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CIS Photovoltaic Technology

**Annual Technical Report for the Period
12 January 1995 - 11 January 1996**

A.E. Delahoy, J.S. Britt, A.M. Gabor,
and Z.J. Kiss

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A national laboratory of the U.S. Department of Energy

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Preface

This report describes work performed during the first year (January 12, 1995 - January 11, 1996) of a three-phase, three-year, cost-shared subcontract with NREL entitled "CIS Photovoltaic Technology". The subcontract is one component of the NREL Thin Film Partnership Program. Remarkably high efficiencies (15 - 17.6%) have been demonstrated for small area Cu(In,Ga)Se₂ devices in the U.S., Europe and Japan. A major objective of this program is to demonstrate the preparation of high quality CIGS material over large areas (0.43 m²) using novel equipment and processes that are adaptable to high throughput manufacturing. Using this material, prototype CIGS PV modules will be produced. Research results generated by other components of the Thin Film Partnership Program will be incorporated as required.

Needless to say, the results described here could not have been achieved without the diligent efforts of the EPV research and engineering staff. Other institutions and individuals have also contributed significantly. At NREL we would like to thank R. Hulstrom and D. Myers for performing the solar radiation data analysis, S. Asher, H. Field, A. Franz, R. Matson, and A. Mason for invaluable material and device characterization, J. Tuttle for helpful technical discussions, and especially R. Noufi for his consistent help to industry to advance CIGS technology. On the program side, we are indebted to H. Ullal and K. Zweibel for their unflagging interest and support. We have benefitted also through interaction with individuals at the Institute of Energy Conversion, University of Delaware, and Sandia National Laboratories.

Summary

EPV's overall strategy in developing CIGS photovoltaic technology has been to define and construct a flexible set of large area vacuum deposition equipment and to explore CIGS formation recipes that can be implemented on this equipment. This is the inverse of the conventional approach in which manufacturing techniques are sought that can reproduce a high efficiency laboratory scale process over large areas. A feature of this equipment is the use of proprietary linear sources capable of downwards evaporation.

Using recipes generated within this program, CIGS cells with efficiencies up to 13.9% were prepared by EPV under a separate CRADA with NREL. Entirely within this program, an aperture area efficiency of 9.6% was achieved for a laminated submodule of area 135.2 cm². Considerable effort has gone into the preparation and characterization of CIGS prepared on substrates measuring 96.5 cm x 44.5 cm, and good compositional uniformity has been achieved along both the short and long directions of the plate. Despite this, the material has not yet achieved the efficiency levels demonstrated in smaller scale equipment, and recipe development is ongoing.

As part of a program to eliminate, if possible, the use of CdS, alternative buffer layers such as InSe, In_xS_y, and ZnSe have been explored, and, to gain insight into junction formation, CdSe. Of these compounds, ZnSe has shown the most promise, and further experiments are being conducted to optimize material and device properties.

A new technique to measure cell internal resistance based on a high intensity laser spot was devised in order to study the CIGS/Mo contact. It was concluded that the performance of good CIS or CIGS cells is not limited by internal resistance.

For the required large area transparent conductor, Al-doped ZnO was prepared at an equivalent static rate of 20 Å/s by bipolar sputtering from an oxide target using an Ar/O₂ gas mixture. For high volume production, reactive sputtering from a metallic target is preferred, and a basic understanding of this process has been achieved. Using a Zn-Al target, low absorption films with a sheet resistance of 16Ω/□ were produced.

A substantial modeling effort was mounted to explore the optimal design of CIS and CIGS modules using annual energy delivery as the performance criterion. By condensing 30 years of irradiance data into an irradiance distribution function, the expectation value of the annual and seasonal energy delivery could be easily calculated. One of the results obtained demonstrated that cells could usefully be made 20%-30% wider than the width that gives maximum power under standard test conditions. Another significant result was that, for a module sited in NJ, the energy contribution for irradiances less than 600 W/m² exceeds that generated by irradiances greater than 600 W/m².

A comparative study of various PV technologies highlighted significant differences in performance at reduced light intensities. Thin film technologies performed well in this regard.

Scale-up of all deposition (Mo, CIGS, CdS, ZnO:Al) and patterning (P1, P2, P3) processes was accomplished to enable fabrication of 0.43 m² monolithically interconnected modules. Both mechanical and laser scribing techniques have been employed.

Good outdoor stability was demonstrated for a 930 cm² laminated CIGS module during 5500 hours exposure. Subsequent to this, a new and complete encapsulation and lead-out process was developed for CIGS plates. This process remains to be fully qualified.

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Introduction

Technology Status

Energy Photovoltaics, Inc. (EPV) has pioneered the production of Cu(In,Ga)Se_2 photovoltaic modules using vacuum processing but without the use of H_2Se . Prior to this subcontract, an efficiency of 9.0% had been achieved for unencapsulated modules of about 200 cm^2 , and a pilot line for the production of 0.43 m^2 encapsulated modules had been completed [Delahoy '96 (i)]. The heart of the pilot line is a computer-controlled large area compound formation machine (Zeus) in which CIGS is formed at temperatures close to the softening point of glass without glass warpage. The machine consists of a deposition and reaction chamber containing a novel dual linear source for material delivery, a load-lock chamber, means for heating and transporting the glass, and appropriate sensors. Sequential CIGS formation schemes have been defined that are better suited to manufacturing than co-deposition of the elements involved.

Program Objectives

The overall project goal is the demonstration of encapsulated and qualified large area CIGS photovoltaic modules prepared in prototype manufacturing equipment, and with powers of about 40W. Another significant goal concerns the development of alternative materials and techniques for contact layers and encapsulation that would result in useful cost reductions if transferred to manufacturing. A further important objective is the development of an alternative junction formation scheme to the traditional CdS/CIGS approach in order to reduce or eliminate the use of Cd. Modeling and performance monitoring will be used to fully characterize CIGS modules.

Approach

The tasks most crucial to the fabrication of high performance CIGS modules are:

1. The preparation of a CIGS active layer (absorber) capable of yielding high efficiency devices over the entire $96.5 \text{ cm} \times 44.5 \text{ cm}$ (0.43 m^2) substrate.
2. The preparation of ZnO transparent conductor over similar areas with 10 - 12 ohms/square sheet resistance and minimal absorption.
3. Patterning of the layers to effect serial interconnection without defects and losses.
4. Robust encapsulation and lead out of the CIGS plate.

Absorber recipe development is being carried out in three programs: R&D using equipment scaled for 930 cm^2 (1 ft^2) substrates, a CRADA in collaboration with NREL, and process development carried out directly on the 0.43 m^2 equipment (Zeus and in-line sputtering system). Different absorbers are judged on the basis of device performance, uniformity, adhesion and reproducibility. In the area of uniformity alone, a significant diagnostics effort has been established to monitor the uniformity of the constituent layers, the thickness and compositional uniformity of the CIGS layer, and device performance as a function of position across the substrate. In parallel with these activities, in-house engineering continues to improve the reliability and reproducibility of the Zeus hardware.

The elimination of CdS requires a method of effecting the same passivation of the CIGS as that provided by the usual chemical bath deposition of CdS, followed by appropriate deposition of ZnO, possibly with an intervening window material.

High quality doped ZnO is being produced over 930 cm² by RF sputtering from a ZnO:Al₂O₃ target. For large area depositions, DC sputtering of ZnO:Al₂O₃ is being performed and improved to satisfy short-term needs, while in the long-term ZnO will be produced by high rate DC reactive sputtering from a metallic target.

For patterning, EPV's previously reported process has been scaled up to large areas and is performing satisfactorily. Meanwhile, research is underway to demonstrate an all-laser approach in order to minimize area loss. For encapsulation, a vacuum lamination process using sheet EVA has been developed, although lower cost processes are envisaged in the future.

Finally, module design is being tailored to fit specific alloy properties and module end uses. This is accomplished through calculation of exact module I-V curves as a function of cell and module parameters, and through calculation of integrated energy delivery based on irradiance and temperature distribution functions [Delahoy '95].

CIGS Formation Routes

Principles

The highest-efficiency Cu(In,Ga)Se₂-based PV cell to date was formed by the simultaneous coevaporation of Cu, In, Ga, and Se (17.7%, total area, with AR coating) [Tuttle '96]. Such codeposition is difficult to scale up. Slightly lower efficiencies have been achieved by separating the deposition into stages containing either In, Ga, and Se or Cu and Se [Gabor '94, Tuttle '94, Zweigart '94]. This represents an improvement in manufacturability but is still difficult to implement. For example, sputtering is preferred for Cu deposition, since evaporation of Cu requires such high temperatures. However, it is difficult to sputter Cu with simultaneous Se activity. Fortunately, recipes incorporating elemental Cu layers have also yielded cells with good efficiencies [Zweigart '94, Britt '94, Tarrant '93, Kessler '92, Britt '95]. In the past, EPV has explored the selenization of sputtered Cu and In metallic precursors by elemental Se [Delahoy '93, Britt '94].

Under this contract we have explored sequential recipes comprising steps of 1) the evaporation of binary compounds such as In-Se and Ga-Se, 2) selenization with Se vapor, and 3) the sputtering of Cu. These general routes are displayed within the box in Fig. 1 of the module processing flow chart.

