

Application of CIS to High-Efficiency PV Module Fabrication

Phase 3 Final Technical Report

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1.0 SUMMARY

This is the Phase III Final Technical Report of the subcontract titled "Application of CIS to High Efficiency PV Module fabrication." The general objectives of the program are the development of a novel, non-vacuum process for CIS film deposition, optimization of the various layers forming the CIS device structure, and fabrication of high efficiency submodules. The specific goals of the project are the development of 15% efficient small area cells and 10% efficient submodules using a novel, low-cost CIS deposition approach.

During this research period, we concentrated our efforts on three different areas of research. Within the National CIS Partnership Program, we participated in the "substrate/Mo interactions" working group and investigated issues such as Na diffusion from the soda-lime glass substrate into the Mo layers and CIS films. It was determined that the Na content within the Mo layers was not a strong function of the nature of the Mo film. However, diffusion through the Mo layers was found to be a function of the Mo film characteristics as well as a very strong function of the CIS growth process itself. It was conclusively shown that Na resided on the grain boundaries of CIS layers.

Another team activity involved evaluation of CdS-free solar cells. ZnO/CIS junctions prepared by the two-stage process showed light soaking effects. Cells left under illumination improved in efficiency and were similar to the CdS/CIS junctions. After storage in dark however, efficiency deteriorated greatly for the ZnO/CIS device, most of the decline coming from the open circuit voltage values.

Much of the effort was spent on the development of a low-cost, non-vacuum CIS deposition technique. The method developed involves particulate deposition and formation of precursor layers followed by the conversion of these layers into CIS. During this period attention was concentrated on yields rather than efficiencies since we observed deterioration of yield when we moved the technology into a pilot line for module fabrication. Test modules of 40-60 cm² area were adapted to understand the issues involved in this novel technology. At the present time the submodule efficiencies are 6-7%. Single cell efficiencies are in the 10-13% range.

Future work will concentrate on the bandgap enhancement through S and Ga addition into the absorber layers. With the base built for this novel technology using the CIS absorbers we will now be able to improve the efficiencies of the single cells as well as the modules fabricated from them using larger bandgap absorbers.

2.0 INTRODUCTION

This is the Phase III Final Technical Report of a subcontract titled "Application of CIS to High Efficiency PV Module Fabrication". The objective of this program is to develop understanding and solutions for certain issues related to cost-effective production of CIS-based PV modules. The most important task is the development and demonstration of a novel, low-cost method for CIS film growth that does not employ expensive vacuum processing. Other tasks involve module integration and bandgap engineering.

Recent advances made in CIS and related compound solar cell fabrication processes have clearly shown that these materials and device structures can yield power conversion efficiencies greater than 17%. However, despite these very impressive laboratory results, CIS type of solar cells and modules are not yet in production. Part of the reason for this is the fact that the techniques employed in fabricating high efficiency CIS type solar cells are costly and/or they are not well suited for large scale film deposition. ISET's Phase II program is specifically gear low cost deposition technique for the growth of CIS absorbers. The vacuum based two-stage processing that was the subject of our Phase I effort has been replaced by this novel non-vacuum approach in the Phase II program. The vacuum based two-stage process was, however, still used in tasks studying some basic phenomena such as substrate/film interactions and bandgap engineering. The approach we selected was to carry out certain initial experiments with the vacuum based processing approach and after understanding the phenomena, to try to apply this knowledge to the new non-vacuum technique.

The specific goals of this 12-month program as listed in our "Statement of Work" and the "Schedule of Deliverables" were: The development of 15% efficient cells of 1 cm² area and 10% efficient submodules of 6"x6" area using ISET's novel, low-cost, non-vacuum CIS growth technique.

3.0 TECHNICAL DISCUSSION

In this program ISET's efforts were concentrated on the development of a novel, low-cost non-vacuum deposition process for CIS absorber layers. However, we also had a task as part of the National CIS team. The team work was on studying the "CIS-Mo-substrate interactions" and the sub-team formed to work on this task included ISET, EPV, Lockheed/Martin, U. of Illinois, NREL and CSU. Although the bulk of the ISET activity during this period was concentrated on the non-vacuum process, we continued to prepare small size samples by the vacuum-based two-stage process, specifically for the above mentioned task which was formulated to study the CIS-Mo-substrate interactions.

Details of ISET's vacuum-based two-stage selenization technique and the device fabrication steps have been previously described [1]. In summary, these baseline processes involved vacuum deposited metallic precursors and vapor phase selenization in H₂Se. Cu-In precursors of various stoichiometries were deposited onto the Mo-coated soda-lime glass substrates at room temperature using the e-beam evaporation method. If needed, gallium addition into the absorber layers was achieved by adding a thin layer of Ga into the Cu-In precursor stack. Selenization of the precursors was carried out in a reactor kept at a temperature of about 450 °C. The reactive atmosphere in the selenization chamber contained a mixture of H₂Se gas and N₂. For device fabrication, CIS films were coated with a thin (600-2000 Å) CdS layer using the solution growth technique. This step was then followed by the deposition of a conductive ZnO window layer using the MOCVD method.

As stated before, tasks involving the development of a novel CIS growth approach did not have any vacuum deposition step. In these tasks, films were grown through a new non-vacuum technique as will be described later in this report. Device fabrication steps, however, were common to CIS absorbers obtained by both vacuum and non-vacuum approaches.

3.1 CIS-Mo-Substrate Interactions

This task was shared by the "Substrate/Mo Impact" working group that was formed within the National CIS Partnership Team. ISET was a member of this group which also included EPV, Lockheed/Martin, University of Illinois, CSU and NREL. The goal was identification and study of the chemical interactions between the glass substrate, Mo layer and the CIS absorber film. Experiments were set up to try to find answers to the questions of the nature of the Na diffusion from the substrate, through the Mo layer and into the CIS absorbers. For each experiment several samples were prepared by the working group members and results on each sample were analyzed with the aim of coming up with a universal explanation for the observed phenomena. In this report we will only present the relevant results obtained from the samples prepared at ISET's laboratory.

