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High Efficiency Copper Ternary Thin Film Solar Cells

Final Subcontract Report
1 March 1987 - 31 July 1990

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Vijay K. Kapur
International Solar Electric Technology
Inglewood, California

Prepared under Subcontract No. XL-7-06031-6

Solar Energy Research Institute
A Division of Midwest Research Institute

1617 Cole Boulevard
Golden, Colorado 80401

Operated for the
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1.0 SUMMARY

This is the Fin' ' Report for a forty-one-month research program entitled " High Efficiency Cu-Ternary Thin Film Solar Cells ". The goal of this project is to develop a high efficiency thin film $CuInSe_2$ (CIS) solar cell using a potentially low-cost two-stage process. The two-stage process involves depositing the metallic elements of CIS (i.e. Cu and In) on a substrate in the form of stacked layers and then selenizing these stacked metallic layers in an atmosphere containing Se to form a CIS film. During the first eighteen months of this research program we concentrated our efforts on using electrodeposition techniques for depositing the Cu and In films on Mo coated glass substrates. These efforts resulted in a process by which small area solar cells with conversion efficiencies close to 10% could be fabricated. These results established the fact that the two-stage process using electrodeposition/selenization technique can yield CIS films with good electrical and optical properties, and efficient solar cells can be fabricated using these layers. In addition to the small area high efficiency cells the early part of the program also concentrated on the scale-up of the electrodeposition/selenization approach. The reader is referred to our recent Annual Report [1] for the details of this work which will not be repeated in this manuscript.

This report summarizes the results of the last 23 months of research during which we have concentrated our efforts on the evaporation/selenization approach. In this technique, controlled thicknesses of Cu and In were evaporated on Mo coated glass substrates and selenization was carried out in a H_2Se atmosphere at 400°C. The microstructure of the CIS films was found to be a strong function of how the Cu-In precursors were processed. Specifically, we have shown that sequentially evaporated Cu-In films were alloyed and their order of deposition determined the degree of alloying as well as the morphology of the composite film. The grain size in the CIS layers was also found to be a function of the stoichiometry. Near stoichiometric or Cu-rich compositions promoted grain growth in these films. Solar cells with around 11% active area efficiency were successfully demonstrated using the two-stage process.

2.0 INTRODUCTION

The overall objective of this project is to develop thin film copper ternary solar cells with conversion efficiencies approaching 12.0%. A two-stage process has been developed for this purpose and high efficiency solar cells with conversion efficiencies of about 11% (active area) have been demonstrated using this very promising technique.

The two-stage process involves deposition of some or all of the elemental components of a compound in the form of stacked layers onto a substrate followed by a reaction of these elemental components to form the desired compound. In the case of $CuInSe_2$ (CIS), either Cu/In/Se or Cu/In stacked layers can be utilized in a two-stage process. If a Cu/In/Se stack is used, the reaction of the elements can be carried out in an inert atmosphere. If, on the other hand, a Cu/In stack is employed, then the reaction should be carried out in a reactive atmosphere containing H_2Se gas or Se vapor. Although, standard furnace annealing is the commonly used

method for forming CIS by the two-stage process, there has also been some work on reacting ultra-thin layers of Cu, In and Se by pulsed laser radiation.

The elemental layers in a two-stage process can be deposited by various techniques. However, the technique chosen should have a demonstrated ability to deposit layers with tightly controlled thicknesses. Such control is important for obtaining material of proper stoichiometry especially for the case of Group I-III-VI_2 semiconductors. The two-stage process employed by our group in this research program consisted of two basic processing steps:

(a) deposition of a thin Cu/In metal stack on a substrate;
(b) selenization of this metal stack in an atmosphere containing H_2Se gas.

The substrate for the CIS devices typically consisted of a glass sheet metallized on one side by an evaporated or sputtered Mo layer. Cu and In layers were either electrodeposited or evaporated. The selenization process was carried out in a H_2Se containing atmosphere at around 400°C.

Following our initial work on the electroplated and selenized CIS layers, we have concentrated our efforts on the evaporation/selenization process during the last 18 months of the project. This approach uses evaporated Cu-In layers as precursors for the selenization step. In this work Cu and In layers were evaporated onto Mo coated substrates and they were then selenized in the same manner as the electrodeposited films. This effort led to very encouraging results and highly efficient solar cells were fabricated on films processed by this technique. Work on the evaporation/selenization approach constitutes the bulk of this report and it is presented in Section 3.2. Section 3.3 contains results on solar cell window layers and device measurements.

3.0 TECHNICAL DISCUSSION

3.1 Substrates

The majority of the substrates used in this work were Mo coated glass sheets. We used both 7059 Corning and soda-lime glass substrates in this work. Mo layers were either E-Beam evaporated or sputter deposited on 6"x 6" glass substrates. E-beam evaporated Mo layers were usually found to contain more oxygen than the sputtered layers, especially when they were deposited at low substrate temperatures. The details of the Mo deposition process have been previously published and they will not be repeated here. The thickness of the Mo film was typically 2.0-2.5 microns and its sheet resistance changed between 0.05-0.1 ohms per square. The Mo films were stress free and they adhered well to the glass substrates without any interlayer of Cr between the glass surface and the Mo film.

3.2 Evaporation/Selenization Process

During the last twenty three months of this project we directed our research efforts towards obtaining CIS films of various stoichiometries by the two-stage process using the vacuum evaporation/selenization technique. In this method, Cu and In layers were first evaporated onto the Mo-coated glass substrates, and then they were selenized in an H_2Se containing atmosphere at 400°C to form the CIS films. Heterojunction solar cells with a structure of Transparent Conductive Oxide (TCO)/thin CdS/CIS or a structure of CdS/CIS were fabricated on these films and conversion efficiencies close to 11% were obtained with both structures. The following sections will present the details of this evaporation/selenization approach.

3.2.1 Cu-In Precursors

Mo coated substrates were degreased and prepared for Cu and In evaporation. In the early experiments with evaporation, metal depositions were carried out in a thermal evaporator at a pressure of $5x10^{-5}$ Torr [2]. A Mo dimple boat with alumina barriers was employed as the evaporation source in these experiments. Cu and In layers were deposited on the Mo coated substrates and glass witness slides using 4-9's pure Cu and In charges. Substrates were not intentionally heated during the evaporation. Deposition rates were monitored by a crystal rate monitor and they were kept at around 30Å/second. The thicknesses of the Cu and In layers were varied to obtain CIS films of differing stoichiometries.

During the later part of the program we have prepared our E-beam evaporation system for Cu and In evaporations. The existing tooling in this machine was modified to permit the addition of a thickness monitor. The rotating mechanism of the four-pocket hearth was activated so that the Cu and In evaporations could be carried out in one pumpdown. The thickness of the Cu film was typically 0.2μm. The thickness of the In layer was changed depending upon the desired stoichiometry of the compound. Details of our E-beam evaporation/selenization process may be found in some of our recently published papers [3,4,5].

The nature of the evaporated Cu-In films was studied by XRD, SEM and Auger analysis. As a result of these investigations it was discovered that unlike the electrodeposited Cu/In stacks, which mostly consist of two separate elemental phases (Cu and In), the Cu-In films evaporated on uncooled substrates were, to a large extent, alloyed. The degree of alloying depended upon the deposition conditions and the deposition sequence.