Fig. 1. A processing flow chart for CIS module fabrication

EPV staff have also explored this class of recipes using the advanced equipment and characterization facilities at NREL under a cooperative research and development agreement (CRADA). Cell efficiencies over 13% have been achieved using the NREL equipment as is displayed in JV curve in Fig. 2.

EPV ZnO/CdS/CIGS

Sample: M1394-14-#1
Nov 8, 1995 4:58 PM
ASTM E 892-87 Global

Temperature = 25.0°C
Area = 0.4224 cm²
Irradiance: 1000.0 Wm⁻²

$V_{oc} = 0.6331$ V
 $I_{sc} = 13.33$ mA
 $J_{sc} = 31.55$ mAcm⁻²
Fill Factor = 69.60 %

$V_{max} = 0.5070$ V
 $I_{max} = 11.58$ mA
 $P_{max} = 5.873$ mW
Efficiency = 13.9 %

Figure 2. A JV curve of a cell made by EPV staff with NREL equipment using methods compatible with EPV's manufacturing equipment.

Compositional depth profiles

In the current pilot line system, an air break is necessary between sputtering and evaporation steps. We have employed Secondary Ion Mass Spectroscopy (SIMS) to examine the degree of contamination related to these breaks between stages. A SIMS depth profile through a CIS film in Fig. 3 shows contamination of C, O, Cl, and Mo as a result of the break between stages. We are evaluating the effects of this contamination.

A significant body of work exists concerning the grading of the absorber composition as a function of depth through the film. Variations in the ratio Ga/(In+Ga) correspond to variations in the band gap and other material parameters. The challenge in recipe development is to find a recipe that is both manufacturable, and which also yields high-quality films with compositional profiles that aid device performance. An example of a profile through a CIGS film formed by our sequential recipes is shown in Fig. 4a. This film displays some degree of alloying of CIS and CGS throughout the depth with more Ga present in the back half of the film. The graded composition could potentially act to push electrons toward the junction to be collected. A Cu-rich part of this same sample shown in Fig. 4b shows the excess Cu-Se phase to exist not just at the surface but at the back of the film as well. In addition, the Cu-Se appears to have promoted better alloying of the CIS and CGS.

Fig. 3. A compositional depth profile through a glass/Mo/CIS film by SIMS.

Fig. 4a. An AES compositional depth profile of a Cu-poor CIGS film.

Fig. 4b. An AES compositional depth profile of a Cu-rich CIGS film.

Phase Makeup

Some pathways toward CIGS formation promote significant segregation of the In and Ga containing material such that the system is phase segregated, often with a CGS layer adjacent to the Mo, and CIS on top [Birkmire '95, Zweigart '95]. The recipes we are employing do not exhibit such a degree of segregation, as can be concluded from the above depth profile, and additionally from the x-ray diffraction pattern in Fig. 5. The film analyzed was of CIGS formed in the large-area pilot line system. Were phase segregation present, a double set of peaks or significant peak broadening would have been observed.

Fig. 5. An XRD spectrum for a CIGS film grown in the pilot line system

CIGS Spatial Uniformity

Material Delivery

Linear Source

Modeling

The design and use of the linear source is crucial for obtaining good CIGS uniformity along the length and across the width of a substrate. The linear source has been optimized with the aid of computer models and by empirical methods. Flux distributions have been calculated for various linear source designs, assuming a cosine law emission from each element. Figure 6 shows the calculated thickness of deposit on a substrate that is translated past a linear source for one particular source design. This demonstrates that excellent uniformity can be achieved by proper source design in conjunction with an appropriate source-substrate distance.

Figure 6. Thickness distribution on substrate for computer-designed linear source.

Experimental Results

Film thickness have been measured with a Dektak IIA stylus profilometer. The thickness profile of an InSe film deposited in the ZEUS system across the width of a substrate is shown in Figure 7. The decline in thickness near the plate edges, also observed in the models, can be corrected by extending the linear source, usually at the expense of the most efficient material usage.

Figure 7: The uniformity of InSe thickness across the substrate width of an InSe film deposited in the ZEUS system from a linear source.

Sputtering

Cu is deposited in the pilot system by DC magnetron sputtering. The uniformity of the Cu film will in part determine the uniformity of CIGS thickness and Cu/(In+Ga) across the substrate. Because the direction of substrate motion relative to the Cu cathode and the linear sources is perpendicular, and because the material flux and scan speeds are constant, there is little non-uniformity in film thickness along that axis. The thickness profile of a Cu film sputtered in the pilot system across the width of a substrate is shown in Figure 8. The slight increase in Cu thickness near the edges of the substrate is believed to be due to increased sputtering yields from the ends of the cathode racetrack.

Figure 8: The uniformity of Cu thickness across the substrate width of a Cu film deposited by DC magnetron sputtering.

CIGS Properties

Thickness Distribution

The CIGS thickness profile is determined primarily by the Group III selenide, Cu, Se, and temperature profiles across the substrate. The Cu and selenide depositions are adjusted to yield a CIGS thickness of about 2.0 μm . In practice, there are only small variations in the CIGS thickness along the substrate length due to the nature of the linear source deposition. The CIGS thickness profile across the substrate width of a film deposited in the ZEUS system is shown in Fig. 9. The cause for the decline in CIGS thickness along the substrate edge is primarily due to a non-uniform distribution of the Group III selenide.

Figure 9: The uniformity of CIGS thickness across the substrate width of a CIGS film formed in the ZEUS system.

Compositional Uniformity

The $\text{Cu}/(\text{In}+\text{Ga})$ and $\text{Ga}/(\text{In}+\text{Ga})$ distributions across the substrate are a convolution of the Cu and Group III selenide distributions. If loss of In through volatilization is significant, the uniformity of the temperature and the Se flux must also be considered. For optimum device performance, a composition of about $0.83 < \text{Cu}/(\text{In}+\text{Ga}) < 0.97$ is required. Less critical but also important is control of $\text{Ga}/(\text{In}+\text{Ga})$ across the substrate. Deviations of this ratio in the direction perpendicular to the module scribes would lead to variations in the short-circuit current of each interconnect, possibly limiting module output current.

The composition of CIGS films has been measured by EPMA (20kV) at NREL. The uniformity of $\text{Cu}/(\text{In}+\text{Ga})$ and $\text{Ga}/(\text{In}+\text{Ga})$ along the substrate length of a CIGS film formed in the ZEUS system is shown in Figure 10. The uniformity is seen to be good along the entire substrate length. The $\text{Ga}/(\text{In}+\text{Ga})$ profile of a CIGS film, also formed in the ZEUS system, shows excellent uniformity across the substrate width (Fig. 11). Nevertheless, we continue our efforts to further improve the uniformity of film properties during all deposition stages.

Figure 10: The uniformity of Cu/(In+Ga) and Ga/(In+Ga) along the substrate length of a CIGS film formed in the ZEUS system as measured by EPMA at 20kV.

Figure 11: The uniformity of Ga/(In+Ga) across the substrate width of a CIGS film formed in the ZEUS system as measured by EPMA at 20kV.

Experience with various recipes for making CIGS has shown us that the micro-uniformity can be poor under some conditions. Poor micro-uniformity can be gauged by large standard deviations of atomic concentrations as measured by a technique such as EPMA. We have developed robust recipes to make CIGS films that have good micro-uniformity over the entire substrate. For example, Table I lists the atomic concentrations and standard deviations of several EPMA measurements made on a CIGS film deposited in the ZEUS system at different locations along the substrate length.

Table I: EPMA of a CIGS film deposited in the ZEUS system at different locations along the substrate length.

Position (cm)	atomic concentration (20kV)				standard deviation			
	Cu	In	Ga	Se	Cu	In	Ga	Se
5.1	22.27	25.59	1.88	50.26	0.1562	0.1013	0.0406	0.1411
24.1	22.75	25.47	1.80	49.98	0.1751	0.1419	0.0263	0.0864
43.2	23.49	24.92	1.80	49.79	0.1223	0.121	0.0549	0.0589
67.3	22.82	25.14	1.79	50.25	0.1641	0.1922	0.0387	0.0688
91.4	22.65	25.32	1.73	50.30	0.0938	0.1305	0.0562	0.1076

Resistance Maps

The highest efficiency CIGS films have a slightly Cu-poor composition, such that the ratio Cu/(In+Ga) is in the range 0.85 to 0.97. A convenient non-destructive technique for estimating the Cu/(In+Ga) of a CIGS film is measurement of the resistance in a direction perpendicular to the film surface. In practice, the resistance is measured by lightly contacting the CIGS surface with two fine wires and measuring the resistance between them. CIGS films with a slightly Cu-poor composition generally have a resistance between 0.1-2M Ω when measured in this way. Stoichiometric or Cu-rich CIGS films have a resistance less than 1k Ω and the resistance of very Cu-poor films is greater than 2M Ω . The resistance of CIGS films deposited in the ZEUS system is routinely mapped at 25 points distributed across the substrate. An example of resistance mapping for one film deposited in the ZEUS system is shown in Figure 12.

1.7	1.2	1.8	1.4	0.8
0.6	1.1	1.3	1.4	0.6
0.9	1.2	1.6	1.4	1.0
0.4	0.8	0.5	0.6	0.7
0.5	0.6	0.8	0.8	0.7

Figure 12: The resistance map of a CIGS film deposited in the ZEUS system (M Ω).