During the last period of research we had carried out measurements on sputter deposited Mo films and CIS absorbers to study the distribution of Na in these layers and reported these results in our annual technical progress report [2]. For completeness we will briefly summarize these results and then concentrate on the new findings of the present research period.

SIMS measurement of Na levels in Mo layers prepared in various laboratories showed that there was a quantitative increase in the Na levels in these layers resulting from heat treatments but there was no qualitative change in the Na profiles which were relatively flat in all the studied samples. The suggestion was that the Na diffusion took place along the grain boundaries and it was fast. It was also determined that Na levels in all Mo layers were roughly identical despite the fact that the deposition conditions and the selenization character of these layers were very different. Na signal and O signal tracked each other, suggesting that Na was in the form of an oxide in the Mo layer.

After studying the Na diffusion into the Mo layers, CIS films were formed on the glass/Mo structures by the two-stage selenization approach. SIMS profiles were taken at NREL through both the CIS and the Mo layers using Cs⁺ primary ions, 10kV, with nominal impact energy of 5.5 kV. Profiles were normalized to the ⁸²Se+Cs signal so that direct comparison between levels could be made. The results indicated that the Na concentrations in the CIS films were a strong function of the nature of the Mo layers. For example, thin Mo films of 0.5 μm thickness let 3-4 times more Na to diffuse into the CIS layer than films that were 2.0-2.5 μm thick. It was also observed that there was a high level of Na near the Mo/CIS interface in all samples. High Na content near the Mo/CIS interface and the decreased Na concentration in the bulk of the CIS layer appeared like a Na diffusion profile. However, we believe that this profile was an artifact of the micro structure of the CIS layer.

As can be seen from the SEM of Fig. 1 the grain structure of the CIS layers obtained by the two-stage technique is typically small near the Mo interface. Then the grains grow as one moves into the bulk of the absorber. If Na resides primarily on the grain boundaries, then it is conceivable that what we were observing in the Na SIMS profiles was actually the effective grain boundary areas in various portions of the studied films. To find further proof that Na resides on the grain boundaries of our CIS absorbers we set up an experiment within the national CIS team activity. In this experiment four samples were prepared at ISET:

1901-135 (0.6 μm CIS + 0.6 μm CIS deposited on ISET Mo-135)
1901-375 (0.6 μm CIS + 0.6 μm CIS deposited on ISET Mo-375)
1902-135 (1.2 μm CIS + 1.2 μm CIS deposited on ISET Mo-135)
1902-375 (1.2 μm CIS + 1.2 μm CIS deposited on ISET Mo-375)

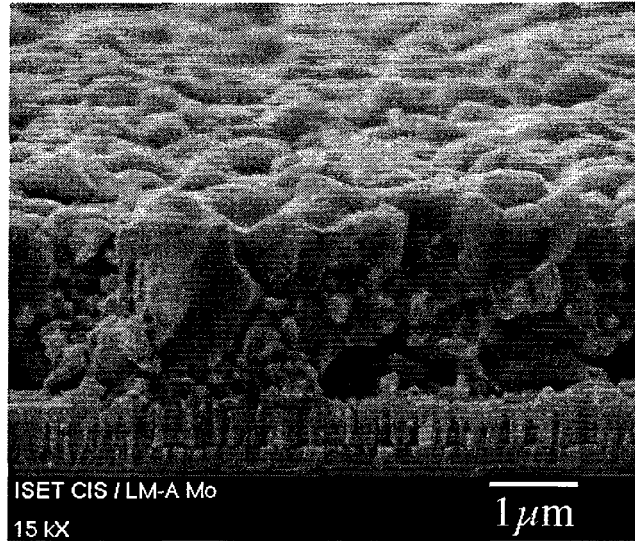


Fig.1 Cross-sectional SEM of ISET's CIS layer grown on 1.0 μm thick Mo film prepared by Lockheed-Martin.

The purpose of the experiment was to grow a double-layer CIS film and introduce a small-grained region at the interface of these two layers. The SIMS analysis would then show a peak in Na content in the middle of the film, if in fact, Na resides on the grain boundaries.

The cross-sectional SEMs for the two samples labeled 1902-135 and 1902-375 are shown in Fig. 2. The double-layer nature of the CIS films in the other two samples was not apparent, probably because these were very thin films. In the SEM's of Fig. 2 there are two distinctly visible layers. The crystalline quality (grain size) of the first CIS layer deposited on the Mo film is superior to the second CIS layer which is deposited on top of the first CIS

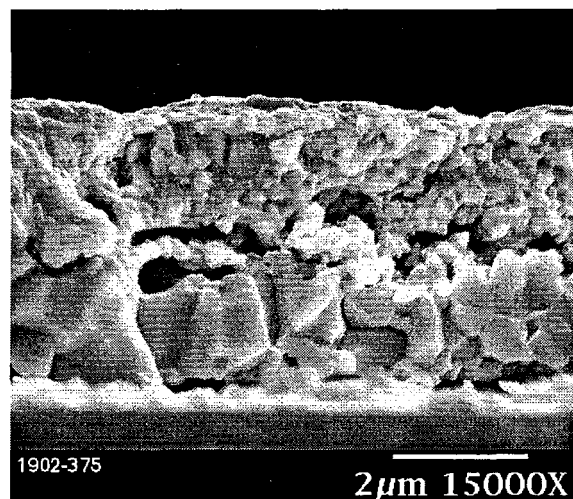
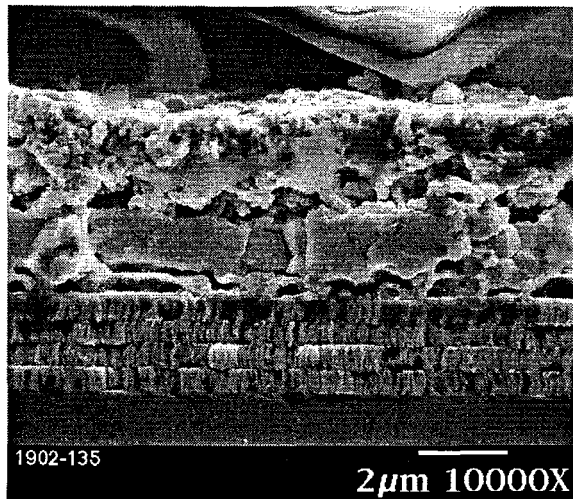


Fig. 2 Cross-sectional SEMs of two double-layer CIS structures grown on Mo-135 and Mo-375 substrates.

layer after taking this sample out of the selenization reactor, and washing and drying it. The differences between the morphologies of the stacked layers may be due to different film nucleation on Mo and CIS surfaces, or due to the possible effect of Na. It has been shown for CIS layers grown by the co-evaporation technique that Na enhances film crystallization. In the films of Fig. 2 the first layer which is closer to the glass substrate may be receiving more Na during growth and thus its crystallization is better. This issue was later clarified when the SIMS data was obtained from the samples of Fig. 2 and correlated with the SEM data.