Fig. 1 shows the XRD data taken from four samples prepared on Mo/glass substrates. Sample A was obtained by evaporating an In layer over the Cu film which was previously deposited on the Mo layer. The evaporation sequence was reversed for Sample B. The Cu-to-In ratio in both of these films was 0.9. Samples C and D consisted of Cu/Mo/glass and In/Mo/glass structures respectively. The XRD data of Samples A and B show many peaks which are not associated with the Cu and In peaks of Samples C and D. These extra reflections are due to Cu-In alloys some of which have been identified in Fig. 1. In the case of In-on-Cu film (Sample A), there

are peaks belonging to the CuIn phase as well as to the Cu phase. An additional set of peaks (labeled as ?) could not be identified using the JCPDS sets 1-38, but they were tentatively

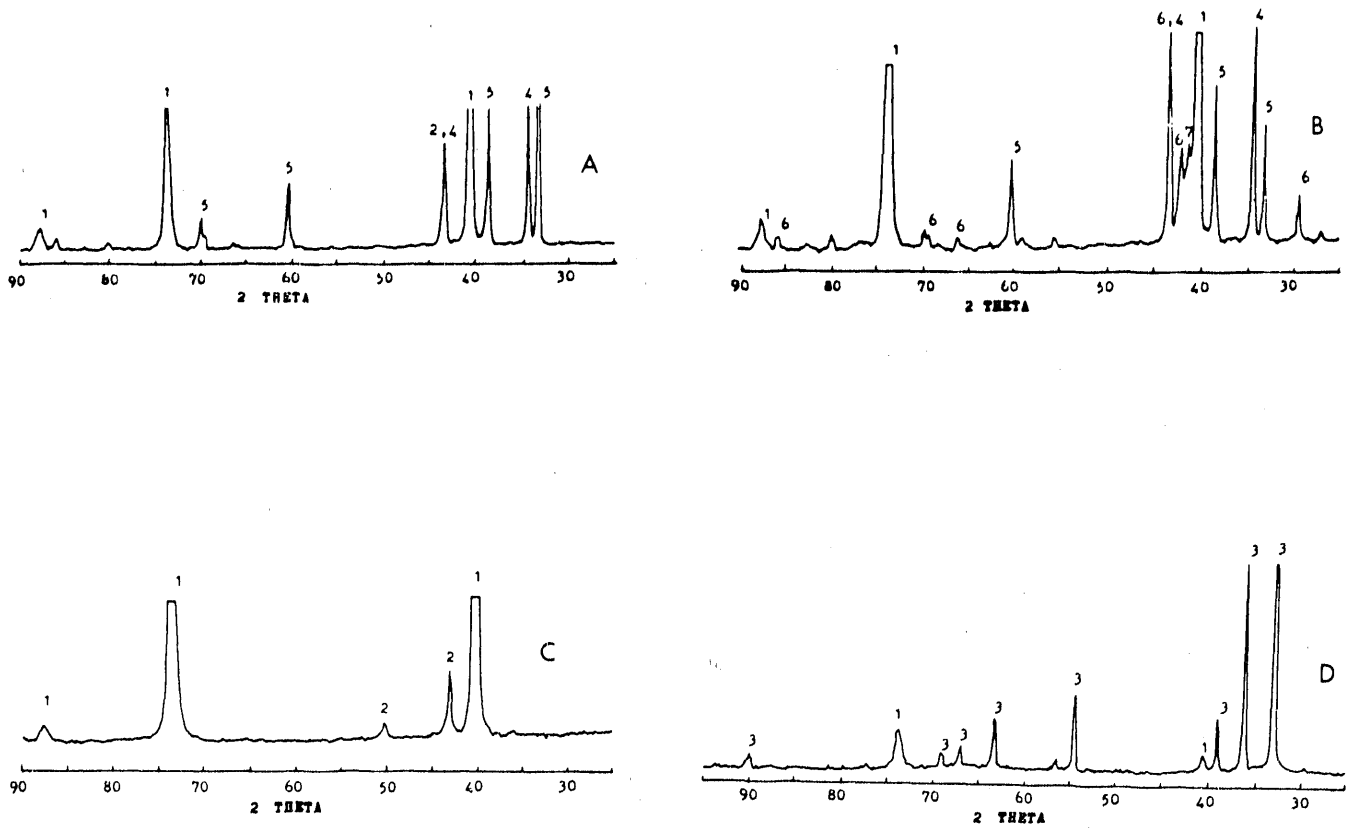


Fig. 1. XRD data taken from, Sample A:In/Cu/Mo/glass; Sample B: Cu/In/Mo/glass; Sample C: Cu/Mo/glass; Sample D: In/Mo/glass (1:Mo; 2:Cu; 3:In; 4:CuIn; 5:?; 6:Cu_4In; 7:Cu_7In_4).

attributed to a cubic phase with a lattice parameter of a=4.657Å. In addition to the alloy peaks seen in Sample A, Sample B also exhibits peaks associated with Cu-rich phases of Cu-In alloys (Cu_4In and Cu_7In_4). Lack of a Cu peak in this sample suggests better alloying between the two elements. This can be explained by the fact that the energy transferred from the incoming Cu atoms to the low-melting In is probably enough to cause more substantial alloying in Sample B

compared to Sample A. It should be noted that the alloying between the evaporated Cu-In films was recently studied by the University of Stuttgart group [6]. The differences between our results and that of Ref.6, in terms of the identified alloy peaks, indicate that the nature of these Cu-In layers depends strongly on the deposition parameters. Low evaporation rates and high substrate temperatures, for example, are expected to favor higher degree of alloying. The Auger depth profile of Fig. 2a was taken from a Cu-In film obtained by evaporating a 0.2μm thick Cu layer over a 0.45μm In film. The evaporation rate for Cu was around 3Å/sec for this sample. Although a distinct gradient in the Cu-to-In ratio of this film can be observed, the intermixing

