

Novel Thin-Film CuInSe_2 Fabrication

Annual Subcontract Report 1 May 1991 – 30 April 1992

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PREFACE

This is an annual report of research carried out from May 1, 1991, to April 30, 1992, under subcontract No. XC-0-10012-1 to the University of Colorado, Boulder. The principal investigator is Allen Hermann, and Andrew Gabor is the co-investigator.

SUMMARY

Thin films of CuInSe_2 were formed by annealing precursor films containing Cu, In, and Se in a rapid thermal processor. These precursors were made by three-source coevaporation and by evaporating a sequence of elemental layers. Adhesion problems limited device performance, and the coevaporated precursors displayed unintended segregation of Cu and In in a direction normal to the film plane. The best cell efficiency was 3.5%.

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INTRODUCTION

The work performed under this subcontract involved a two step method for CIS formation. In the first step, a precursor containing Cu, In, and Se is deposited on unheated substrates such that CIS does not form during this deposition step. In the second step, the precursor is annealed in a rapid thermal processor to crystallize the CIS. Advantages of this process are: 1) no H_2Se is used; 2) concentration gradients can potentially be built into the film due to the rapid anneal; 3) the precursor can potentially be deposited using scalable methods such as sputtering, solution growth, and electrodeposition. Details of the apparatus are included the annual report covering the previous year's work.

The deposition method available to us was three-source, elemental physical vapor deposition. At the outset of the work, we considered such a method when done at room temperature to be a flexible way to deposit a precursor that would be fairly typical of precursors deposited by more scalable techniques. We have since found this assumption to be erroneous as is discussed below. Precursors were made both by the stacked elemental layer (SEL)¹ approach where one element at a time was evaporated, as well as by a co-evaporation method.

We also found problems in the adhesion of the films to the Mo-coated substrates during the anneal. Below, we shall discuss these adhesion problems and then address issues concerning the precursor composition and the anneal temperature. The last section of the report consists of a paper presented at the NREL 11th Photovoltaic Advanced Research & Development Review Meeting in Denver, May 13-15, 1992. This paper contains the quantitative results discussed in this report.

RESULTS and DISCUSSION

Adhesion

Most of the films experienced adhesion problems during the anneal. The source of the poor adhesion is related to mismatches in the coefficients of thermal expansion (CTEs) of the precursor films to the substrates. Soda-lime silica (SLS) glass and alumina (Al_2O_3) are the two substrates with which NREL has performed most of its CIS research, and they are well suited to CIS formation methods in which CIS is formed during heated deposition. The CTEs of these substrates are well matched to that of the CIS, and as the sample cools, both film and substrate shrink at about the same rate. However, in our method the precursor film may expand more than the substrate during the rise in temperature in the anneal. This can result in the film peeling off or bubbling.

The films adhered better to alumina than to glass, and as we moved into annealing co-evaporated precursors, we used alumina almost exclusively. This better adhesion can be explained through the rougher surface morphology of the alumina which gives the films more surface area to "grab" onto. The substrate cost is a very significant fraction of the total cost of thin film modules. SLS glass is much cheaper than alumina, and thus we intended to develop the process using alumina, but then later transfer the results back to glass substrates, perhaps textured or coated with an interfacial metal layers (Ga or Te) to increase adhesion. For this reason we kept most of the processing at temperatures $\leq 500^\circ\text{C}$ which is near the *anneal point* of the glass, the point beyond which its CTE increases greatly.

Adhesion with SEL precursors was found to depend on the order of the layers, with particularly poor adhesion resulting from a first layer of Se followed by a second layer of Cu.

In general, the faster the ramp rate during the rapid anneal, the worse the adhesion in films that experienced adhesion problems. This is reasonable since the faster the ramp rate, the less the diffusion and plastic deformation that can take place in the film to accommodate the stress. However, as we reduce the ramp rate, we veer away from the regime of rapid thermal annealing and thus lose the motivation of limited diffusion.