Photovoltaic Characteristics

Open-circuit Voltage and Short-circuit Current Mapping

Non-destructive techniques have also been devised for quickly mapping the photovoltaic characteristics of CIGS films deposited in the ZEUS system. These techniques provide timely feedback to the deposition process and accelerate module throughput by allowing plates with poor characteristics to be culled. The open-circuit voltage and short-circuit current are routinely mapped at identical locations at 25 points distributed across the substrate. The open-circuit voltage map of a CIGS film deposited in the ZEUS system is shown in Figure 13. The non-uniformity across the width is due to a gradient in the Cu/(In+Ga). The normalized short-circuit current density of a CIGS film is shown in Figure 14.

480	520	500	510	470
485	510	465	510	470
465	440	485	490	510
420	440	425	430	480
400	440	395	395	400

Figure 13: The open-circuit voltage map of a CIGS film deposited in the ZEUS system (mV).

0.88	1.00	0.88	0.88	0.88
1.00	1.00	0.88	1.00	1.00
0.88	0.83	0.83	0.71	0.83
1.00	1.00	0.88	0.88	1.00
0.83	1.00	1.00	1.00	0.53

Figure 14: The normalized short-circuit current density map of a CIGS film deposited in the ZEUS system.

Junction Formation and Contacts

CdS Preparation

Chemical Bath Deposition

The deposition of CdS films by chemical bath deposition has been scaled up so that four ZEUS substrates (total area: 1.7m^2) can be coated at one time. The CdS thickness is typically uniform over all four substrates and reproducible from run to run. However, the process is inefficient in material usage and generates a significant amount of waste material. By far the most expensive component of the CBD process is ammonium hydroxide, which is depleted through reaction and evaporation. A more tightly sealed reaction vessel is being constructed to reduce loss through evaporation. Experiments have been conducted that demonstrate that reuse of the filtered liquid waste is possible, but addition of nearly the original amounts of starting materials (thiourea, cadmium acetate, and ammonium hydroxide) is required. The CBD process is expensive and incompatible with subsequent vacuum deposition steps and alternatives continue to be explored.

Linear source

Deposition of CdS through use of linear source was demonstrated in the experimental 1 ft^2 linear source system. Films of uniform thickness were deposited upon unheated bare glass substrates which were translated relative to the linear source. The deposition of CdS upon CIS is generally performed between 155° and 195°C . Deposition at higher temperatures is difficult as the CdS flux tends not to stick to the substrate. Deposition upon heated substrates was attempted by first using lamp heaters to bring a glass substrate up to the desired temperature ($\sim 170^\circ\text{C}$) and by then depositing the material from the linear source. However, radiation from the linear source provides additional heating of the substrate. Even without additional lamp heating, the substrate temperature subsequently can rise above 195° during the CdS deposition, such that non-reproducible sticking of CdS to the substrate occurs. By preheating the substrate to a lower temperature, heating of the substrate by the linear source does not bring the substrate above 195°C . However, the temperature is not held constant during the deposition by such a scheme. Improvements have been made to subsequent generations of the linear source in the pilot line system such that less heating of the substrate occurs and such that low temperature depositions can be performed at a steady temperature. Thus reproducible deposition of CdS at a controlled temperature is possible with the correct linear source design.

Alternative Buffer Layers

Based on the results of Ohtake et. al. [Ohtake, 1995], a preliminary investigation of InSe as a buffer layer (to replace CdS) was made. Thin films of InSe ($< 50\text{nm}$) were deposited by co-evaporating In_2Se_3 and selenium at substrate temperatures from 225° to 375°C . Devices were completed by sputtering a conductive ZnO film. InSe devices with InSe films deposited at 300° or 375° are superior to those deposited at 225°C . In nearly all cases, the direct ZnO devices were superior to the devices with a thin InSe film.

In_xS_y films have also been investigated as a potential buffer layer. In_2S_3 was used as the source material without additional S and the substrate temperature was generally 275°C . The conductivity type of an In_xS_y film deposited on a Mo/glass substrate under these conditions was n-type, as measured by the hot-probe technique. The band gap of an In_xS_y film deposited on glass was estimated to be between 2-2.3eV based on optical transmission measurements. Although the In_xS_y films were photo-conductive, ZnO/ In_xS_y /CIGS devices were found to have very poor photovoltaic characteristics.

In another set of experiments, CdSe was utilized as the buffer layer in an attempt to identify if an interface reaction between Cd and CIGS was responsible for the good characteristics of the CdS/CIGS junction. CdSe films were deposited from CdSe source material in the presence of additional Se and the substrate temperature was maintained at about 275°C. The ZnO/CdSe/CIGS devices were superior to the direct ZnO devices and comparable to the CBD CdS devices with the exception of smaller short-circuit current densities in the CdSe devices due to significant absorption in the CdSe film ($E_g = 1.70\text{eV}$). These results imply that interface reactions may serve an important function in CdS/CIGS devices.

ZnSe films have also been investigated as a potential buffer layer based on the results of other groups [Olsen, 1994, Ohtake, 1996]. ZnSe films were deposited by co-evaporating Zn and Se at a substrate temperature of 275°C. The device performance of ZnSe films was found to be sensitive to the thickness of the ZnSe film. Devices with a 200nm ZnSe film had low open circuit voltage and poor photocurrent while devices with a 20nm ZnSe film were superior to direct ZnO devices but still inferior to devices with CBD CdS. The high resistivity of ZnSe films deposited in this way may account for the correlation between efficiency and ZnSe film thickness. Future experiments will focus on using thinner ZnSe films or introduction of a suitable dopant.

Device Internal Resistance

The effect of ZnO sheet resistance on CIS and CIGS thin film cell and module performance can be calculated and is well understood. However, series resistance internal to the cell structure is not easily quantified, and is often not clearly differentiated from sheet resistance contributions. For sufficiently high light intensity such internal resistance will reduce the cell fill factor. Possible sources of internal resistance are the CIS/Mo back contact and the bulk resistance of the CIS neutral region or the CdS.

A new method is described to quantify cell internal resistance. A small region of the cell is illuminated by a chopped and focused HeNe laser beam, and the ac current in the external circuit is recorded as a function of cell bias for both forward and reverse polarities. The optical and electrical set-ups are depicted in Figures 15a and 15b. A single element lens specifically optimized for focusing HeNe beams is utilized. The lens is mounted on a translation stage that allows the diameter of the laser spot falling on the cell to be varied, while maintaining constant total optical flux. Figure 16 shows the device equivalent circuit used for the analysis of the experimental data, a typical set of data for an EPV 1cm^2 CIS cell being shown in Figure 17. Analysis of the set of curves obtained by varying the laser spot diameter allows a determination of the internal resistance of the cell, as explained below.

For large beam diameters (e.g. 22 mils in Figure 17, or larger) the photocurrent generated by the cell is fully collected for all values of reverse bias applied to the cell, thereby accounting for the saturated signal. As the test cell is placed under forward bias, some of the photocurrent is shunted by the forward-biased diode (mostly by the large area of the cell that is illuminated), and this reduces the collected current by a factor $(1 + J_F R_{Cq}/nkT)^{-1}$ [Sites '90], where J_F is the DC forward current through the cell, thereby accounting for the observed fall-off in collected current.

Optical arrangement

*External electrical circuit
(R_c is a current sensing resistor)*

*Device equivalent circuit
(within dotted box)*

Figures 15a, 15b and 16. Optical arrangement, external electrical circuit, and device equivalent circuit, respectively.

For a beam diameter of 6 mils, the light intensity at the cell surface is approximately 200 suns equivalent. If the specific internal resistance is r_i ohm cm^2 , and the illuminated area of the cell is A , then the numerical value of the cell internal resistance for the illuminated portion of the cell is $R_i = r_i/A$ ohms. If the light-generated current i_L is fully collected it must pass through R_i , leading to a voltage drop $i_L R_i$. (It can be shown that, because of the low photocurrent involved, about 1mA, the lateral voltage drop in a standard ZnO:Al transparent conductor can be neglected.) However, if the external cell reverse voltage plus $i_L R_i$ is sufficient to drive the illuminated diode into forward bias, the light-generated current will be partially shunted by the diode, and the measured photocurrent will be reduced. From Figure 17, for the case of a 6 mil diameter beam, it can be seen that the photocurrent starts to fall at an applied cell bias of -0.35 V, from which we immediately deduce that the voltage across the internal series resistance R_i must be larger than 0.35 V, and to account for a 1-2% reduction in photocurrent must in fact be about 0.8 V (as estimated from the known diode parameters n , J_x , and V_b). From this we calculate an internal resistance R_i of 500 ohms, and a specific internal resistance of 0.09 ohm cm^2 . Very similar numbers for the specific internal resistance are deduced through analysis of the remaining curves for different beam diameters.

Figure 17. AC current in the external circuit versus DC bias as measured across the test cell, for various laser spot diameters, and for two different total beam fluxes (solid symbols are measurements taken at a reduced beam flux, with AC signal multiplied by 10 for plotting purposes). Measured beam diameters:

<i>open circles</i>	-	<i>22 mils</i>
<i>open triangles</i>	-	<i>6 mils</i>
<i>open squares</i>	-	<i>4 mils</i>
<i>open inverted triangles</i>	-	<i>2 mils</i>

The advantages of the method are that a) it clearly separates internal resistance from sheet resistance effects, b) it can be applied to monolithically interconnected modules, and c) it can probe selected areas of a cell with a resolution of better than 0.02 mm^2 . The method should prove useful for the optimization of both terrestrial and space CIGS devices, for the evaluation of alternative back contact schemes, and is likely to be of interest to those involved in the fabrication of concentrator cells or modules.