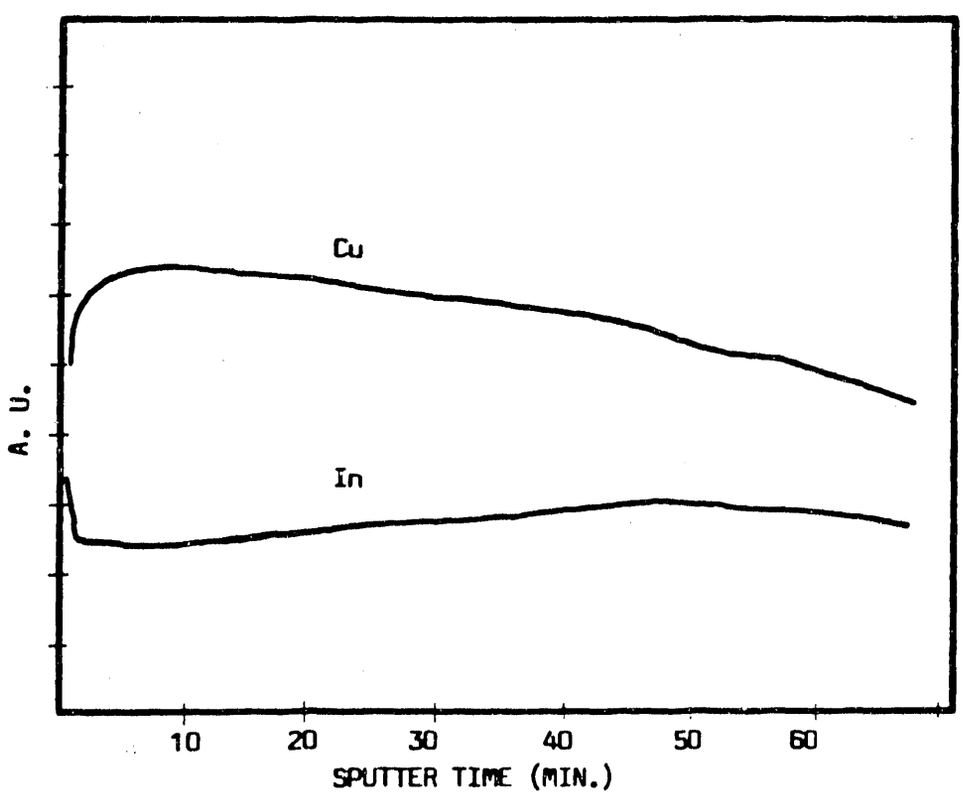


Fig. 2a. Auger depth profile of a Cu-In/Mo/glass structure where the Cu layer was evaporated over the In layer at a rate of 3Å/sec.

between the two elements is complete. The profile of Fig. 2b, on the other hand, was taken from a film that was obtained by evaporating the Cu layer at a rate of 30Å/sec. A Cu-rich surface region can be observed in this sample. The sequence of deposition for the Cu and In films also

affects the morphology of the deposited layers. Films obtained by evaporating In over Cu layers are generally better in terms of their surface micro-structure compared to those obtained by evaporating Cu over In. Fig. 3 is a cross sectional SEM of a Cu/In/Mo sample where a 0.2μm Cu layer was evaporated onto a 0.45μm thick In layer. It is obvious that poor wetting of the Mo surface by the In film has given rise to a very non-uniform Cu-In layer with a rough surface morphology. Selenization of such non-uniform Cu-In films results in non-uniform CIS morphology as will be discussed in a later section.

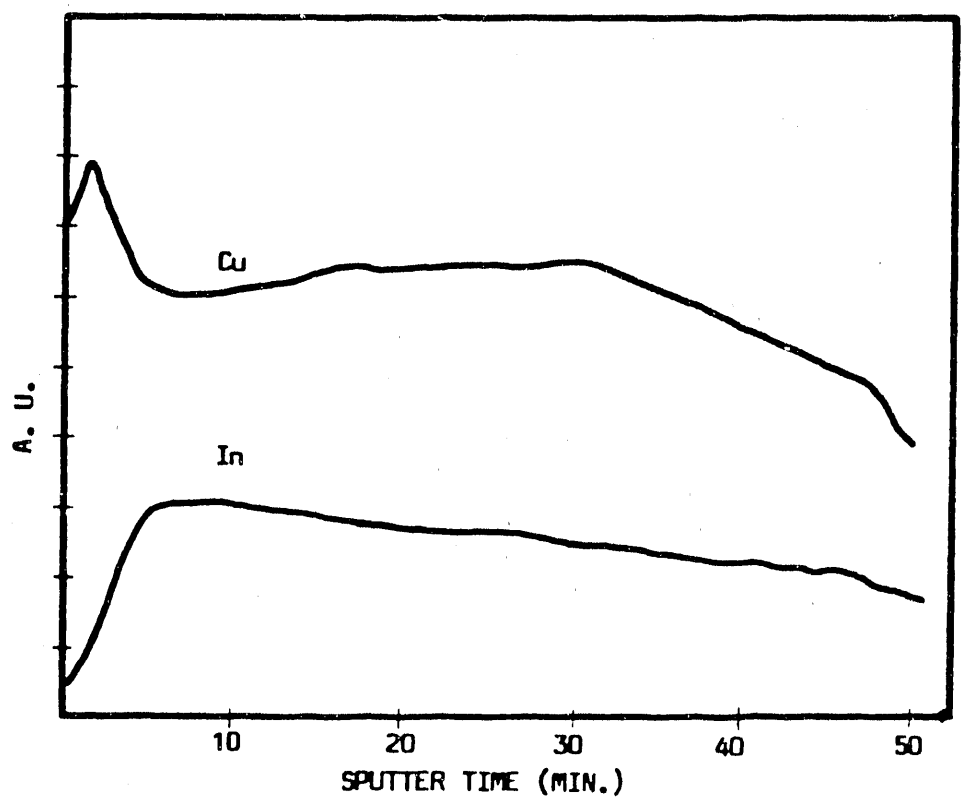


Fig. 2b Auger depth profile of a Cu-In/Mo/glass structure where the Cu layer was evaporated over the In layer at a rate of 30Å/sec.

3.2.2 Selenization

After the evaporation step, the substrates were removed from the vacuum chamber and placed into a tube furnace for selenization. Selenization was carried out for 1 hour at 400°C in a 5-10%

H_2Se (in Ar) atmosphere. In some of the experiments an attempt was made to simulate the double-layer structure of the Boeing cells. In these experiments, first a 2μm thick Cu-rich CIS layer was deposited onto the Mo coated glass substrate. This was achieved by evaporating and selenizing Cu and In layers corresponding to a Cu-to-In ratio of around 1.1. After the selenization step, another elemental layer with Cu-to-In ratio of 0.7 was deposited over the first selenized film and then the whole structure was again selenized briefly for about 10 minutes. The thickness of the second layer in these samples was 0.8μm.

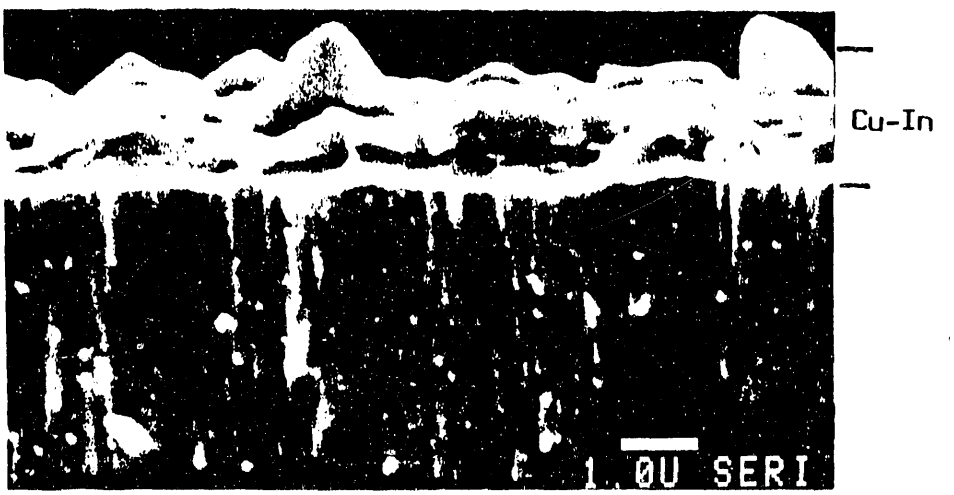


Fig. 3. Non-uniform morphology of a Cu-In layer obtained by evaporating a 0.2μm thick Cu layer on a 0.45μm thick In film.