The best adhesion resulted from annealing codeposited precursors that were very In-rich. In has a very low melting point, and thus its presence in the precursor allows for stress relief during growth. Xray diffraction data showed no elemental crystalline In in the precursor, but free In might still have been present in amorphous form or in very small crystallites not detected by this method. Alternately, In-Se binaries might also aid in the stress relief. The relation between adhesion and film composition was further complicated by the Cu-In segregation found in codeposited precursors, as is discussed below.

Precursor

As determined by depth profiles of codeposited precursors performed by Auger spectroscopy, more Cu is found at the back of the films, and more In is found at the front. This is the case for films deposited with a constant Cu-to-In flux ratio throughout the duration of the deposition and is prior to any annealing. When we view the poorer adhesion found upon annealing precursors with higher overall Cu contents in light of this segregation, we conclude that were the In to be spread more evenly throughout the precursor, better adhesion may occur in all films. We discovered this segregation toward the end of the period of the contract, and thus we have not had sufficient time to investigate how we might better control precursor composition as a function of depth in the film.

One possible explanation for the segregation is that In is more likely to be selenized at room temperature. This leaves the Cu unbound, and because it is a fast diffuser, it is able to make its way to the back of the film. However, we do not currently have an explanation for why the Cu should diffuse to the back. If the Cu were also selenized during the deposition of the precursor, then its diffusion would be limited. Such Cu-Se binary formation is more likely to occur at higher substrate temperatures during deposition, and therefore the effect of substrate temperature on segregation should be explored.

Diffusion also occurs upon deposition for the SEL precursors. Auger depth profiling showed significant mixing of the "elemental" layers prior to any anneal. This runs contrary to the assumptions of another group which

investigated the laser annealing of SEL precursors also deposited by physical vapor deposition.²

These examples illustrate the need to understand the nature of the precursor. How the elements are distributed spatially and how they are bound may strongly affect adhesion, the reaction pathway toward CIS formation, and the final quality of the CIS and devices. Precursors made using other deposition techniques are likely to have different spatial distributions of the elements and likely to have the elements pre-reacted in different forms. Contact has been established with two other groups to supply us with precursors made by sputtering.

A precursor parameter that may be important and that has not yet been thoroughly explored is the effect of precursor Se content on final film quality. Precursors were generally made with some (>20%) Se in excess of what is needed to form CIS if all the Se were to react. Some methods³ of forming CIS from a precursor involve enclosing the precursor in a vessel prior to annealing. This creates a vapor pressure of Se around the film during the anneal. In our method, the Se is free to evaporate from the film. We have found that only a small amount of excess Se is needed in the precursor to form CIS, and any excess Se evaporates from the film during the anneal. However, the relation between the quality of the CIS and the precursor Se content is not clear. A CIS formation process such as three-source, heated coevaporation uses a higher Se flux than is necessary to just achieve CIS of the desired stoichiometry. The high Se flux contributes to good grain structure and morphology. It may be that higher precursor Se contents will also improve films made using our method, and we plan to investigate this variable in future work.

Temperature

As discussed above, even though most of the work was performed with alumina substrates which can withstand very high anneal temperatures, we chose to restrict the anneal range to $\leq 500^{\circ}\text{C}$. The grain sizes we achieved were small, and the grains did not have desired columnar structure.

It may in fact be unreasonable to expect rapid annealing to produce large grain CIS in this temperature regime. Formation techniques that involve heating during the entire duration of the deposition within this temperature

regime experience difficulty achieving such grains. In addition, a two minute anneal of a precursor with greatly segregated In and Cu compositions resulted in a fairly uniform film. So, if we are intending to use the process to retain compositional gradients, we may be limited to anneals times less than two minutes in which to form the CIS.

In the previous year of work on this subcontract, Mooney explored some higher anneal temperatures, as did Albin in his own investigations.⁴ They both found extremely large grain growth, in some cases > 100 μ m. These films were full of voids and secondary phases which prevented device fabrication, yet these results are still highly encouraging. Such exceptional grain sizes warrant the relaxation of the temperature constraint, and we plan to explore an extended temperature range in future work. If high quality devices can be made from these films, then perhaps low cost substrates can be developed which can withstand higher temperatures. Such a high temperature annealing method involves partial melting of the precursor film, and thus the recrystallization aspect of rapid annealing is explored rather than its diffusion limiting aspect.