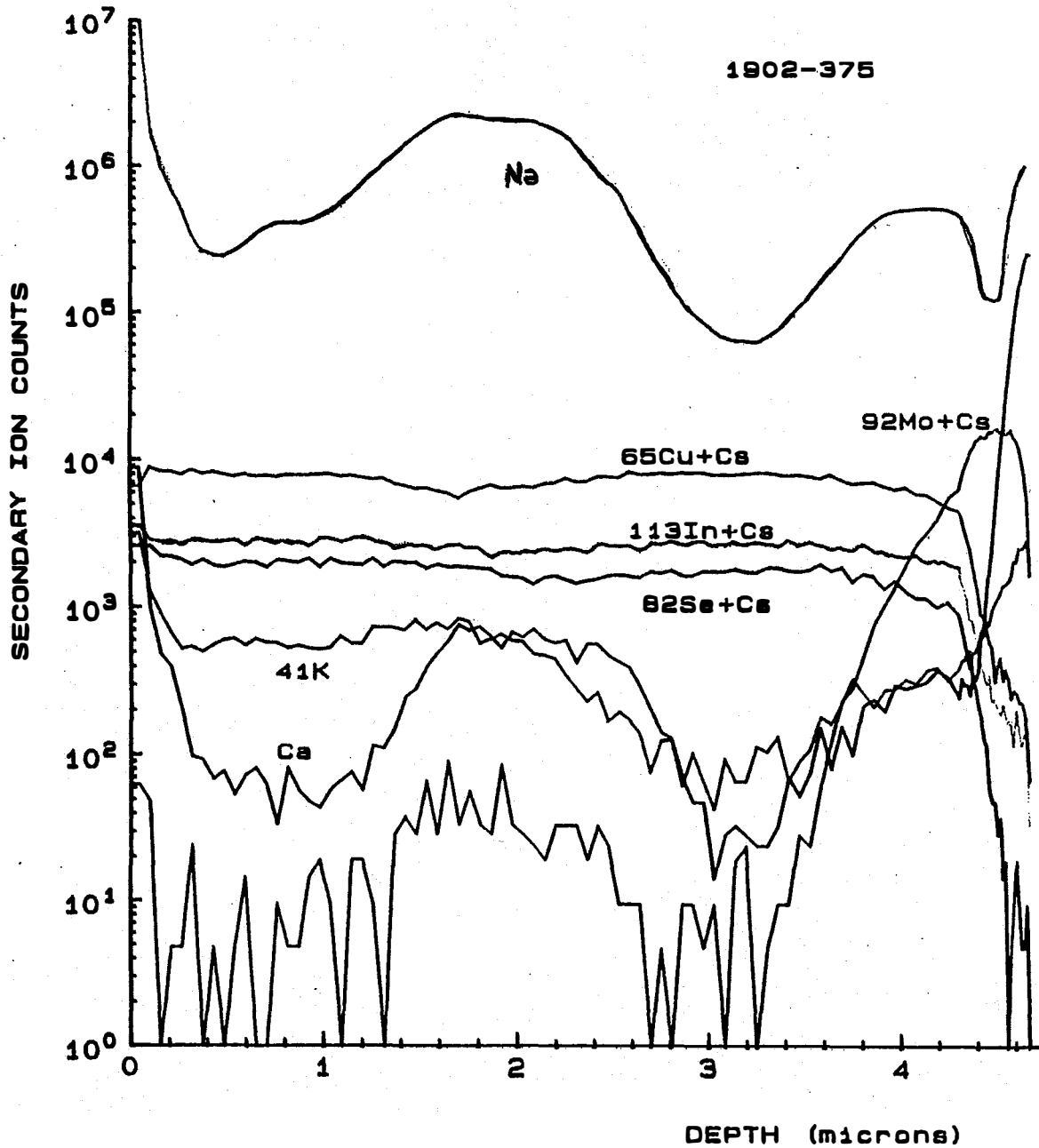


Fig. 3 SIMS data taken from sample 1902-375.

Fig. 3 shows the SIMS data obtained from the sample of 1902-375. The Cu, In and Se signals are relatively flat through the CIS absorber layer. Especially interesting in this data is the “double hump” behavior of the Na signal. Na level is high and saturated near the Mo/CIS interface. The concentration then decreases as one moves from the small grained CIS region near the Mo contact into the larger grain region of the bottom layer. This is the behavior we had observed in single layer CIS films grown on Mo/glass substrates [2]. In the present double-layer film, however, Na signal rises again in the middle of the film, peaks, and then decreases, eventually rising again right at the surface of the sample. In other words, the CIS/CIS interface introduced in the middle of the absorber layer acts just like the Mo/CIS interface in terms of its Na content. If the peak of Na at the CIS/Mo interface was simply due to a diffusion profile then one would expect the Na level to continue to drop towards the surface of the sample 1902-375. However, this did not happen. On the contrary, Na level in the top half of the absorber was found to be higher than the bottom half. SEM of Fig 2 shows that the top half of the double layer structure film has smaller grain size, therefore, proving that the Na content in CIS layers is indeed a strong function of the micro structure of the film and that most of the Na resides on the grain boundaries.

In summary, the Mo substrate impact work carried out within the National CIS Team has pointed out the following important facts.

