdS films deposited on large area substrates, 30 cm x 30 cm, are not uniform or reproducible in thickness.

Figure 1 CdS film thickness as a function of NH_4OH concentration in solution.

Figure 2 CdS film thickness as a function of CdAc_2 concentration in solution.

In the deposition of CdS films ranging in thickness from 700 - 1500 Å, the homogeneous process is suppressed, and the solution is essentially free of CdS precipitates. Scanning electron microscopy indicated that films of these thicknesses deposited on glass substrates are discontinuous, consisting of densely packed microcrystallites less than 0.1 μm in size. These films did not contain large clusters of CdS on the surface, as are found on thicker films. The lack of clusters on these thinner films may be attributed to the lack of homogeneous reactions in the solution. Scanning electron microscopy reveals that thicker films, 5000 - 7000 Å thickness, contain densely packed microcrystallites ranging in size from less than 0.1 μm to about 0.2 μm. In addition, some large clusters formed from the homogeneous reaction in the solution were embedded in these films. CdS films deposited on glass substrates exhibit the smallest grain sizes and many discontinuities due to nucleation problems. Films deposited on commercial SnO₂:F/glass show a slightly larger grain size and are continuous, and films deposited on PEI SnO₂/glass have the largest grain size and are continuous as well.

The crystallographic properties of CdS films deposited on glass and SnO₂:F/glass substrates has been investigated by X-ray diffraction. CdS exists in two crystalline modifications: the hexagonal (wurtzite) phase and the cubic (zincblende) phase. Polycrystalline hexagonal and cubic CdS of random orientations are known to show many strong X-ray diffraction peaks. The X-ray diffraction spectra of CdS films of about 1500 Å thickness on glass substrates and 0.5 - 0.7 μm thickness on SnO₂/glass substrates were obtained using CuKα radiation by scanning 2θ in the

range of 25x - 55x. The results are shown in Fig. 3. The thinner film was deposited under conditions of negligible homogeneous reaction, and the X-ray spectrum shows a single diffraction peak at $2\theta = 26.5^\circ$, indicating a strong preferred orientation. This peak could be associated with the (002) reflection of hexagonal CdS or the (111) reflection of the cubic modification. The preferred orientation of this CdS film is due to the controlled nucleation process associated with the low formation rate of CdS. On the other hand, the homogeneous reaction cannot yet be eliminated during the deposition of the thicker CdS films. As a result, the CdS films on a SnO_2 substrate shows two additional diffraction peaks at 43.8° and 52° . They are associated with the (110) and (112) reflections of the hexagonal modification or the (200) and (311) reflections of the cubic CdS structure.

3.2 Optical Properties

The optical transmission of CdS films on glass substrates was measured by using a Varian Cary 17D spectrophotometer. An example is shown in Fig. 4, where the optical transmission of a CdS film of 5000 Å thickness is reproducible. The bandgap energy deduced from the α_2 (α is the absorption coefficient) versus photon energy plot in the wavelength range 450 - 520 nm is about (2.35 - 0.05) eV (Fig. 5), slightly lower than the bandgap energy of single crystalline CdS, 2.42 eV.

3.3 Electrical Properties

The lateral resistivity of CdS films deposited on glass substrates were measured by the conventional potential probe tech-

Figure 3 X-ray diffraction spectra of CdS films (A) and SnO_2 /glass (B) substrates.

Figure 4 Optical transmission of a CdS film of 5000 Å thickness on a glass substrate.

Figure 5 The optical absorption of a CdS film for bandgap energy determination.

nique. A solution of 25% In in Ga, a liquid at room temperature, was used as contacts to CdS films. Four collinear contacts were applied to the surface of each sample, and approximately 1.2 V was applied across the outer contacts. The current through the sample was measured with a Keithley picoammeter, and voltage drop across the two inner contacts was measured with a high input impedance voltmeter. Since no current flows through the voltage probes, the measurements are not affected by contact resistance. The dark resistivity of undoped CdS films is always higher than 10^4 ohm-cm.