Transparent Conductor

Approaches to Large Area ZnO Deposition

Zinc oxide has been the most widely used transparent conducting oxide for CIGS, although indium tin oxide (ITO) has also been employed. The conventional method of deposition is RF magnetron sputtering from an oxide target doped with alumina ($\text{ZnO}:\text{Al}_2\text{O}_3$) [Minami, '85]. Several serious drawbacks of the conventional method of depositing ZnO:Al become apparent upon designing an in-line sputtering system capable of coating CIGS modules with the throughput necessary to support a 5MW_P /year manufacturing line. With the usual overall target utilization of 25%, the materials cost for the ZnO alone would be $8 \text{ c}/\text{W}_\text{P}$ (at 8% module efficiency, $1.0 \text{ }\mu\text{m}$ ZnO thickness). This is almost three times the materials cost for the In,

and is greater even than the cost of the glass substrate (about 5 c/W_P). How many magnetron cathodes are required? For a static rate of 20 Å/s, and even doubling the target width, 26 cathodes would be needed to meet the line speed and 2 minute cycle time required for 5 MW_P/year production. An alternative method is clearly required.

Promising approaches to high rate, large area ZnO deposition include DC reactive sputtering from a metallic target [Menner '88, Schaffler '93, Ellmer '93 & '94, Zafar '94], and, because zinc can be readily evaporated at low temperatures (vapor pressure of 0.1 Torr at 400 °C), reactive activated evaporation [Menner '88]. As an interim method of large area ZnO production, EPV has investigated DC sputtering of a doped ZnO target using both conventional and bipolar sputtering supplies. The following sections describe results in this area, and report preliminary results using a metallic target.

Deposition Equipment

Reactively sputtered films were prepared in a five chamber, diffusion-pumped, in-line, planar magnetron sputtering system with substrate translation and a base pressure in the 10⁻⁷ Torr range. The target size was 22 in x 4 in and the standard substrate size 96.5 cm x 44.5 cm. Targets were clamped, not bonded, to a water-cooled cathode. For comparison, 30 cm x 30 cm reference samples were prepared (non-reactively) by RF magnetron sputtering in a separate system using a bonded target.

Bipolar Sputtering of an Oxide Target

For the purpose of coating large area (0.43 m²) CIGS modules with a transparent conductor we have been exploring the deposition of ZnO:Al onto unheated substrates by DC sputtering of a ZnO:Al₂O₃ (1.3% wt.) target. Standard DC sputtering resulted in arcing problems that left visible blotches on the deposited film. The recent successful use of bipolar sputtering supplies in the preparation of oxides and nitrides [Graham '94], in which a reverse (positive-going) voltage is applied periodically to the target resulting in the preferential sputtering of arc-prone insulating regions and prevention of charge build-up, suggested the evaluation of such a supply for the preparation of ZnO. Use of a bipolar supply with arc suppression (ENI RPG-50) indeed resulted in a stable sputtering process. A frequency of 90 kHz and a reverse pulse length of 2.5 μs were used. Film properties were initially unsatisfactory, however. The films were grey and had an optical transmission of only 55-60% at the usual test thickness of about 5,000 Å. Addition of a small amount of oxygen to the discharge lightened the films somewhat but increased the sheet resistance. Other deposition parameters were explored but at this stage none resulted in obvious improvement of film quality.

It was conjectured that if the transparency of the films could be improved sufficiently through oxygen addition the sheet resistance of the film could be brought back to reasonable values by depositing thicker films. This strategy was pursued and has led so far to a seven-fold increase in the amount of added oxygen and a doubling of film thickness to compensate for the lower material conductivity. A significant improvement in transparent conducting oxide (TCO) quality was thereby achieved.

Oxygen was added by mass flow control of an Ar/0.5% O₂ source gas with separate control of an Ar source to achieve the desired sputtering pressure. The dependence of the visible transmission T_{VIS} (defined below) and electrical conductivity $\sigma = (R_{\square}t)^{-1}$ of the ZnO:Al films on the amount of oxygen added to the sputtering gas is shown in Figure 18. In this figure, each data point represents the average T_{VIS} and σ obtained for several films deposited at a given O₂/Ar ratio. The depositions were largely conducted in order of increasing oxygen. For O₂/Ar ratios greater than 1 x 10⁻³, T_{VIS} increased and σ decreased with increasing oxygen. A decrease in doping efficiency with increasing oxygen addition is commonly observed in the deposition of transparent conductors. During the early runs (O₂/Ar < 1 x 10⁻³) it is believed that evolution of the target properties (either oxygen loss or changes in surface morphology) outweighed the

effects of added oxygen. Properties of representative films are summarized in Table II. Target conditioning (sputtering in Ar/0.5% O₂) between successive scans appeared to increase the electron mobility. It is notable that the average deposition rate of about 2 Å/s achieved over the entire plate at a power of 750 W corresponds to a static deposition rate under the target of about 20 Å/s.

Figure 18. Dependence of ZnO:Al visible transmission and electrical conductivity on the O₂/Ar ratio of the sputtering gas for bipolar sputtering at 90 kHz from a ZnO:Al₂O₃ target.

Table II. Properties of representative ZnO:Al films prepared by RF sputtering from an oxide target, and by bipolar reactive sputtering from oxide and metallic targets.

Target	Mode	O ₂ /Ar	t	R _□	T _{IR}	T _{VIS}	T _W *	λ _p (T=0.3)	N	σ	μ
			Å	Ω/□	%	%	%	nm	10 ²⁰ /cm ³	S/cm	cm ² /Vs
ZnO:Al ₂ O ₃	RF	0	5,900	12	83	91	86	1600	6.9	1400	12.8
ZnO:Al ₂ O ₃	bipolar	0.0006	5,000	38	56	53	55			530	
ZnO:Al ₂ O ₃	bipolar	0.0020	8,800	30	78	69	75	1880	5.0	380	4.8
ZnO:Al ₂ O ₃	bipolar ^a	0.0029	10,300	36	89	84	87	2050	4.1	270	4.0
ZnO:Al ₂ O ₃	bipolar ^b	0.0029	8,600	26	83	77	81	2100	4.0	450	7.1
Zn:Al	bipolar	0.06	10,000	45	92	90	91	2650	2.5	220	5.5

* $T_W = (2 T_{IR} + T_{VIS})/3$

^a with periodic target conditioning

^b substrate temperature = 170 °C

Quantification of Film Improvement

A useful method of displaying and comparing the TCO properties of films from different runs is to plot points on a sheet resistance versus transmission scatter plot. Earlier work had shown that for constant deposition conditions, points representing films of different thickness tended to fall on a straight line if a logarithmic scale for sheet resistance is used. Figure 19 shows data points for 24 runs using the oxide target on such a plot.

In order to conduct the film optimization process and to select deposition conditions for future runs, a criterion is needed for deciding whether or not a film with 30 ohms/sq. resistance and 75% transmission, for example, is more desirable than a film with 50 ohms/sq. resistance but 80% transmission. One such criterion is module efficiency at 1 sun calculated (for constant CIGS material parameters and scribing widths) as a function of ZnO resistance and transmission. Using a distributed cell model [Delahoy '95, and the section *Module Calculations* in this report], calculations were carried out for high performance CIGS assuming a total cell width of 0.5 cm, and contours of equal efficiency are plotted in Figure 19 for efficiencies of 8%, 9%, 10%, 11%, 12% and 13%. This plot allows the improvement in ZnO quality to be quantified. From Figure 19 it can now be seen that the improved ZnO prepared by reactive, bipolar sputtering from an oxide target is capable of 11% module efficiency using high quality CIGS, compared to a starting value of 8% before intensive ZnO optimization and a target value of 13%.

Figure 19. Scatter plot of the sheet resistance and weighted transmission $(2T_{IR} + T_{VIS})/3$ of bipolar sputtered ZnO:Al films superimposed on calculated contour lines of equal CIGS PV module efficiency.

Optical Transmission

The determination of ZnO transmission deserves comment. A quick procedure extensively employed at EPV to characterize ZnO transmission utilizes a tungsten bulb with reflector as light source and a CIS cell as detector, with ZnO transmission (T_{IR}) calculated as the ratio of detector short-circuit current for glass plus film relative to uncoated glass. This method has the advantage of automatically averaging over interference fringes, but probably represents an average transmission in the wavelength range of about 800 - 1200 nm. However, it was realized that the rather absorbing ZnO films produced by DC (or bipolar) sputtering possessed increasing absorption at shorter wavelengths. To monitor this characteristic a second transmission set up was constructed consisting of a tungsten-halogen bulb with dichroic reflector and a Hamamatsu silicon photodiode with integral glass filter whose overall response is similar to that of the human eye (visible region sensitivity only). Transmissions derived from these two set ups are denoted T_{IR} and T_{VIS} respectively. T_{VIS} represents an average transmission in the range 550-650 nm.