3.2.3 CIS Films

We have already stated that the nature of the selenized compound layers strongly depends on the nature of the Cu-In precursors. Specifically, the microstructure of a CIS film is, to a large extent, determined by the processes and procedures used in depositing the Cu-In layers. The grain size of a CIS film is also a function of its stoichiometry.

Fig. 4 shows SEM data taken from three CIS films of different stoichiometries. It is clear from this data that the CIS films become more and more granular as the Cu-to-In ratio is increased from 0.77 to 0.95. Although not shown in this figure, when the Cu-to-In ratio is raised above

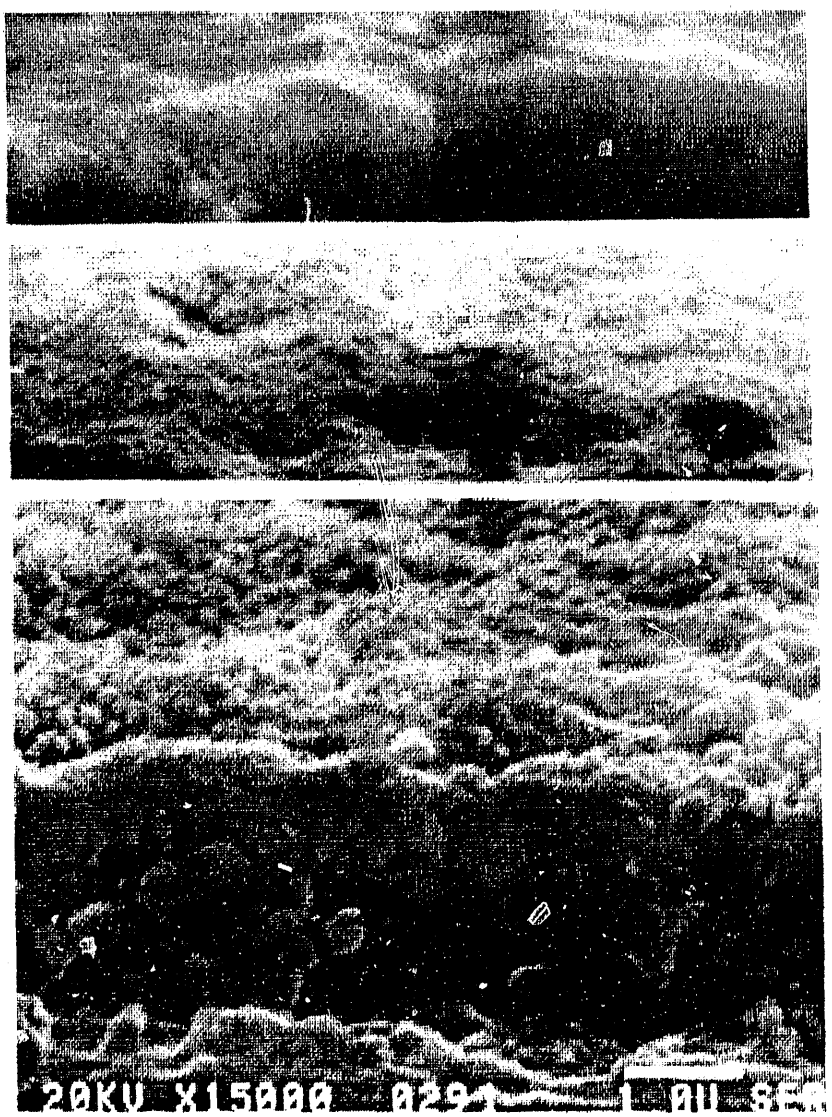


Fig. 4. SEM's of CIS films obtained by the selenization of evaporated Cu-In layers. The Cu-to-In ratio for these samples were: A(0.77), B(0.90), C(0.95).

1.0, faceted crystals associated with the Cu-selenide phase become dominant. These results are very similar to those obtained from coevaporated CIS films and they suggest that the grain structure of CIS is sensitive to the stoichiometry of the film whether it is grown by the coevaporation method or the selenization technique. It is not clear how the higher Cu-to-In ratios promote grain growth in CIS. However, Cu is known to be an effective "sensitizer" for grain growth in II-VI compounds such as CdS.

Fig. 5 is a SEM picture of a CIS film obtained by selenizing a Cu-In film similar to the one depicted in Fig. 3. The non-uniformity of the grain structure observed in Fig. 5 can be directly

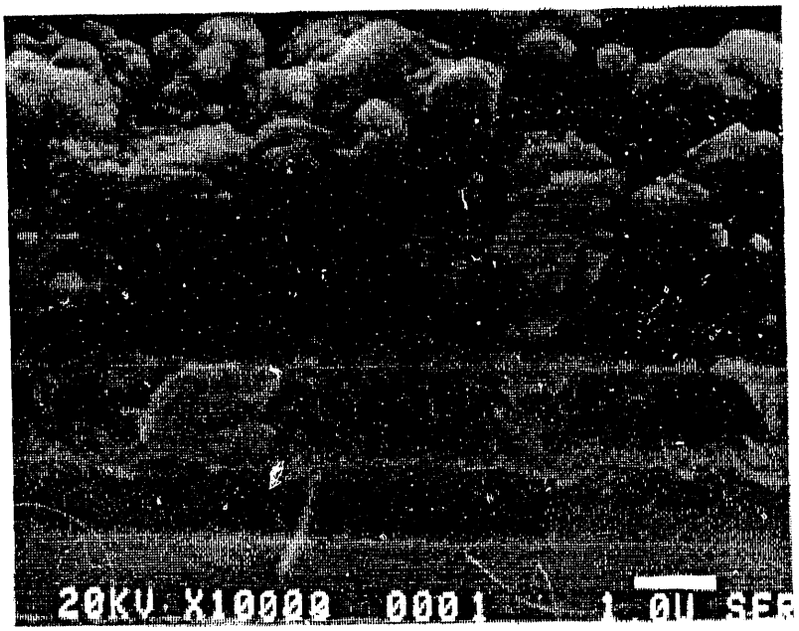


Fig. 5. Morphology of a CIS film obtained by the selenization of a Cu-In layer similar to that of Fig. 3.

translated into the stoichiometric non-uniformities in the grains of this film. As we stated earlier, large grains in CIS are usually associated with near-stoichiometric or Cu-rich compositions of this material, whereas, smaller grains are typical of In-rich stoichiometry. It should be noted that solar cells fabricated on such non-uniform films display poor fill factors and low open circuit

voltage values due to the shunting effects by the Cu-rich grains which most probably contain Cu-selenide phase.

We have carried out studies to determine how the deposition technique of the Cu-In layers affects the grain structure of the CIS films. The film of Fig. 6a was obtained by selenizing an electrodeposited Cu/In stacked layer. The film of Fig. 6b, on the other hand, was prepared using an alloyed Cu-In film. It is observed that the electrodeposited and selenized CIS film has well defined grains that are 2.0-3.0μm in size. The evaporated/selenized film, on the other hand, has a submicron grain size. This observation can be explained by the fact that the selenization of a Cu/In stacked layer gets initiated at the surface of the In film which is in the form of a liquid at above 157°C. Therefore, during the early stages of the process both the selenization of In and the diffusion of Cu takes place into a liquid medium. As a result, large grains are formed. In the case of the evaporated and alloyed Cu-In films with high melting points there is no liquid medium and the alloy film is transferred into CIS by the gas/solid reactions and solid/solid diffusion processes. As a result, the grain size is smaller.