The addition of boric acid to the solution during the growth of CdS has been found to have a pronounced effect on the dark resistivity of CdS films. Figure 6 shows the dark resistivity of B-doped CdS films as a function of the $H_3BO_3/CdAc_2$ in solution. The addition of boron into the solution reduces the resistivity of CdS films. A minimum in dark resistivity is observed at a $H_3BO_3/CdAc_2$ ratio of 0.001. As boron concentration in solution increases, the dark resistivity increases and approaches that of undoped films (1.9 vs. 2.1×10^4 ohm-cm). Figure 7 shows the resistivity of CdS films measured under illumination with ELH lamps at 100 mW/cm^2 . The minimum is again seen at a $H_3BO_3/CdAc_2$ ratio of 0.001. However, the illuminated resistivity of boron doped CdS films deposited at large $H_3BO_3/CdAc_2$ ratios is essentially independent of the boron concentration.

Figure 6 Dark resistivities of CdS films deposited at different $\text{H}_3\text{BO}_3/\text{CdAc}_2$ ratios.

Figure 7 Illuminated resistivity of CdS films deposited at different $\text{H}_3\text{BO}_3/\text{CdAc}_2$ ratios.

Figure 8 The increase of resistivity of an undoped CdS film with time after removal of the ELH light source.

Figure 9 Time constant, τ , of B-doped CdS films grown at different $H_3BO_3/CdAc_2$ ratios.

After the removal of the ELH light source, the decay of photogenerated carriers in all CdS films takes place very slowly. Figure 8 shows the rate of increase of electrical resistivity of an undoped CdS film after the removal of the light source. To show the effect of B-doping, a time constant, τ , is defined as the time required for the resistivity to increase by a factor of 10. In undoped CdS films, τ can be seen to be about 35 minutes. Figure 9 shows the effect of boron doping on time constant τ . The incorporation of boron into CdS films increases the time constant appreciably indicating the introduction of slow states in the CdAc₂ in the concentration range $(5-30) \times 10^{-4}$ M, ZnAc₂ in the concentration range $(5-5000) \times 10^{-4}$ M, thiourea in the concentration range $(5-5000) \times 10^{-2}$ M, and NH₃ in the bandgap. The maximum τ is found in CdS films deposited at a H₃BO₃/CdAc₂ ratio of 0.001, where the photoconductivity ratio is the lowest. When comparing Fig. 6 with Fig. 9, it is interesting to note that dark resistivities at a H₃BO₃/CdAc₂ ratio of 0.01 are similar, 2.1×10^4 ohm-cm, and 1.9×10^4 ohm-cm, respectively; however the time required to achieve these values is increased by a factor of about 16 in the boron doped film.

4. Solution-Grown CdS for Solar Cells

Many CdS films of various thickness deposited on SnO₂/glass substrates were used for the fabrication of CdS/CdTe solar cells at Photon Energy, Inc. Under global AM 1.5 conditions, the best cell had a V_{OC} of 0.8384 V, J_{SC} of 23.08 mA/cm², and FF of 57.8%, corresponding to a conversion efficiency of 11.2%. Further work to improve the reproducibility of using solution-grown CdS for the manufacture of thin film solar cells.

5. Deposition of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ Films From Aqueous Solutions

The deposition of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ films from an aqueous solution has been reported [7]. However, attempts to duplicate this report were not successful. In the present work, ammonia and triethanolamine (TEA), were used as the complexing agent, CdAc_2 and ZnAc_2 were used as the Cd and Zn sources, respectively, thiourea was the sulfur source, and NH_4Ac was used as a buffer. Concentration range (0.5-4) M were used. The glass and $\text{SnO}_2/\text{glass}$ substrates were thoroughly cleaned in the usual manner and suspended vertically in a beaker. In the first few experiments, a simple substitution of ZnAc_2 for one half of the CdAc_2 was made in the starting solution of a standard process. The resultant films were not adherent and separated from the substrates during ultrasonic cleaning. Through altering the parameters and slowing the rate of formation, adherent films were eventually deposited with CdAc_2 and ZnAc_2 in a 3:1 molar ratio. The bandgap energy deduced from the α^2 vs. photon energy curve was consistent with that of CdS only. This was attributed to the fact that CdS is more stable than ZnS; the solubility products of ZnS and CdS at room temperature are 1.2×10^{-23} and 3.4×10^{-29} , respectively. To compensate for this large difference, Zn/Cd ratios of up to 1000 in the starting solution were used. However, adherent films of sufficient thickness for characterization cannot be obtained at ZnAc/CdAc molar ratios greater than the 3:1 ratio noted above.

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