Using natural sunlight and a CIS cell as detector, average transmissions T_{SUN} were determined for a set of ZnO samples. It was found that the quantity $(2T_{IR} + T_{VIS})/3$ provided an excellent estimate of the average transmission T_{SUN} obtained using sunlight as the incident spectrum. The horizontal axis of Figure 19 (labeled weighted transmission) is in fact the quantity $(2T_{IR} + T_{VIS})/3$ for the various films.

The spectral transmittances of ZnO:Al films reactively sputtered from an oxide target for low and high values of the added oxygen and for an RF sputtered control sample are shown in Figure 20. The plasma frequency ω_p of the free electron gas in the ZnO:Al is related to the electron concentration N by the equation [Qu '93]:

$$N = m^* \epsilon_0 \epsilon_1 \omega_p^2 / e^2 \quad (1)$$

In the vicinity of the plasma wavelength $\lambda_p = 2\pi c/\omega_p$ the transmission declines and the reflectivity rises for increasing wavelength, while the absorption passes through a maximum. This maximum tends to occur at a wavelength at which the transmission is about 30%. Using this approximate criterion for identifying the plasma wavelength we have estimated the carrier concentration using eq. (1) for several of the ZnO:Al films (see Table II). An effective mass $m^* = 0.35 \times m_e$ and a high frequency dielectric constant equal to 4.5 were assumed.

The RF sample (curve a in Fig. 20) exhibits the shortest plasma wavelength and highest carrier concentration. Its transmission at short wavelengths does not decline until about 450 nm. The band edge at 350 nm is slightly blue-shifted relative to the other samples because of the high carrier concentration (possible Burstein-Moss effect) and implies a bandgap of about 3.5 eV. The sample reactively sputtered from an oxide target in a low concentration of oxygen (curve b) exhibits broad band absorption, with an onset of additional short wavelength absorption at about 750 nm. For the highest oxygen concentration so far used the samples exhibit very good transmission for wavelengths longer than 600 nm but are slightly absorbing below 600 nm, leading to a straw-colored tint (see curve c).

Figure 20. Optical transmission as a function of wavelength for ZnO:Al films prepared by different techniques: curve a, RF sputtering from a ZnO:Al₂O₃ bonded target; curves b and c, bipolar reactive sputtering from a ZnO:Al₂O₃ unbonded target at O₂/Ar flow ratios of 0.62×10^{-3} and 2.9×10^{-3} , respectively; curve d, bipolar reactive sputtering from a Zn:Al target.

Optical Emission Studies

Equipment was constructed to allow measurement of the optical emission from Zn, O, and Ar atoms excited in the discharge during various ZnO sputtering processes. Appropriate interference filters were mounted on a filter wheel adjacent to a collimating tube and Si photodiode. The collimating tube looked at the plasma glow along and just under the target racetrack through a window port of the sputtering system. Figure 21 shows the photodiode currents recorded during sputtering of a ZnO:Al₂O₃ target in bipolar mode at 375, 750, and 1000 W. The bandwidth of the Ar and O filters were 1-2 nm compared to 10 nm for the filter for Zn. It is of interest that the Zn signal increases faster than the Ar signal with increasing discharge power. It is not clear whether this represents a superlinear increase in the number density of Zn atoms, an increase in their excitation efficiency, or simply a sublinear dependence of Ar emission on discharge power due to indirect excitation [Savas '86].

Figure 21. Optical emission (current from photodiode) from Ar, Zn, and O atoms excited in the discharge during sputtering from a ZnO:Al₂O₃ target as a function of discharge power and for two compositions of sputtering gas.

Three other points were noted. Firstly, the data indicated that while sputtering in pure Ar, the window transmission steadily declined. (This problem will be addressed in future work.) Three sets of data were taken at 750 W in Ar, two sets initially and the third immediately after sputtering in Ar/O₂. However, the final Zn signal was 10% smaller than anticipated on the basis of the reduction of window transmission. It has been conjectured at EPV that the near surface composition (Zn/O ratio) of oxide targets depends on their recent history of operation, and that sputtering in pure Ar without oxygen activity leads to oxygen loss from the surface region. The aforementioned smaller Zn signal observed after sputtering in Ar/O₂ is attributed to a reduction of free Zn on the target surface through oxidation.

Finally, after initiating sputtering in Ar alone at 1000 W, the Ar signal declined slightly with time, while the Zn signal increased slightly with time. The latter observation clearly implies that conditions at the target surface are changing. Without doubt the target temperature is increasing, and probably also the target is losing oxygen at the surface. The increasing Zn signal could be due to evaporation of Zn from the target or an increased sputtering rate of Zn atoms. Experiments will be designed to further document these effects.

Temperature Dependence of Resistivity of ZnO:Al

The temperature dependence of the resistivity of ZnO:Al films was explored using a vacuum dewar. Top surface Mo contacts were sputtered onto the films in a gap cell configuration and In was applied to further lower the sheet resistance of the contact. A four-wire configuration was used to measure the film resistance. A current of 10 mA was applied to the In pads from a precision constant current source and the voltage on the In pads was picked up separately. Three films were examined, and while initial annealings at 140-150 °C could either irreversibly decrease or increase film resistivity, subsequent cooling and heating

cycles confirmed the reversibility of resistivity changes for temperatures less than 100°C. Data from the final heating cycle for an RF sample are shown in Figure 22. The temperature coefficient of resistance is generally small and positive ($+2.9 \times 10^{-4}/^\circ\text{K}$ at room temperature) and falls to zero at low temperature (at 125°K for the RF sample). It could not be confirmed that the resistivity would rise at even lower temperatures. The TCRs for ZnO reactively sputtered from oxide and metallic targets were $+1.2 \times 10^{-4}/^\circ\text{K}$ and $+5.5 \times 10^{-4}/^\circ\text{K}$, respectively. At around room temperature degenerately doped ZnO is seen to exhibit metallic behavior. For doped films the carrier mobility is presumably fundamentally limited by ionized impurity scattering, while around room temperature additional lattice scattering appears to reduce the mobility for increasing temperature. The sign of the temperature coefficient suggests grain boundary scattering is not significant.

Figure 22. Resistivity of RF sputtered ZnO:Al as a function of temperature.

Bipolar Reactive Sputtering of a Metallic Target

Oxidation State of the Target Surface

Reactive sputtering of a Zn:Al (2.7% wt.) target onto heated substrates was conducted using Ar/O₂ sputtering gas mixtures obtained through separate mass flow control of Ar and O₂ source gases. The vast majority of operating conditions were found to yield either conductive, non-transparent films (presumably containing unoxidized micro-particles of metallic zinc) or completely insulating, transparent films of zinc oxide. Upon investigating the target (discharge) voltage V_d as a function of oxygen flow for ordinary DC sputtering of the Zn:Al target at a fixed discharge current of 0.8A, the voltage was found to decline linearly from 870 V in pure Ar to about 460 V at an O₂/Ar ratio of 0.05, and to remain constant at 460 V for larger O₂ flows. It was then discovered that conductive, transparent films of ZnO:Al could be reliably produced by maintenance of the discharge at the appropriate point of the discharge voltage/oxygen flow curve. In terms of oxygen flow this desirable operating point was not fixed, but shifted depending on pumping speed,

substrate temperature, and discharge current. Rather, the operating point appeared to be defined by an appropriate discharge voltage, which was slightly higher than that at the breakpoint of the curve.

The inference was made that low discharge voltages correspond to sputtering from a fully oxidized surface of the Zn target, that high voltages correspond to sputtering from a metallic surface of the Zn target, and that the discharge voltage in general reflects the average state of oxidation of the target surface. (The associated change in plasma impedance implies a higher secondary electron yield for ZnO compared to Zn.)

The following work was conducted in bipolar mode. To increase the deposition rate the discharge current was increased from 0.8 to 1.4 A. Upon reducing the oxygen flow from high values to low to plot the new curve of V_d vs. O_2 flow, a fast, runaway transition to high voltage was encountered at an oxygen flow of 13.2 sccm. At 0.8 A, V_d began to rise at 8.7 sccm, although no runaway occurred. Clearly, the physical quantity determining the oxidation state of the target is the actual oxygen partial pressure, not the oxygen flow rate. At higher sputtering rates the increased oxygen consumption by the growing ZnO film results in the critical partial pressure being obtained at a higher oxygen flow rate.

To further verify that V_d controls the oxidation state of the target depositions were conducted in a constant voltage mode. By this means it was hoped to force the target surface to the oxidation state corresponding to the particular discharge voltage, and to avoid the instabilities inherent in the constant current mode. At a constant voltage of 452 V, the discharge current was found to depend approximately linearly on oxygen flow (see Fig. 23). This remarkable result is interpreted as follows. The discharge voltage approximately fixes the degree of oxidation of the target surface which in turn requires a certain partial pressure of oxygen. Increasing the oxygen flow must then increase the deposition rate (i.e. discharge current) in order to consume the extra oxygen by incorporation in the growing film.

Figure 23. Dependence of discharge current on oxygen flow for reactive sputtering of a Zn:Al target in Ar/ O_2 in constant voltage mode.

The optical emission at 636.2 nm from excited Zn atoms was monitored while passing through the unstable region in constant current mode. This experiment was performed at a reduced pumping speed by employing only one diffusion pump instead of the usual two. Figure 24 shows the strong hysteresis loop that was observed for the discharge voltage as oxygen flow was first decreased (points A-B) until runaway occurred (points C-D) and was then increased (points D-E-F). (Such a pronounced hysteresis had not previously been observed, implying that the reactive sputtering process is sensitive to pumping speed.)