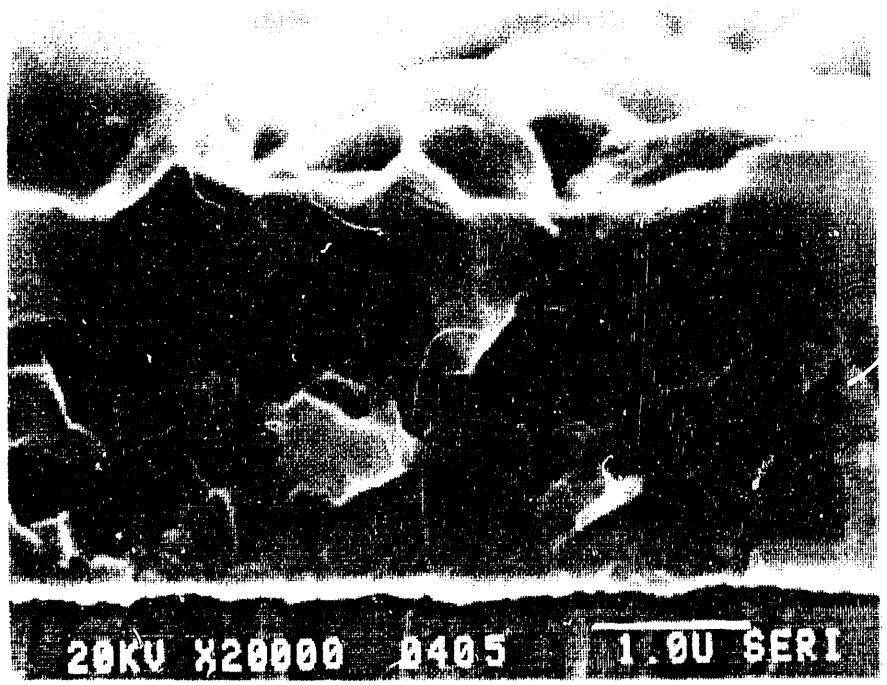


Fig. 6a. Cross-sectional SEM of a CIS film obtained by the selenization of an electrodeposited Cu/In stack.

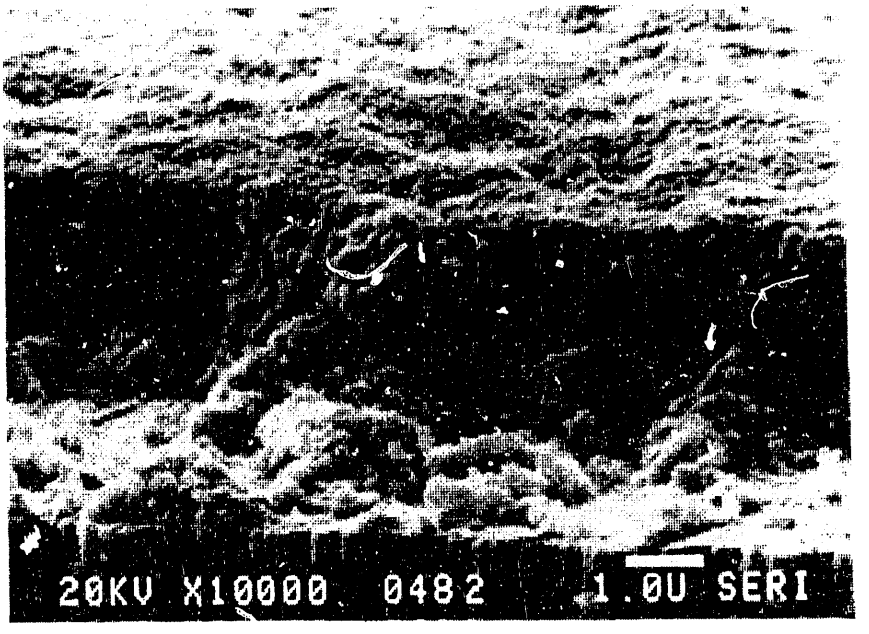


Fig. 6b. Cross-sectional SEM of a CIS film obtained by the selenization of an evaporated Cu-In layer.

Alloying of the evaporated Cu-In layers may have another effect on the CIS film properties. As we had reported previously, one of the problems associated with the electrodeposited/selenized CIS films is their poor adhesion to the Mo coated substrates [1]. The reason for the poor adhesion is believed to be the nearly 3-fold volume expansion caused by the incorporation of Se into the Cu/In layers during the selenization process. This volume expansion exerts considerable stress on the already weak Mo/CIS interface and causes the films to peel. Measurements made on the evaporated Cu-In layers showed that the density of these alloyed layers was much less than the individual densities of the Cu and In films. An alloy film obtained by evaporating a 0.2μm thick Cu film and a 0.4μm thick In layer, for example, had a thickness of 1.1μm. This corresponds to a volume expansion of almost 2-fold and Se can be more easily incorporated into these films without exerting much stress on the Mo/CIS interface.

3.3 Device Fabrication

3.3.1 Window Layers

Both evaporated and chemically deposited CdS layers and evaporated CdZnS films were used as junction partners to the CIS films. The evaporated CdZnS layers were In-doped. They were 1.1 microns thick and they contained 15% Zn. The sheet resistance of the CdZnS films was 175 ohms/square. A 2000Å thick Indium Tin Oxide (ITO) layer was sputter deposited over the CdZnS film to bring the sheet resistance down to about 20 ohms/square.

The evaporated CdS films had the commonly used two-layer structure that was obtained by first evaporating a 0.4-0.8μm thick undoped layer and then depositing on top of it a 0.8-1.0μm thick In-doped region. The substrate temperature and the deposition rate for the CdS evaporations were 200°C and 60-100Å/sec respectively and the nominal sheet resistance of the composite CdS layer was 30 ohms/square. Aluminum was used as the top contact material in devices with evaporated CdS window layers.

Chemically deposited CdS layers were 500-3000Å thick and they were obtained by the solution growth method. Chemical deposition (also known as dip-coating or solution growth) is a technique that is known to yield thin layers of near-stoichiometric, highly transparent CdS films. In our work we have used a solution with cadmium acetate, ammonium hydroxide and TEA. These reagents were mixed with deionized water and warmed up to 65°C. A CIS coated substrate was placed in the container with the above solution mixture, and a thiourea solution was then added into the container with stirring. After 5-20 minutes, a coating of CdS that was 500-3000Å was obtained. The thickness of this layer could be further changed by controlling the deposition temperature and the deposition time.