- i) Na content of Mo layers prepared in different laboratories using different conditions was approximately the same.
- ii) Despite the fact that the Na content was the same in Mo layers, Na diffusion through these layers into CIS were very different, diffusion being faster through the thinner Mo films.
- iii) Na primarily resides on the grain boundaries and is associated with oxygen especially when it is in Mo layers. In CIS layers, Na mostly resides on grain boundaries.
- iv) When different selenization techniques were studied (not reported here) Na content in the CIS films was found to be a very strong function of the selenization method. H₂Se selenization promoted the highest degree of Na diffusion into the CIS layers. This result suggested that the most important factor determining Na diffusion into CIS was the process used in growing the CIS layers rather than the nature of the Mo layer.

Using the above information and recognizing the influence of the processing technique on Na diffusion, ISET was able to formulate a Mo contact for its devices. This contact gave us well adhering CIS layers and high efficiency devices.

3.2 CdS-free Junctions

Prof. Larry Olson's group at Washington State University had previously shown that the CdS buffer layer in the CIS device structure could be replaced by an undoped ZnO film,

especially if this ZnO film is deposited in a H₂ environment, or if the CIS layer is annealed in H₂ before the deposition of the ZnO layer. Accordingly, we tested the importance of the H₂ annealing step in the specific MOCVD technique that we employ to deposit the ZnO layers. This work was also carried out within the National CIS Team.

A Mo/soda lime glass substrate was coated with CIS layer with a Cu:In ratio of 0.90. The Ga content in the film was 10%. Selenization was carried out at 440 °C for 30 minutes for this sample. After the selenization step, part of the sample was coated with dip CdS as the control and on the other portions ZnO was deposited under the following conditions.

Condition #1

- Load the samples (without CdS) into the ZnO Chamber.
- Flow 25% H₂ balance Argon as a carrier gas.
- Raise the temperature from 175 °C to 250 °C.
- Hold the temperature (250 °) for 15 minutes.
- Bring back the temperature to 175 °C.
- Deposit high rho ZnO for 3 minutes and low rho for 11 minutes.
- Measure the devices after the photo resist step.

Condition #2

- Repeat all the steps using 100% Argon as Carrier gas instead of 25 % H₂.

Condition # 3

- Load the samples (without CdS) into the ZnO Chamber.
- Flow Argon as a carrier gas.
- Raise the temperature from 175 °C to 300 °C.
- Hold the temperature (300 °C) for 15 minutes.
- Deposit undoped ZnO for 5 minutes at 300 ° C.
- Bring back the temperature to 175 °C.
- Deposit low rho ZnO for 13 minutes.
- Measure the devices after the photo resist step.

The device measurement results for the three conditions of processing are given in Table 1.

Table 1. Device parameters for cells with and without the CdS buffer layer.

	1917 A1 (Control)	1917A2 Condition #1	1917 B1 Condition # 2	1917 B3 Condition # 3
Voc (mV)	455	370	385	320
Jsc (mA/cm ²)	35.00	35.50	35.50	34.40
FF (%)	68.70	59.12	63.50	56.45
Eff (%)	10.95	7.77	8.70	6.20

As can be seen from this table, the control sample has the highest voltage and efficiency. The H₂ and Ar annealed samples are similar. In fact, Ar annealed sample has better efficiency. Therefore, observing these results we initially concluded that there was no clear benefit in annealing the samples in hydrogen in our process. However, it later became clear that a much larger effect was masking the results of these experiments.

The factor influencing our measurements was observed when the CdS-free ZnO/CIS junctions were placed under illumination under open circuit conditions. This light soaking improved the cell efficiency by improving mostly the open circuit voltage. For example, the cell 1917 B3 of Table 1 had a starting efficiency of 6.2% ($V_{oc}=320$ mV, $J_{sc}=34.4$ mA/cm², FF=56.45). After 120 hours under light, the efficiency of this device went to 10.31% with V_{oc} value increasing to 415 mV. This is indicative of changes in the junction region resulting from light generated carriers and their population of surface/bulk states. When the improved device was later stored in dark for about three days its I-V characteristics went back to nearly the original one we had measured before illumination. Therefore, the observed effects are reversible. Control samples with CdS buffer layers did not show this behavior.

The above observations prompted a study on CdS-free junctions jointly with Washington State University and the Institute of Energy Conversion. In our MOCVD ZnO deposition system the resistivity of undoped layers is about 100 ohm-cm. The undoped layers deposited at WSU are truly insulating films with resistivities above 10,000 ohm-cm. Therefore experiments were set up to replace the CdS buffer layer with the truly high resistivity ZnO layers deposited at WSU to see if the resistivity of the buffer layer was playing a role in the observed voltage transient phenomenon. WSU group carried out the ZnO depositions on our films. Some of these films were then sent to IEC and completed into cells by depositing sputtered ZnO. Some of the samples were made into cells by the deposition of doped ZnO at ISET by MOCVD. The experiment was designed to determine if the type of the doped ZnO layer had any influence on the device performance. The summary of the results obtained on a representative sample is given below.

Sample 1941-F had a CIS absorber that was coated with a thin layer of (about 500Å) intrinsic ZnO at WSU. When the cells were completed at ISET by MOCVD ZnO, the device efficiencies were poor (3-5%). Parts of the sample were completed into cells at IEC by sputtered ZnO and measurements at IEC showed cell efficiencies varying from 6.7% to 9%. This was an encouraging result and we thought it may have suggested that ZnO deposition process had an effect on the device behavior. After keeping these IEC finished devices in the dark and re-measuring them however, it became clear that the light induced effects were prominent even in these cells with intrinsic ZnO buffer layers and sputter deposited doped ZnO windows. The high efficiency measured at IEC was probably due to the pre-soaking procedure before the measurement. The I-V data obtained from one typical cell is given in Fig. 4. The various curves on this data are as follows.

- A: The I-V of the cell after storage in lab for 20 days (eff=7.3%).
- B: After leaving under light for 24 hours (9.2%).
- C: After storage in a dark box for 24 hours (8%).
- D: After storage in a dark box for an additional 48 hours (6.7%).

As can be seen from this data, the major change in the device efficiency is due to the change in the voltage values. These experiments suggest that high resistivity ZnO layers as buffer layers may be problematic for CIS cells fabricated by the two-stage process because of these large transient effects.