Figure 24. Discharge voltage and optical emission from excited Zn as a function of oxygen flow during reactive sputtering of Zn:Al in constant current mode.

It is notable that despite almost no change in discharge voltage as the runaway point *C* was approached, the approach *B-C* to the transition *C-D* was heralded by an easily observable increase in the optical emission of excited Zn atoms, the sensor current increasing from 8.3 nA to 11 nA.

During the transition *C-D* the photocurrent jumped to 30 nA. In order to re-oxidize the target, the oxygen flow had to be increased by 40%, at which point the discharge voltage fell precipitously. During this latter transition the chamber pressure increased from 8 mTorr to 14 mTorr despite no change in Ar or O₂ flows. This reflected the sudden drop in sputtering rate upon passing from a metallic to an oxidized target surface and hence the sudden drop in oxygen consumption.

The effects just described are responsible for the runaway nature of the process. During the transition *E-F* in Fig. 24, the sputtering rate falls, oxygen consumption falls, the partial pressure of oxygen rises, thus leading to faster oxidation of the target surface, and further reduction of the sputtering rate. Under these conditions, intermediate oxidation states of the target cannot be maintained by conventional control variables such as discharge current and oxygen flow. Such states may be termed the forbidden zone of reactive sputtering, and correspond to film compositions that may be desirable (as appears to be the case for ZnO transparent conductors) but are normally unattainable. Such intermediate states can be accessed, however, if control signals are derived from either the oxygen partial pressure, or equivalently, optical emission from oxygen (possibly normalized to the discharge power).

Film Properties

The lowest sheet resistance obtained so far for ZnO:Al films reactively sputtered from a Zn:Al target is 16 ohms/sq. (stationary substrate, $T_s = 170^\circ\text{C}$). This film had a transmittance T_{IR} of 90.5% and possessed a combination of sheet resistance and transmission values indistinguishable from those of good RF sputtered ZnO:Al films. It was found that the sheet resistance of these ZnO:Al films prepared in a static mode varied strongly with position on the substrate in a direction perpendicular to the long axis of the target racetrack. This is shown in Figure 25. Coexisting on this substrate within a few cm of each other are film regions with sheet resistances ranging between 24 ohms/sq. and infinity. The central low resistance region at $x = 0$ cm occurs directly under the central long axis of the target. The overall shape of the curve in Fig. 25 could be viewed as a U-shaped curve (with resistance rising at the edges of the deposit) modulated by two resistive regions that in fact occur directly under the racetracks. This modulation is not due to a thickness effect. A series of SEM micrographs of film regions spaced 0.5 cm apart around the $x = 4$ cm position of Figure 25 showed the film morphology to evolve continuously from a large grain structure for $x = 1-3$ cm through an intermediate grain size for $x = 3.5 - 4.5$ cm to small grains for $x \geq 5$ cm [Delahoy '96]. A similar spatial variation in resistance, although much less pronounced, was also found with use of oxide targets in a static mode (see Figure 26).

Low resistance films could not be prepared in a scanned mode (i.e. with substrate translation) by reactive sputtering of the metallic target. This is presumably related to the effective layering of favorable and unfavorable growth conditions as the substrate passes under the cathode. The spatial dependence of material quality in the static mode is clearly related to the nature, flux, and energy of the particles arriving at the substrate. Both target and plasma effects could be relevant. Negative ion bombardment (e.g. by O^- ions) could alter film properties (by disrupting either crystal growth or substitutional dopant incorporation), as could the supply of highly reactive atomic oxygen. The strong modification of film properties directly under the racetrack suggests film bombardment by negative ions accelerated away from the cathode by the electric field in the cathode fall.

Figure 25. Modulation of sheet resistance under the target racetrack for ZnO:Al films reactively sputtered from a Zn:Al target (static mode).

Figure 26. Modulation of sheet resistance under the target racetrack for reactive sputtering from a $\text{ZnO}:\text{Al}_2\text{O}_3$ target (static mode).

Module Issues and Results

Substrate

Soda-lime float glass is formed on a molten bed of tin, and the side of the glass touching the tin has a small amount of tin incorporated into the surface. Previously, we had not paid attention onto which side of the glass we deposited the thin films. We are now using a UV lamp to identify the tin-side of the glass. We then clean the glass on a commercial glass washer with the tin-side touching the rollers, and subsequent deposition of the thin films is performed on the non-tin side.

Patterning

The common interconnect structure used in CIS modules comprises three scribes per cell, designated as *S1*, *S2*, and *S3* in Fig. 27. Scribe *S1* is performed subsequent to the Mo deposition, scribe *S2* is performed subsequent to the absorber deposition and does not penetrate through the Mo, and scribe *S3* is performed subsequent to the transparent conductor formation and also does not penetrate the Mo. Scribes *S2* and *S3* can be performed with a blade, but blade scribing of the Mo film in *S1* is difficult. In general, we consider laser scribing to be the preferred scribing method for all three scribes for reasons of high throughput, high reproducibility, and thinness of scribe lines. By having good scribing table control and thin scribe lines, the dead area of a cell between *S1* and *S3* can be minimized, thus yielding a smaller percentage of dead area in the module.

Figure 27. The common interconnect structure for CIS modules.

The radiation used for our experiments was from a Nd YAG laser (IR) and a frequency-doubled Nd YAG laser (green). The Mo was scribed through the glass, and the CIGS was scribed from the top film surface. The direct variables which we can control are 1) the pulse rate from the laser (higher rates translate to lower energy per pulse), 2) the feed rate, which is the translation rate between the laser beam and the plate, and 3) the beam focus. These variables determine the shape and quality of the scribe lines. Most combinations explored so far yield scribes with oscillating width, as is depicted in Fig. 28. The period of this oscillation is determined by the degree of pulse overlap which is in turn determined by the combination of pulse rate and feed rate.

Figure 28. A depiction of a scribe line with oscillating width.

Mo Scribing

In scribing Mo, the scribe widths were generally greater than 50 μm . One problem observed has been curl of the Mo at the narrowest points in the scribe pattern, as is depicted in the SEM analysis of Fig. 29a and in the surface profilometer scan of Fig. 30. Such curl may represent shorting paths between cells in a complete module. Washing the plate subsequent to Mo scribing removes most of the curl, but a wash step subsequent to Mo deposition represents an additional undesired step which as yet has unknown effects on subsequent absorber film growth. Further exploration of the parameter space has enabled us to minimize the curl as is shown in Figure 29b.

Figure 29. SEM analysis of laser scribes through the Mo film on glass for a) a scribe with excessive curl, and b) a scribe with minimal curl.

Figure 30. A surface profilometer scan across a Mo scribe showing curl of the Mo at one edge.

Given sufficient pulse energy, pits have also been observed in the glass, but these might not detrimentally affect the interconnects.

CIGS and ZnO Scribing

In scribing CIGS, a melted phase was often observed along the edge of the scribe. The melt likely consists of Cu-rich, Se-deficient phases, and such phases would be conducting. Surface profilometer scans of CIGS scribes with and without the melted phase are shown in Fig. 31 and SEM micrographs of these scribes are shown in Fig. 32.

Figure 31. Surface profilometer scans across CIGS scribes with and without an edge phase.

Figure 32. SEM micrographs of laser scribes through CIGS on glass/Mo.

The presence of this edge phase does not necessarily represent a problem for scribe S2. However, this phase could be a problem in scribe S3 if it is present on the right edge of scribe S3 in the above Fig. 27, since a conductive phase present at this location could short the TCO to the Mo.

Figure 27 above depicts scribe S3 as penetrating through the TCO and CIGS down to the Mo surface. However, this scribe need only penetrate through the TCO. We have successfully adjusted the scribing parameters so that this scribe only penetrates about half way through the CIGS. By this method we can potentially avoid shorting along the right wall of the scribe from the TCO to the Mo.

Encapsulation and Termination

After patterning, border isolation is accomplished by removing all thin films (including Mo) within 1 cm of the module perimeter. An abrasion technique, such as sandblasting, is typically employed for this. Electrical contacts are made by bonding two Al foil strips parallel to the scribes along opposite sides of the module. The foil strips are brought out behind the module through a hole drilled in the glass substrate. The CIS circuits are laminated to another glass plate with an EVA sheet (12 mil nominal thickness) in a vacuum laminator. A two conductor cable is attached to the foil strips and the entire lead-out area is electrically and environmentally isolated by forming a boot from a two-part thermally-cured silicone RTV. Optionally, the glass sheets are framed with a notched plastic casing.

Module Performance

A mini-module encapsulated and terminated using the procedure described above has been tested after 500 hours of light-soaking. The aperture area efficiency of the mini-module was 9.6%. The illuminated IV characteristics of this module are shown in Figure 33.

Figure 33: Laminated mini-module with an efficiency of 9.6% after 500 hours light-soaking.