Because of their excessive sheet resistance the chemically deposited CdS films need to be contacted by TCO layers. We have used both ITO and ZnO films for this purpose. ZnO layers were deposited by the magnetron sputtering technique from a 6" diameter target. The target material was doped with 1% (by weight) Al_2O_3 and the deposition rate was around 200Å/min. The surface of the target was first conditioned by sputtering onto the shutter in a 10% O_2 + 90% Ar plasma. The oxygen flow was then cut off and the shutter was opened for deposition over the substrates. Although we were able to obtain films with resistivity values as low as 8×10^{-4} ohm-cm by this approach, the uniformity of the resistivity was poor across the 6 " diameter substrate holder. The resistivity was as high as 10^{-2} ohm-cm in some parts of the substrate. We believe that this non-uniformity can be avoided by using a more heavily doped target.

3.3.2 Devices

The early experiments on evaporated/selenized CIS films utilized Cu-In layers that were prepared using resistively heated evaporation boats. Fig. 7 shows the I-V characteristics of the first

efficient CdS/CIS cell that we obtained by this approach. The solar cell parameters of this device are; V_{oc}=0.332 V, J_{sc}=32.24 mA/cm^2, FF=56.91% and η=6.96%.

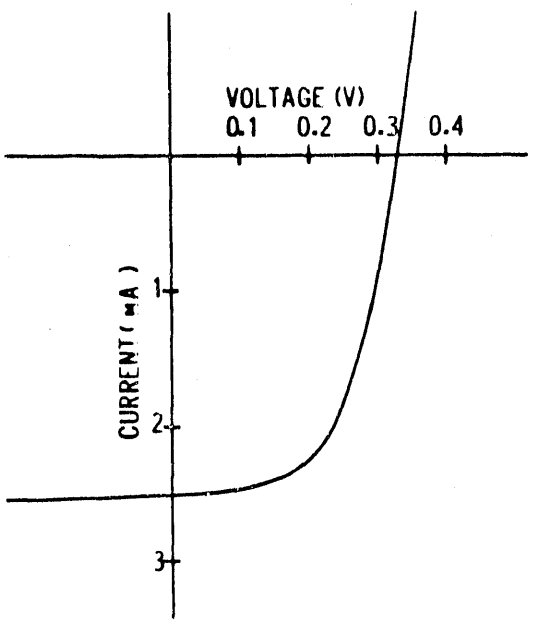
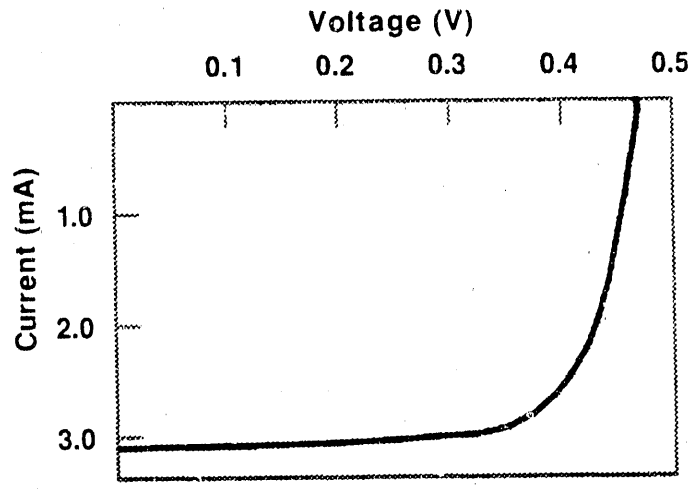


Fig. 7. Illuminated I-V characteristics of an ITO/CdZnS/CIS solar cell made by the two-stage process. A=0.08 cm^2, V_{oc}=0.332 V, J_{sc}=32.24 mA/cm^2, FF=56.91% and η=6.96%.

A solar cell was also prepared with a double-layer absorber structure similar to that of Boeing's. A resistively heated Mo boat was used in evaporating the Cu and In layers for this device which also employed an evaporated CdS layer. The cell parameters were measured under 100 mW/cm^2 ELH illumination. The V_{oc} (0.45 V) and the FF (63 %) values of this solar cell were quite good. However, the J_{sc} (25 mA/cm^2) value limited the active area efficiency of the device to 7%. Poor long wavelength response of this cell led us to believe that the break introduced into the film growth process for the purpose of simulating the double layer structure also caused a break in the grain structure of the material and effectively limited the current collection to the top 0.5-0.8μm of the absorber layer.

The illuminated I-V characteristics of one of the most efficient CIS solar cells prepared using thick, evaporated CdS layers is given in Fig. 8. This cell has the solar cell parameters of V_{oc} = 0.47 V, J_{sc} = 30.50 mA/cm^2, FF = 71.50 % and η = 10.26%. The active area efficiency of this device is 10.8 %. It should be noted that the current density values in cells with thick CdS window layers are rather low. Improvement of these values to over 35 mA/cm^2, which is our near term goal, will improve the efficiency to over 12 %.



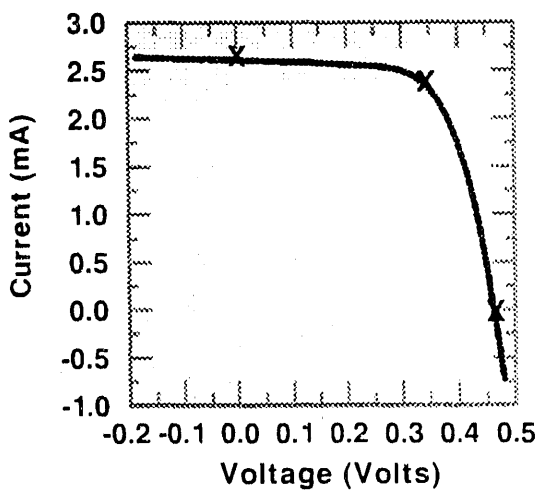
CdS / CIS / Mo / Glass
V_{OC} = 0.470 V
J_{SC} = 30.50 mA / cm^2
FF = 71.50%
Eff = 10.26%
Eff(Active Area) = 10.80%

Fig. 8. Illuminated I-V characteristics of a CIS cell (measured at ISET).

One way to improve the current density values in a CIS solar cell is to use more transparent window layer over the CIS film. The illuminated I-V characteristics of Fig. 9 belongs to a cell with an ITO/ZnO/CdS window layer [7] where the thickness of the CdS film was about 0.1μm. Thicknesses of the ZnO and ITO layers were 0.8 and 0.2μm respectively. The active area of

the device was only 0.075 cm^2 due to two large contacting pads along its two edges. The solar cell parameters of Fig. 9 are: V_{oc}= 0.4627 V, J_{sc}= 35.36 mA/cm^2, FF= 66.59% and η = 10.89% (active area). Another group of cells fabricated on a similarly prepared film has yielded devices with active area efficiency values of 10.47%, 10.68%, 10.74% and 10.74%. The external quantum efficiency of the cell of Fig. 9 is shown in Fig. 10. Good collection in the blue region of the spectra is due to the use of highly transparent CdS/ZnO/ITO window layer. Response at long wavelength region again extends to 1.3μm as expected from a CIS cell. Reduction of the CdS thickness below 1000Å is expected to further improve the short circuit current value. The best solar cell parameters observed during this period of research were; V_{oc} = 0.49 V, J_{sc} = 36.36 mA/cm^2 and FF = 71.59%. These results clearly demonstrate the near term potential of this very promising technology.