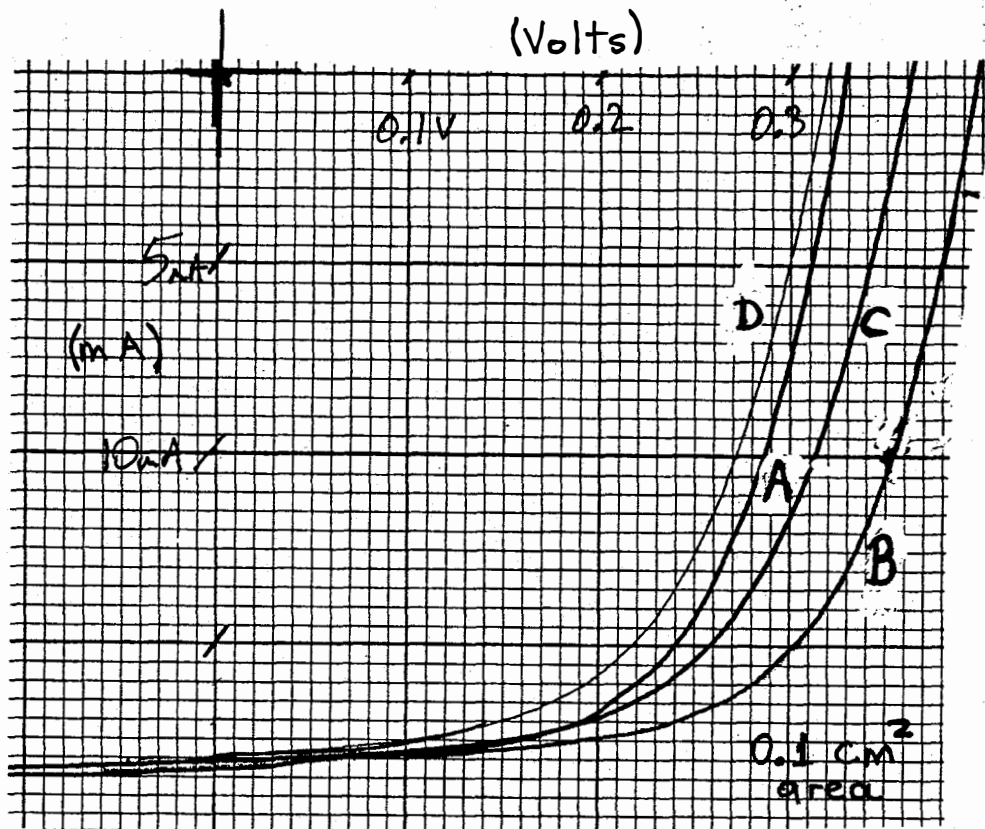


Fig. 4 I-V measurements made on a CIS/ZnO junction after various light soaking experiments.

3.3 Non-vacuum CIS Deposition Technique

As stated before, CIS and related Group I-III-VI compound absorbers have been used in thin film solar cell structures and devices with over 17% conversion efficiency have been demonstrated. A review of the literature shows that high efficiency CIS cells have so far been fabricated on layers grown by the vacuum co-evaporation technique or by various versions of the two-stage selenization method employing evaporated or sputter deposited precursor films. Evaporation techniques are difficult to scale up because of film uniformity and material utilization considerations. Sputtering techniques are better suited for large area deposition, however, they require expensive vacuum equipment and sputtering targets. Materials utilization in sputtering targets is also poor. Therefore, a low cost, non-vacuum technique with the capability of processing large area substrates would be very attractive for the growth of CIS layers for photovoltaic applications. During this project ISET has developed such a new non-vacuum deposition technique.

ISET's novel technique involves particle deposition. The basic idea is to fix the stoichiometry of the material in a "starting powder" which can later be deposited on the selected substrate in the form of a precursor film. This in effect is similar to screen printing which to date has not given any good results due to the fact that there is no good sintering agent for CIS type materials. In ISET's approach sintering and densification of the deposited films do not present a big problem. The key is to have a very small (sub-micron) particle size in the starting powder and to utilize a film deposition technique that can put down a thin (1-4 μm) layer of this powder for further processing. The stoichiometry is fixed within the deposited powder layer and therefore the uniformity of the deposited layer is not of concern. The thickness, however, needs to be controlled to a certain extent within the range indicated above.

The general steps of depositing CIS layers by the non-vacuum technique is given in Fig. 5. The advantages and unique features of this process are (i) the uniformity and the composition control in the deposited CIS film which is easily achieved since the composition of the precursor is fixed at the molecular level, (ii) Material utilization is over 85%, and (iii) the capital equipment required is relatively low cost [3].

Fig. 6 shows the SEM of a powder film (precursor film) deposited on a Mo/glass substrate. The typical particle size is about 0.2 μm . When this film is further processed to form CIS the resulting layer has a grain size of 0.5-2.0 μm . We had presented several SEM studies of the CIS layers grown by the non-vacuum technique in our previous annual report [2].

Fig. 5 General processing steps for ISET's non-vacuum technique.