Dark Shunt Resistance of Cells in Modules

The determination of cell dark shunt resistances based on the shading method of McMahon and Basso [see McMahon '96] was performed on an unencapsulated CIS plate consisting of twenty one 23 cm long cells. The plate was illuminated with steady light from an ELH lamp, and the small signal ac module resistance at close to open-circuit conditions was determined at 35 Hz with and without shading of individual cells. The difference between these resistances represents the dark shunt resistance of the cell in question. In contrast to the published method, it was found to be important to ensure that the measured cell was placed under reverse bias in order to accurately determine the resistance of cells having a high shunt resistance. The results including measurements of individual cell V_{OC} 's, are shown in Figure 34. A clear correlation is seen between the values deduced for cell shunt resistance and the cell's open-circuit voltage, lending credibility to the data. Shunt resistances below 200 ohms clearly lead to diminished V_{OC} . Further work will be conducted to evaluate the usefulness of the technique in detecting changes of shunt resistance after encapsulation or extended ageing.

Figure 34. Cell open-circuit voltage in mV (solid circles) and shunt resistance in ohms (bars) versus cell number of module.

Outdoor Stability

The long term stability of these modules is expected to be excellent. This expectation is based on data accumulated for glass-glass encapsulated 1 ft² CIS modules that have been mounted permanently on an outdoor test rack. Performance data are collected under natural sunlight illumination and are normalized with respect to the power produced by a reference CIS module that is normally kept indoors but which is taken outdoors to monitor the irradiance (powers are translated to 25 °C before normalization). The performance of such a module mounted outdoors is shown in Figure 35 for over 5500 hours of exposure.

Within the accuracy of the data (the origin of the scatter being the variable natural conditions of temperature, irradiance and spectral content, and differences in the test and reference module dependencies on these factors) no deterioration in performance was observed due to the outdoor light soaking, thermal cycling and other environmental stresses over the duration of the test. This is in line with other published reports of the stability of CIS [Zweibel '95]. The test was terminated after delamination of the encapsulant occurred. The encapsulant used in these early modules was UV-cured acrylic. As a result of this observation, EVA was adopted as the encapsulating material.

Figure 35. Performance of a 1 ft² CIS module during 5500 hours outdoor exposure.

Energy Delivery

Frequency Distribution of Irradiance

We have compiled data on the relative distribution of plane of array (POA) irradiance for high, intermediate, and relatively low irradiance sites within the U.S. (El Paso, TX; Dodge City, KS; and Newark, NJ). These sites are represented in the 30 year hourly National Solar Radiation Data Base (NSRDB). The array is assumed to be tilted south at an angle equal to the latitude of the site. To obtain POA irradiance, we multiplied direct normal radiation by the cosine of the incident angle (computed for the midpoint of the hour) and added diffuse irradiance (DPOA) calculated using the Perez Anisotropic Model [Perez '90]. For every daylight hour, the POA irradiance was assigned to one of twenty four, 50 watt/m² wide bins (i.e. 0-50, 50-100,...600-650,...etc), from which a percent frequency distribution was derived representing the percent of the daylight hours the POA radiation was within the bin limits for the 30 year period.

Figure 36 shows the percent frequency distribution of irradiance as seen by a fixed plate array at latitude tilt for the three selected sites. The three vertical bars are centered on the mid-bin irradiance value, e.g. for the 100-150 W/m² bin the bars are centered on 125 W/m². Of note are the strong rise in the percent occurrence of low irradiance values, the widely different occurrence of high irradiance values (>900 W/m²) depending on site, and the surprising structure in the distribution for El Paso. The latter feature presumably implies the existence of certain well-defined weather or cloud patterns. On the other hand, for Newark, NJ, the distribution is smoothly varying.

Figure 36: Frequency distribution of irradiance for three sites (Newark, Dodge City, El Paso) for the years 1961-1990.

Energy Delivery Calculations

A direct, although laborious, calculation of the annual integrated energy production of a PV array (assuming perfect tracking of the maximum power point) would sum the product of irradiance and module efficiency for every hour throughout year, using the NSRDB hourly data base for irradiance and temperature at the site for the chosen year. In this work we have advantageously used a distribution function for the irradiance in order to avoid lengthy summations over the entire 30 year NSRDB database. For 50 W wide bins, an annual irradiance distribution function compresses 135,000 irradiance readings taken over 30 years into about 25 numbers.

Because of the importance of ambient temperature we decided to deal with four seasonal distribution functions, and to calculate the average ambient temperature for all observations in each irradiance bin. Obviously there is a gross difference in temperature from season to season, but within each season a correlation was found between temperature and POA irradiance. We believe that seasonal irradiance distribution functions together with seasonal average temperature versus irradiance plots provide a useful and compact data set for realistic PV calculations.

Examples of such manageable data sets are shown in Figures 37 and 38 for Newark, NJ. For the irradiance distribution functions ϕ , the bin width is again 50 W/m², and the total seasonal insolation is $\sum I \phi N$ Wh/m² where I is the POA irradiance (W/m²), $\phi(I)$ is the irradiance distribution (fraction of daylight hours the irradiance is within a given bin) and N is the total number of daylight hours in the season. These normalization constants are given in Figure 37. From Figure 38 we see that for 3 of the 4 seasons there is a rough positive correlation of ambient temperature with irradiance.

Figure 37: Seasonal frequency distribution of irradiance for Newark, NJ for the years 1961-1990.

Figure 38: Seasonal average temperature for irradiances within 50 W/m² bins for Newark, NJ for the years 1961 - 1990.

The expectation value of the annual integrated energy production E can thus be easily calculated as

$$E = \sum_s \sum_I I \cdot \text{Eff}(I, T) \cdot \phi_s(I) \cdot N_s \text{ Wh/m}^2/\text{y} \quad (1)$$

where the first summation is over the irradiance range, the second summation is over the 4 seasons, and $\text{Eff}(I, T)$ is the module conversion efficiency as a function of irradiance and module junction temperature.

Module Calculations

As an example of the utility of the compact data sets described above, we have calculated the expected seasonal and annual energy delivery of thin film CIS modules (sited in Newark, NJ) as a function of cell width. We will first briefly describe and illustrate the computer model of CIS modules employed to calculate $\text{Eff}(I, T)$.

The I-V curve of a module can be calculated by representing the module as a series string of identical unit cells. The I-V curve of a unit cell is degraded relative to that of an elementary CIS cell by the finite sheet resistance of the ZnO (R_s , in ohms/square), the series resistance of the ZnO lying between the end of the active cell and the ZnO/Mo contact (R_t , in ohm cm), and the internal resistance of the cell (R_{sr} , in ohm cm^2). The equivalent circuit of a unit cell of the module is therefore as shown in Figure 39. Shunting mechanisms are not included in this model since they are presumed avoidable by careful processing. This 1-dimensional model consists of repeated units extending in the x direction, this direction being perpendicular to the scribes, and the unit consisting of an elementary CIS cell plus a resistive element of ZnO. Starting with an assumed voltage V at $x = 0$, the voltage $V(x)$ and the current $i(x)$ in the zinc oxide at a point x are calculated iteratively. In this way terminal current and voltage pairs are determined, thereby allowing calculation of J_{sc} , P_{max} , FF, active and aperture area efficiency etc. The input parameters are the irradiance (from which the cell photocurrent j_{ph} is estimated based on material type, CIS or CIGS, and on ZnO transmission), the cell temperature T , the diode parameters V_b , n , and J_{00} , ZnO sheet resistance R_s , R_t , R_{sr} , and relevant cell and interconnect dimensions.

Figure 39: Equivalent circuit of a unit cell of a thin film module used for computer I-V modeling.

Figure 40 shows the calculated aperture area efficiency of CIS modules as a function of cell width from 0.4 to 0.7 cm, and irradiance from 50 to 1000 W/m², assuming ZnO of 12 ohms/square sheet resistance, diode parameters $V_b = 1.01$ V, $n = 1.54$, $J_{00} = 3.4 \times 10^4$ A/cm², and other pertinent parameters. In this calculation an *ambient* temperature of 300 K was assumed, with the module temperature rising linearly with irradiance: $T_{mod} - T_{amb} = 27.5C \times I/1000$ where I is the irradiance in W/m². The decline in module efficiency shown in Figure 40 for irradiances greater than 400 W/m² is principally due to the rise in module temperature. For a *constant* module temperature of 300 K the efficiency for a cell width of 0.5 cm rises monotonically from 7.27% to 9.55% for the irradiances shown, while for a cell width of 0.7 cm the efficiency peaks at 9.19% at 600 W/m² and declines to 8.95% at 1000 W/m².

Figure 40: Aperture area efficiency of a CIS module deployed at an ambient temperature of 300 K as a function of unit cell width and irradiance.

Using the above program we have also modeled the performance of CIS and CIGS (unencapsulated) plates as a function of temperature. The following parameters were assumed: high quality CIS and CIGS material, a ZnO sheet resistance of 12 ohms/square, and a cell width of 0.5 cm for CIS and 0.55 cm for CIGS. The temperature coefficients for efficiency $(1/Eff)dEff/dT$ were found to be -0.61 %/°C for CIS and -0.49 %/°C for CIGS referenced to 25 °C.