Although we have demonstrated high efficiency solar cells using both the evaporated and chemically deposited CdS layers, these devices were generally made on films with Cu-to-In ratios of close to 0.9. However, the influence of the CdS deposition process on the device behavior became pronounced when working with CIS films of near-stoichiometric compositions (Cu-to-In



ITO / ZnO / CdS / CIS / Mo / Glass
V_{oc} = 0.463 V
J_{sc} = 26.52 mA / cm^2
FF = 66.59%
Eff = 8.18%
Eff(Active Area) = 10.89%

Fig. 9. Illuminated I-V characteristics of a CIS cell (measured at SERI).

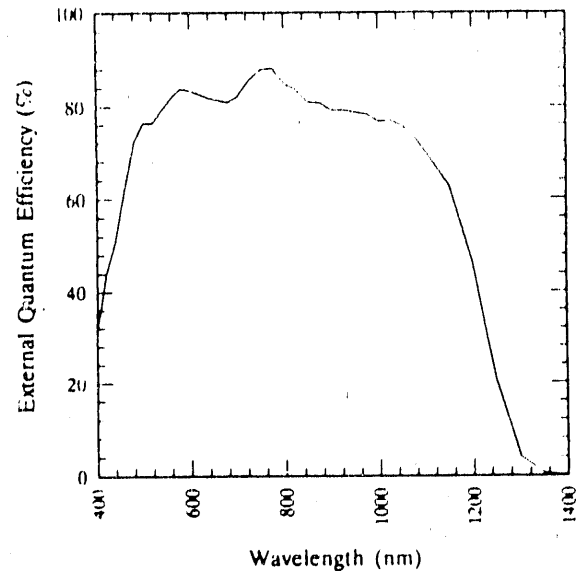


Fig. 10. Spectral response of the cell of Fig. 9.

ratios of about 0.97-1.00). Figure 11 shows the illuminated I-V characteristics obtained from two small area (0.1 cm^2) cells made on a CIS film with a Cu-to-In ratio of 0.97. Device A was processed by evaporating a two-layer CdS film (a 0.4μm thick undoped layer followed by a 1.6μm thick doped layer) on the CIS surface at 200°C. A 0.3μm thick CdS layer was chemically grown on the absorber surface of Device B before the evaporation of the two-layer CdS film. It is clear that the device with the chemically grown CdS inter-layer has a higher V_{oc} value and a better fill factor.

The Boeing group had previously reported the formation of Cu-rich nodules at the CdS/CIS interface when the CdS film was evaporated over near-stoichiometric, low-resistivity CIS surfaces. These nodules deteriorated the device performance. Formation of nodules was avoided by using a double-layer device structure where an In-rich CIS surface was provided at the CdS/CIS interface. A similar phenomenon may be responsible for the low V_{oc} and fill factor values in Device A of Fig. 11. The chemically deposited CdS film of Device B, on the other hand, may be acting as a shield protecting the CdS/CIS interface from the incoming Cd and S vapors during the evaporation of the top CdS layer. It should be noted that unlike the

evaporation technique which involves reaction of elemental Cd and S on the substrate surface which is heated to 200°C, the chemical dip method deposits a highly stoichiometric CdS compound film on the substrate at low temperatures (50-60°C).

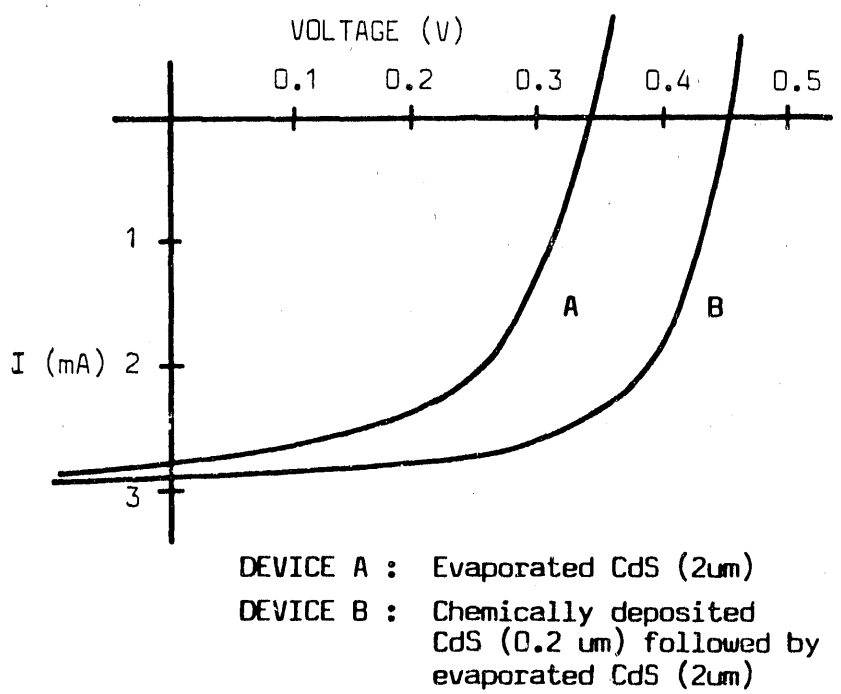


Fig. 11. Illuminated I-V characteristics of two CIS devices demonstrating the effect of the window layer on cell efficiency.

3.3.3. Submodule Fabrication Steps

Having achieved the deposition of up to 50 cm2 area CIS films that adhered well to their substrates we have started some preliminary experiments on the submodule fabrication steps. The submodule fabrication process consisted of 6 major steps (Fig. 12).