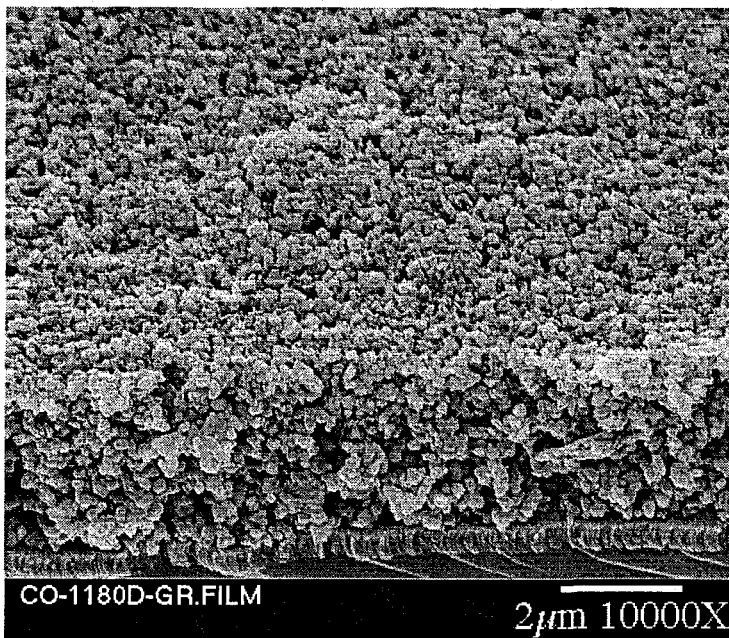
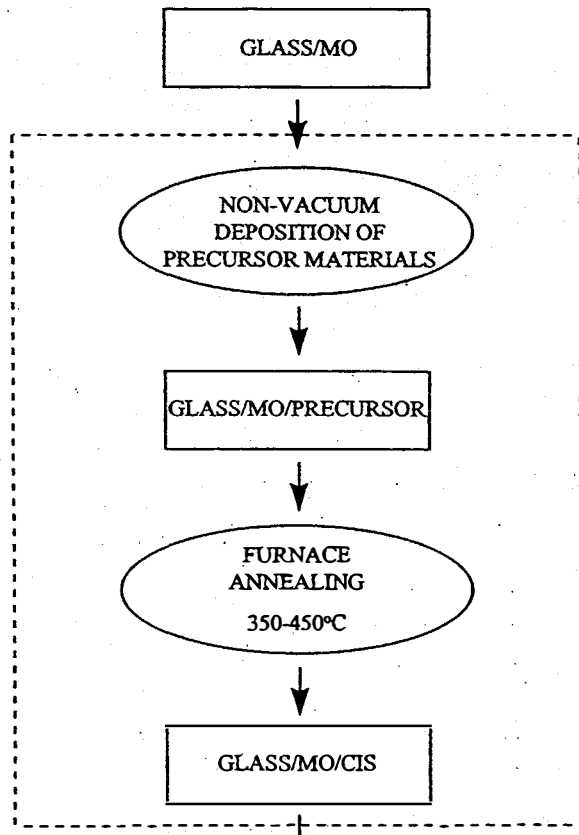


Fig. 6 SEM of a precursor layer that is later converted into a dense CIS absorber.

3.4 Device Processing

Soda-lime glass substrates were used in this work. Mo contact layers were deposited on the soda-lime glass substrates by D.C. magnetron sputtering. CIS films were grown on the Mo surface by the non-vacuum technique. Solar cell fabrication steps included deposition of a thin CdS layer by the commonly used chemical bath deposition approach. A ZnO layer was then deposited on the CdS surface using a MOCVD method. Solar cells of 0.09-1.00 cm² area were defined on the substrates using photolithographic techniques. Modules were also fabricated using films of typically 50 cm² area.

Single cell fabrication continued during this period, mostly for yield studies rather than efficiency improvement. Higher efficiency devices require the development of CIGS or CIGSS layers by the non-vacuum technique. The chemistry utilized and the deposition system used did not allow us to include Ga into the absorber layers in a simple way. We also detected problems in efficiency yields while moving from small area cells to large area modules. Therefore, the attention was turned to yields and producibility rather than efficiency.

CIS cells without S and Ga were fabricated with efficiencies ranging from 10%-13%. In this range of efficiencies the main difference between the high and low efficiency cells was the voltage which, through device analysis, could be directly correlated with the carrier densities in the absorbers. High voltage cells always showed higher carrier densities as determined by capacitance measurements. Correlation of the carrier densities in the absorbers to the film processing parameters, however, has not been 100% successful. The statistical data so far indicates that the efficiencies of the devices fabricated on CIS absorbers will be at best in the 10-13% range. Higher efficiency and tighter yields will require the development of higher bandgap absorbers. I-V characteristics of over 12% efficient cells fabricated on CIS absorbers grown by the non-vacuum technique were previously given in our annual report and will not be repeated here [2].

Module integration for devices fabricated by the non-vacuum technique offered unique challenges. In the general module integration approach the Mo layer is first scribed by laser forming isolated Mo pads, and then a CIS layer is grown over the whole substrate. In our non-vacuum approach, however, we determined that the film nucleation on the glass surface was very different from its nucleation on the Mo layer. The SEM of Fig. 7 shows the surface view of a CIS layer deposited near a scribed Mo region. The white line on the SEM indicates the glass/Mo boundary. To the left of this boundary is the glass/CIS structure and to the right is the glass/Mo/CIS region. Clearly, the CIS layer grown directly on the glass surface by the non-vacuum technique is discontinuous and the glass surface is visible through the large nodules of CIS. The adhesion between the CIS nodules and the glass substrate is not good and the portions of the CIS film within the scribed lines peel off, especially during the ZnO deposition. Exposed Mo edges then give rise to low shunt resistance between adjacent devices.

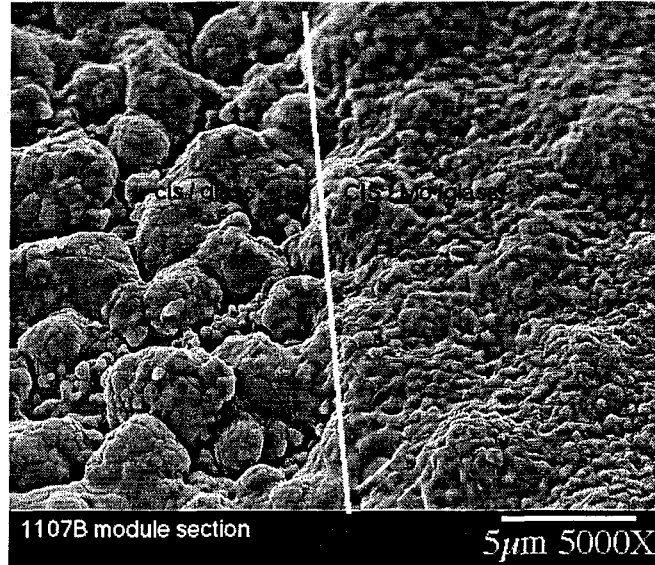


Fig. 7 CIS layer grown near a scribed Mo line. Region on the left is the CIS grown on glass surface. Region on the right shows the CIS grown over the Mo layer.