Energy Delivery Calculations

By performing the summation $\sum I \cdot Eff(I, T) \cdot \theta_s(I) \cdot N_s$ we have calculated the seasonal and annual energy delivery for CIS modules having a 0.5 cm cell width sited in Newark, NJ. The results are shown in Table III. The module efficiency was calculated as described above, with the average module temperature at each irradiance calculated from the ambient temperature data of Figure 38, assuming average seasonal wind speeds of 5.1, 4.1, 4.4, and 4.9 m/s for spring, summer, fall, and winter, and assuming a 5 m/s wind results

in a 4.75% decline in $T_{\text{mod}} - T_{\text{amb}}$. The seasonal irradiance distributions were shown in Figure 37. Also shown in Table III is the total seasonal insolation calculated from the distributions, and the overall module efficiency for the relevant time period.

Table III: Seasonal and annual energy delivery calculated for a flat plate PV array consisting of CIS modules with a 0.5 cm cell width rated at 9.55% efficiency (STC) using irradiance and temperature distribution functions for Newark, New Jersey.

Time period	Insolation (kWh/m ²)	Integrated array energy (kWh/m ²)	Average efficiency (%)
Spring (M,A,M)	455.8	41.3	9.06
Summer (J,J,A)	491.5	41	8.34
Fall (S,O,N)	380.6	33.8	8.88
Winter (D,J,F)	299.2	29.6	9.88
Year	1,627.1	145.7	8.95

Because of the manageable nature of these calculations it is easy to analyze other aspects of the energy delivery, such as the distribution of energy contributions from each irradiance bin. Figure 41 shows such a distribution for the fall season in Newark and for an increased cell width of 0.6 cm. It is perhaps startling to note that *the overall energy contribution for irradiances less than 600 W/m² (17.5 kWh/m²) exceeds that generated by irradiances greater than 600 W/m² (15.8 kWh/m²)*. The reasons, of course, are the rising irradiance distribution for small irradiances (see Figure 37) and the now slightly *higher* module efficiency at the lower irradiances e.g. 9.22% at 300 W/m² compared to 8.41% at 900 W/m². The latter situation results firstly from much lower module temperatures (about 290 K at 100 W/m² compared to 316 K at 900 W/m², resulting from ambient temperature and irradiance effects), and secondly from the increased cell width which favors higher efficiency at low irradiance (reduced area loss) at the expense of efficiency at high irradiance (increased losses due to voltage drop in the wider ZnO).

Figure 41: Contributions to the energy produced by a CIS module during the Fall in Newark, NJ arising from irradiances falling within 100 W/m² wide irradiance bins.

Prompted by considerations such as those just mentioned, we have investigated how annual energy delivery from CIS modules depends on unit cell width over the range 0.3 - 0.8 cm. The results (for Newark, NJ) are shown as the solid data points in Figure 42. While energy production peaks at 145.7 kWh/m²/yr at a cell width of 0.5 cm, it declines only relatively slowly with increasing cell width, falling to 141.8 kWh/m²/yr at a cell width of 0.7 cm, for example. Traditionally, thin film PV modules are designed to produce the maximum possible power (or close to it) under standard test conditions (STC) of 1000 W/m² and 25°C. The open circles in Figure 42 represent the variation of module efficiency with cell width at STC. The peak efficiency of 9.62% is attained at a cell width of 0.42 cm, with the efficiency falling more rapidly than the energy delivery curve with increasing cell width. The open squares represent module efficiency at 200 W/m²; this rises to a peak at 0.7 cm, thereby slowing the decline in annual energy delivery for larger unit cell widths. Currently, EPV produces CIS modules with a cell width of 0.5 cm [Delahoy '93, Britt], representing a compromise between peak efficiency at STC (which occurs at 0.42 cm) and reduced patterning times. The above calculations suggest that a design criterion based on annual energy delivery would allow the fabrication of modules with a larger cell width (e.g. 0.6 cm) and further reduced patterning times. These issues are significant for high volume production.

Figure 42: Annual energy production for CIS modules in Newark, NJ as a function of unit cell width, contrasted to the dependence of module efficiency on cell width for two irradiances.

Irradiance and Temperature Dependence of PV Technologies

The above calculations, conducted for the case of CIS, suggest that the specific characteristics of a chosen PV technology should be examined with respect to irradiance and temperature dependence in order to accurately predict system performance and energy delivery under operational conditions. For example, in systems involving battery storage (e.g. PV lighting), the low light performance of the PV array is an important factor, since a minimum voltage must be maintained for battery charging. We therefore embarked on a program to experimentally determine the irradiance and temperature behavior of various PV technologies, and especially to compare the behavior of the leading thin films relative to the traditional crystalline and multicrystalline silicon products.

We have so far measured the dependence of open-circuit voltage (at a fixed temperature) on irradiance between 30 W/m^2 and 1000 W/m^2 for high quality solar cells based on the following PV technologies: thin film CIS, CIGS, CdTe, a-Si:H, and bulk multi-crystalline silicon wafers. Similar measurements were also performed on a light-soaked, 25W nominal, single junction a-Si:H module, and on a 10W nominal multicrystalline silicon module, again taking care to hold module temperature constant. The results are shown in Figure 43. Using the usual diode equation we may write $V_{oc} = V_b + n (kT/q) \ln (I_{sc}/I_{00})$, from which the diode ideality factor n can be calculated for each technology using the data of Figure 43. These values are summarized in Table IV. The voltage loss upon reduction of the irradiance from 1000 W/m^2 to, say, 125 W/m^2 can now be calculated as $\Delta V_{oc} = -n (kT/q) \ln 8$, and these values together with the percentage loss of V_{oc} are given also in Table IV. The percentage losses range from 8.7% to 22% depending upon the technology. For light-soaked a-Si, CIGS and CdTe the losses fell in the 11-13% range. For the crystalline Si technologies a loss of 14.7% was measured for the multicrystalline Si module, while data supplied by J. Anderson of Sunset Technologies imply losses of 16.9% for multicrystalline Si and 14.6% for single crystal Si for the factor of 8 reduction in irradiance. The high value of 21% measured for a single cell on a multicrystalline Si wafer suggests that the quality of multicrystalline Si is variable, and may depend on defect passivation.

Figure 43: Dependence of open-circuit voltage on irradiance (at a fixed temperature) for a variety of cell and module technologies.

For some of these technologies we have also measured the temperature dependence of V_{oc} at 1000 W/m^2 irradiance (see Table IV). Results for CuInSe_2 and $\text{CuIn}(\text{Se},\text{S})_2$ cells and for CIS modules have been given in earlier papers [Delahoy '93 & '94]. Here we report measurements of $V_{oc}(T)$ for CuInSe_2 and $\text{Cu}(\text{In,Ga})\text{Se}_2$ cells mounted on a copper block in a vacuum dewar. The addition of Ga is seen to strongly increase V_{oc} and only weakly increase the magnitude of dV_{oc}/dT , so that the percent loss in V_{oc} for increasing T is reduced through the addition of Ga. Outdoor measurements were performed on the light-soaked a-Si:H module and on the multicrystalline Si module. Here values of dV_{oc}/dT slightly higher than those commonly reported were obtained. In summary, however, CIGS, a-Si:H, and multicrystalline Si technologies were found to exhibit similar values of $(1/V_{oc})dV_{oc}/dT$ (about - 0.0036).

Table IV: Voltage-related parameters, including diode ideality factor and percent loss of V_{oc} at 125 W/m^2 relative to 1000 W/m^2 , for various thin film and crystalline solar cell technologies.

cell material	V_{oc} (300K) *	dV_{oc}/dT^*	V_b	n	ΔV_{oc}^{**}	$-\Delta V_{oc}/V_{oc}$
	(mV)	(mV/deg)	(V)		(mV)	(x100%)
CIS	411	-1.96	1.00	1.66	-89	21.7
CIS +Ga	452	-2.09	1.08	1.40	-75	16.7
CIGS	615	-2.18	1.27	1.36	-73	11.9
CdTe	798			1.91	-103	12.9
a-Si:H	859			1.38	-74	8.7
a-Si:H†	817	-2.97		1.66	-89	10.9
Multi-Xtl Si	555			2.16	-116	21.0
Multi-Xtl Si†	577	-2.13		1.58	-85	14.7

* @ 1000 W/m^2

** $\Delta V_{oc} = n(kT/q)\ln(8) = \text{loss in } V_{oc} \text{ @ } 125 \text{ W/m}^2$

† PV module (a-Si:H module in light-soaked state)

The dependence of module fill factor (FF) on irradiance was also determined for a-Si:H and multicrystalline Si modules through computer measurement of I-V curves in natural sunlight. These data are shown in Figure 44. Also shown are data from J. Anderson for a multicrystalline Si module. We would in general expect all PV modules to exhibit a decline in FF at sufficiently low intensities, and, because of series resistance effects, a decline at sufficiently high intensities. For multicrystalline Si the decline in FF at low intensity was particularly pronounced. Also shown in Figure 44 are the computed results for FF versus irradiance for CIS and CIGS modules with a 0.5 cm and 0.55 cm cell width, respectively. It is anticipated that manufactured modules will closely approach these curves. To summarize, in contrast to the generally predictable values of dV_{oc}/dT , $V_{oc}(I)$ and especially $FF(I)$ are seen to vary between technologies and to be process sensitive. As a general rule, the percentage loss in V_{oc} and FF at reduced irradiances (relative to their values at 1000 W/m^2) appears to be lower for the thin film technologies compared to the traditional crystalline Si products.

Figure 44: Dependence of module fill factor on irradiance for multicrystalline Si and amorphous silicon (experimental data), and for CuInSe_2 (calculated).

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