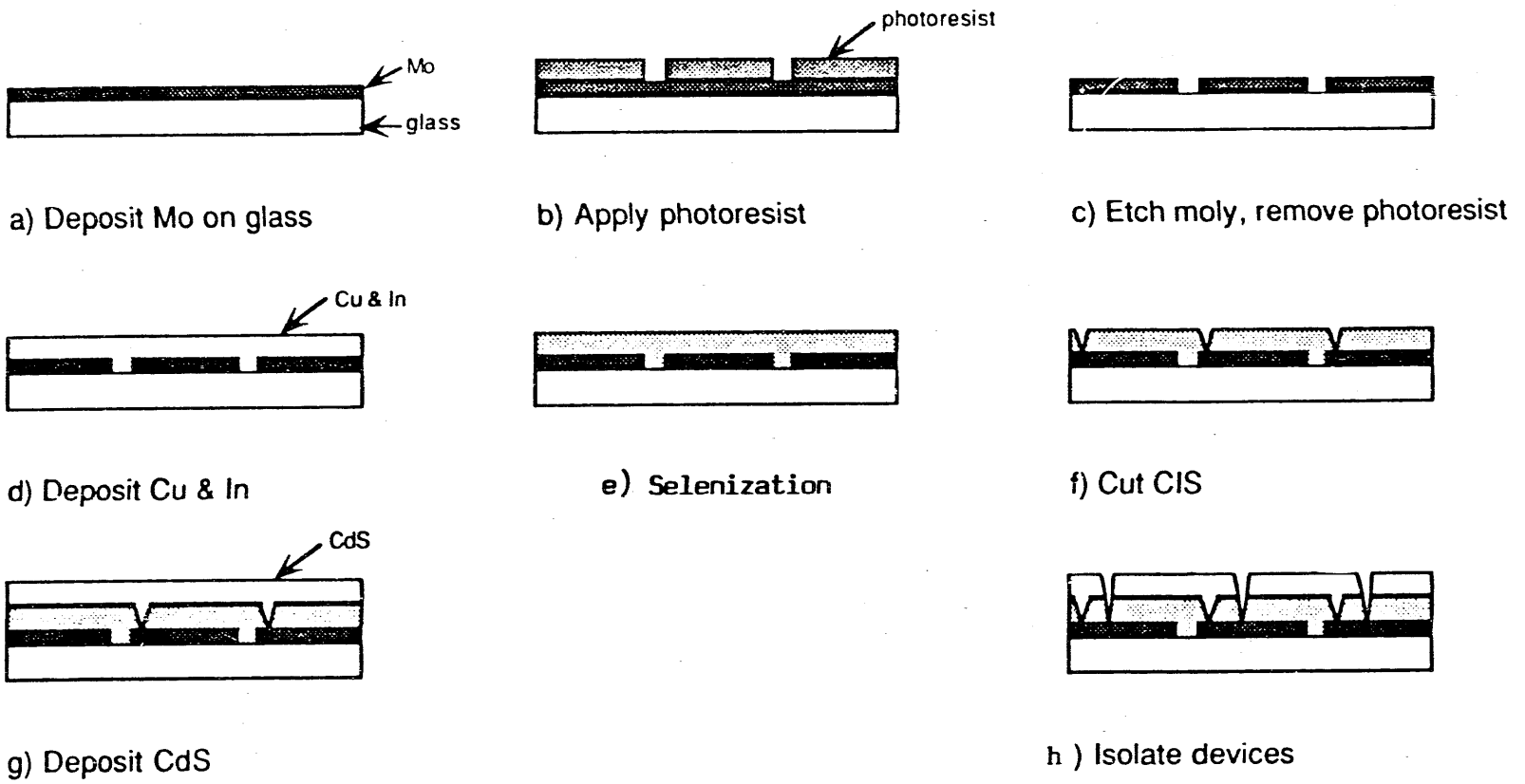


Fig. 12. Module integration steps.

These steps are:

a) substrate preparation
b) metals deposition
c) selenization
d) device interconnection scribe
e) CdS deposition
f) device isolation scribe

We will now briefly describe each step of the processing sequence.

Substrate preparation consisted of isolating discrete Mo pads on the glass substrate. In our work the Mo pads were isolated by first coating the cleaned Mo substrate (Fig. 12a) with Kodak 820 positive photo resist and exposing a pattern defining the layout of the pads (Fig. 12b). After the development of the resist the substrate was etched in a bath consisting of 50:25:25 H_2O:HCl:HNO_3 to remove the Mo strips from the exposed areas. The piece was then well rinsed and the resist was stripped from the part, leaving 0.25 or 0.5 cm-wide Mo pads isolated from each other by 3 mil wide isolation lines (Fig. 12c).

Metals deposition and selenization steps were carried out as explained before in this report. After the selenization step, prior to the deposition of the CdS layer, the CIS films along one edge of the isolated Mo pads were scribed to provide electrical interconnection between the adjacent cells. CdS layer was then coated all over the device. The last step of the process was the isolation of individual devices. This was accomplished using a fine carbide tip and forming another scribe mark parallel to the previous one (Fig. 12h).

Several small modules with areas of 20-50 cm2 were fabricated using these procedures and voltage addition in these units was demonstrated. One of these samples contained twenty interconnected cells of about 3.5 cm wide and 2.5 mm length and it gave an open circuit voltage of 8.8 V. The characteristics of these early cells were dominated by the high CdS resistance. Having demonstrated the feasibility of the module integration process, our future efforts will concentrate on the development of low resistivity TCO layers for these cells. As explained in Section 3.3.1 we have already initiated work on the deposition of low resistivity ZnO layers on small area devices. This work needs to be expanded to be able to coat low resistivity ZnO layers over large area submodules.

4.0 CONCLUSIONS

The two-stage process is a very promising and versatile technique for depositing polycrystalline thin films of I-III-VI_2 compounds for solar cell applications. In this work we have developed two approaches to the two-stage process. In the first approach, we have fabricated solar cells with active area efficiencies around 10% on films prepared by the selenization of electrodeposited Cu/In stacked layers. The evaporation/selenization approach which was developed in the second

half of the project has yielded devices with efficiencies approaching 11%. Further improvements especially in the short circuit current density values of these cells are expected to increase the conversion efficiencies to the 12-15% range in the near future. In our future work we will concentrate on the evaporation and sputtering techniques for the deposition of Cu-In precursors. Using the optimized selenization procedures we will fabricate high efficiency devices and large area (1 ft^2) modules.

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5.0 LIST OF PUBLICATIONS

1. V. K. Kapur, B. M. Basol and R. C. Kullberg, "High Efficiency Copper Ternary Thin Film Solar Cells," Annual Report on SERI Contract XL-7-06031-6, July 1989.

2. B. M. Basol and V. K. Kapur, "High Efficiency Copper Ternary Thin Film Solar Cells," Final Report on SERI Contract XL-7-06031-6, December 1990.

3. B. M. Basol and V. K. Kapur, "CIS Films and Solar Cells Obtained by Selenization of Evaporated Cu-In Layers," Appl. Phys. Lett., 54 (1989) 1918.

4. B. M. Basol, V. K. Kapur and R. C. Kullberg, "High Efficiency CIS Solar Cells Prepared by the Two-Stage Process," Solar Cells, 27 (1989) 299.

5. B. M. Basol and V. K. Kapur, "Deposition of CIS Films by a Two-Stage Process Utilizing E-Beam Evaporation," IEEE Trans. Electron. Dev., 37 (1990) 418.

6. V. K. Kapur and B. M. Basol, "Key Issues and Cost Estimates for the Fabrication of CIS PV Modules by the Two-Stage Process," Proc. 21st IEEE Photovoltaic Specialists Conf., 1990, p. 467.

7. B. M. Basol and V. K. Kapur, "CIS Thin Films and High Efficiency Solar Cells Obtained by Selenization of Metallic Layers," Proc. 21st IEEE Photovoltaic Specialists Conf., 1990, p. 546.

8. B. M. Basol and V. K. Kapur, "CdZnTe and CIS Films and Devices by a Two-Stage Process," Solar Cells, in press.

6.0 REFERENCES

1. V. K. Kapur, B. M. Basol and R. C. Kullberg, "High Efficiency Thin Film Solar Cells," Annual Report on SERI Contract XL-7-06031-6, July 1989.

2. B. M. Basol and V. K. Kapur, Appl. Phys. Lett., 54 (1989) 1918.

3. B. M. Basol, V. K. Kapur and R. C. Kullberg, Solar Cells, 27 (1989) 299.

4. B. M. Basol and V. K. Kapur, IEEE Trans. Electron. Dev., 37 (1990) 418.

5. B. M. Basol and V. K. Kapur, Proc. 21st IEEE Photovoltaic Specialists Conf., Florida, 1990, IEEE, New York, 1990, p. 546.

6. B. Dimmler, H. Dittrich and H.W. Schock, 20th IEEE PVSC, 1988, p. 1426.

7. TCO layers were provided by Dr. Robert Birkmire of IEC, University of Delaware.