Faced by this challenge ISET has adapted another approach to module integration. In this approach Mo/CIS structure was first formed on the glass substrate and then the scribing step was carried out. Two techniques were evaluated for the isolation of adjacent devices, laser scribing and chemical etching. Fig. 8 shows the nature of a laser scribed line through a glass/Mo/CIS structure. There is clearly a melted region along both edges of the scribed line. The composition of this melted region was studied by micro probe and was found to be In and Se poor. Heat generated by the laser beam apparently causes preferential evaporation of In and Se species which are known to have low vapor pressure. What is left behind is a Cu-rich region that is relatively conductive. Such a conductive path would cause low shunt resistance in the finished modules once the top ZnO contact is deposited.

Photolithography followed by chemical etching was another approach that was evaluated to form isolated devices for module integration. In this case a photoresist process and chemical etching was used to form the isolating grooves in CIS/Mo structures. The grooves were then filled with an insulating material and the devices were interconnected using the steps depicted in Fig. 9.

We have fabricated many mini-modules of 40-60 cm² area using this second approach. The illuminated I-V characteristics of a typical device is shown in Fig. 10. This is a 60 cm² device consisting of 16 cells connected in series. The efficiency is about 6.6%.

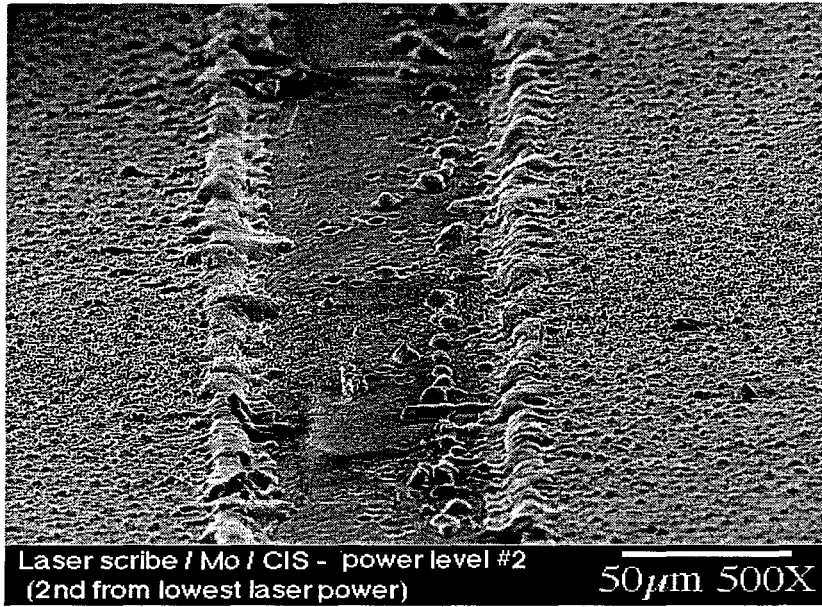


Fig. 8 A Mo/CIS structure scribed by YAG laser. The melted regions along the scribed line were found to be Cu-rich.

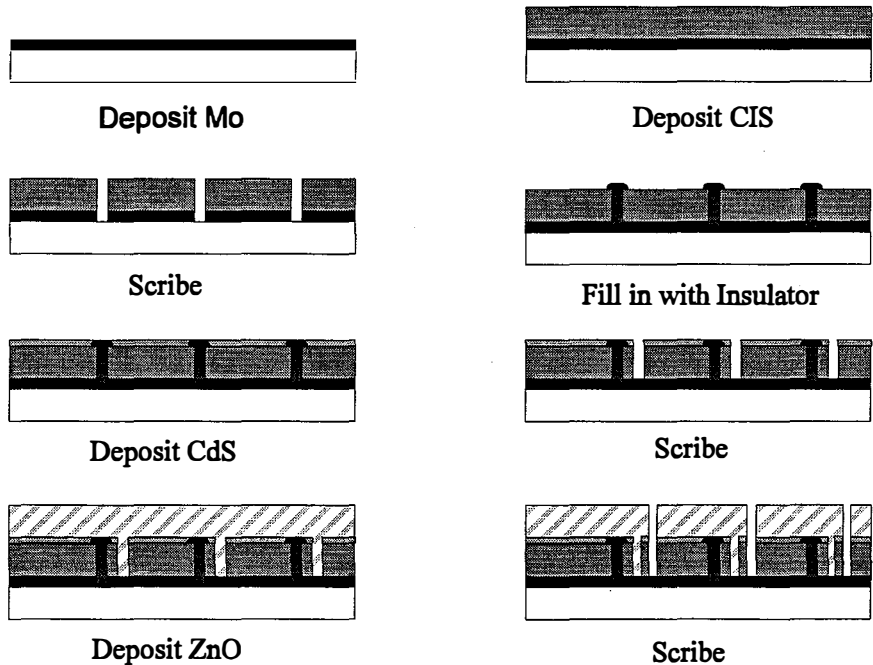


Fig. 9 Integration steps used in the fabrication of the modules.

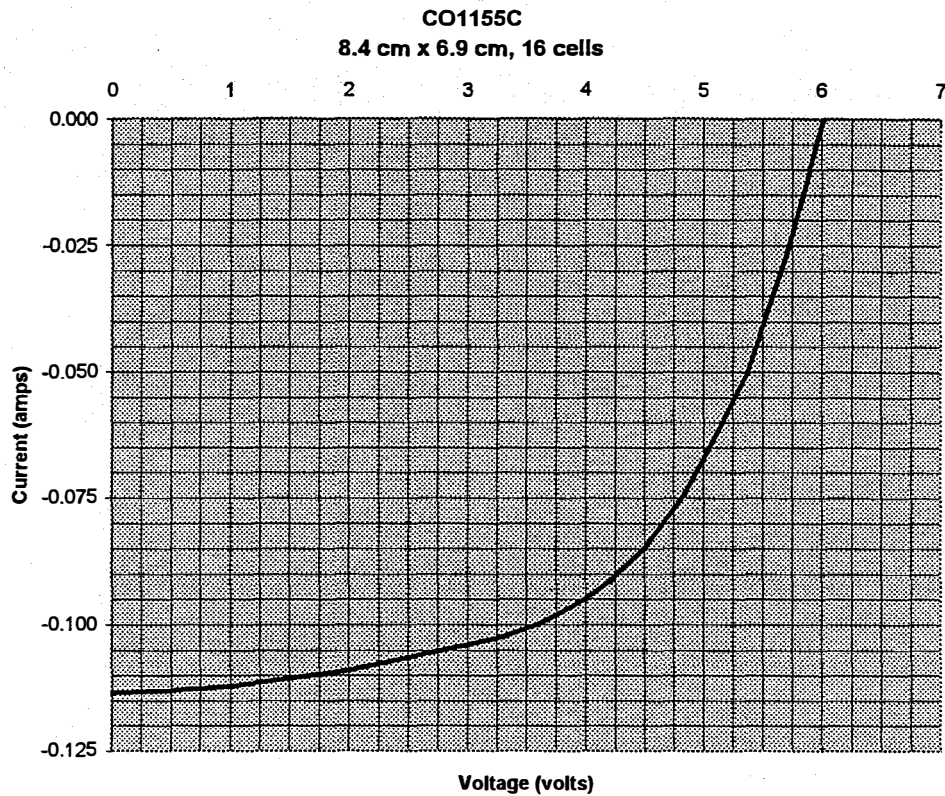


Fig. 10 Illuminated I-V characteristics of a module fabricated on a non-vacuum grown CIS layer.

4.0 CONCLUSIONS AND FUTURE WORK

During this research period ISET has concentrated its efforts on the further development of its novel non-vacuum technique and understanding the glass/Mo/CIS interactions. The second topic was the subject of a team set up under the National CIS Partnership Program. Na diffusion from the glass substrates into the CIS absorbers was found to be a strong function of the nature of the Mo layer and even stronger function of the nature of the CIS growth technique. Put in other words, this result means that there is no unique Mo layer that is appropriate for all CIS coating approaches in terms of its ability to control Na diffusion. Rather, each deposition scheme requires a Mo layer that is tailored for that technique. Using the results of this team effort ISET was able to tailor its substrate for its non-vacuum technique that allowed us to minimize the mechanical peeling problems and at the same time to minimize the Mo layer thickness which was reduced from about 2.5 μm to 0.5 μm .

ISET's non-vacuum technique was fully developed during this research period and patent applications have been submitted. Work on large area (up to 1 ft^2) processing brought with it challenges in terms of uniform processing and low yields. Therefore, attention was turned from efficiency improvement to increasing the processing yields. CIS layers without Ga or

S were used to demonstrate up to 13% efficient solar cells. Modules with 40-60 cm² area were fabricated with efficiencies between 5% and 7%. Problem areas in module integration were identified.

The efficiency limit for devices fabricated on CIS layers grown by the non-vacuum technique appears to be about 13%. To improve this efficiency further, the future work will concentrate on larger bandgap absorbers. Both Ga and S addition to the absorbers grown by the non-vacuum approach will increase the solar cell efficiencies to the 15% range. Future work will also include 1 ft² processing and development of a robust module integration approach. Long term stability of devices fabricated on layers grown by the non-vacuum technique will also be demonstrated.

5.0 ACKNOWLEDGMENTS

Part of this work has been carried out under National CIS Partnership Program. The authors are grateful to the members of the "Mo/substrate interaction" working group which included J. Britt of EPV, T. Gillispie of Lockheed Martin, A. Rockett of University of Illinois, J. Sites of CSU, R. Matson, A. Swartzlander-Franz, S. Asher and M. Al-Jassim of NREL. We are also thankful to K. Emery of NREL for characterization and measurements of films and devices, and to H. Ullal, R. Noufi and K. Zweibel for technical discussions.

6.0 LIST OF PUBLICATIONS

During this research period the following papers were published on thin film solar cells:

- W. Shafarman, B. Basol, J. Britt, R.Hall and R. Rocheleau, "Semiconductor processing and manufacturing", Progress in PV, 5 (1997) 359.
- V. K. Kapur, "Low cost manufacturing of PV modules through improved CIS technology", Proc. World PV Power Conf., San Diego, CA Nov. 10-12, 1997, Gorham Advanced Materials Inc.

We also have two papers in preparation reporting the results of the team activity. They will be published in Solar Energy Materials and Solar Cells. ISET also prepared and submitted a U.S. patent application on its non-vacuum process during this research period.

7.0 REFERENCES

1. B.M. Basol et al., J. Vac. Sci. Technol. A, 14(4), July/Aug 1996, p. 2251.
2. B.M. Basol et al., "Application of CIS to High Efficiency PV Module Fabrication", Annual Technical Progress Report, NREL Contract ZAF-5-14142-07, April 1, 1996-March 31, 1997.
3. V. K. Kapur, "Low cost manufacturing of PV modules through improved CIS technology", Proc. World PV Power Conf., SanDiego, CA Nov. 10-12, 1997, Gorham Advanced Materials Inc.

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13. ABSTRACT (Maximum 200 words) During this research period, researchers at International Solar Electric Technology (ISET) concentrated their efforts on three different areas of research. Within the National CIS R&D Team, ISET participated in the "substrate/Mo interactions" working group and investigated issues such as Na diffusion from the soda-lime glass substrate into the Mo layers and CIS films. Researchers determined that the Na content within the Mo layers was not a strong function of the nature of the Mo film. However, they found that diffusion through the Mo layers was a function of the Mo film characteristics as well as a very strong function of the CIS growth process itself. Researchers showed conclusively that the Na resided on the grain boundaries of CIS layers. Another team activity involved evaluation of CdS-free CIS solar cells. ZnO/CIS junctions prepared by the two-stage process showed light-soaking effects. Cells left under illumination improved in efficiency and were similar to the CdS/CIS junctions. After storage in the dark, however, efficiency deteriorated greatly for the ZnO/CIS device, most of the decline coming from the open-circuit voltage values. Much of the effort during this period was spent on developing a low-cost, non-vacuum CIS deposition technique. The method developed involves particulate deposition and formation of precursor layers followed by the conversion of these layers into CIS. Test modules of 40-60 cm ² were adapted to understand the issues involved in this novel technology. At the present time, the submodule efficiencies are 6%-7%. Single-cell efficiencies are in the 10%-13% range.				
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