Devices

Devices were made by evaporating the CdS heterojunction partner on the CIS. Top Al contacts were evaporated onto the CdS. The best devices were made from very In-rich codeposited films which did not exhibit any adhesion problems. Cell #C63/R296, one of the deliverable of the subcontract, had the best conversion efficiency of 3.5%. Cells with higher Cu contents generally had bubbles and/or cracks which resulted in very low shunt resistances. The best devices were made with films that were more In-rich than is usually considered optimal for devices, and if shunting problems can be overcome in films with higher Cu contents, better efficiencies may be expected. To make sure the shunting was not caused by conductive Cu₂Se paths in the film, we performed a NaCN etch on some samples which should remove any Cu₂Se. The film composition, as determined by electron probe microanalysis (EPMA) before and after the etch showed no changes. This implies that no Cu₂Se existed in the films.

Films formed from SEL precursors with layer orderings of:

Alumina/Mo/Cu/In/Se/Cu/In/Se/Cu/In/Se/Cu or

Alumina/Mo/In/Se/Cu/In/Se/Cu/In/Se/Cu

displayed only CIS peaks from the Xray diffraction characterization, but their morphologies were very rough and irregular. These cells were in general badly shunted. A typical set of layer thickness for the former structure was: 550Å for each Cu layer, 1925Å for each In layer, and 4200Å for each Se layer.

Other uses for rapid annealing:

- Introduction of impurities or alloys near the surface:

If a thin layer of an impurity or alloying element such as Al, Zn, Ga, or S is deposited on already formed CIS, a rapid anneal could be used to shallowly diffuse the layer into the CIS. By creating only a thin higher-bandgap layer near the heteroface, higher open circuit voltages may be obtained without significantly reducing short circuit currents. In addition, the defect chemistry of the CIS can be altered near the critical interface region.

- As a characterization tool:

We believe rapid annealing has much potential as a tool to characterize the evolution of the reactions between elemental and binary constituents in precursor films. The rapid thermal processor allows precise control of temperature ramp rates, soak temperatures, and soak times. We can thus take a precursor of known composition and crystallinity and stop the anneal at a succession of points along the pathway to complete reaction of constituents. By characterizing these partially annealed films using xray diffraction, we can see how reactions proceed. By annealing precursor films containing just two of the elemental constituents, we can possible compare the rates at which various binary reactions proceed. Such characterization will give us a better idea about pathways toward CIS formation and will allow us to design better precursors.

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CuInSe₂ THIN FILM FORMATION BY RAPID ANNEALING OF THE ELEMENTAL PRECURSOR

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ABSTRACT

Cu, In, and Se were coevaporated onto unheated Mo-coated substrates of glass and Al₂O₃. Cu and In partially segregated in these precursors in a direction normal to the film plane. The precursors were annealed in a rapid thermal processor to form CuInSe₂ (CIS). The films adhered better to the Al₂O₃ than to the glass upon annealing. Solar cells were made by evaporating CdS and top contacts onto the CIS. The best cell had an efficiency of 3.5% and was obtained after annealing the as-fabricated device in air.

INTRODUCTION

Solar modules based on polycrystalline thin films of CIS have emerged as a leading candidate for low cost photovoltaic energy production, and CIS/CdS/ZnO heterojunction solar cells have been demonstrated with efficiencies approaching 15%.^{1,2} For the industrial production of solar modules, CIS device fabrication methods are needed that produce high quality material and that are low-cost and scalable to large-area deposition with high throughput. A wide variety of formation techniques have been explored, and one of the most successful involves the selenization of a precursor film of Cu and In using the gas H₂Se.^{3,4} Although this process is scalable for industrial production, safety and cost-related concerns exist over the use of this highly toxic gas. These concerns provide incentive to develop techniques that do not involve H₂Se.⁵

Another desired characteristic of a formation process is that it be able to control composition as a function of depth normal to the film plane. One measure of the composition is the Cu-to-In atomic ratio or film *molecularity*, defined as $X=[Cu]/[In]$. The type and magnitude of the conductivity in a film region, as well as the grain size, are strongly influenced by this parameter, and junction parameters such as junction position and space charge width are related to these conductivities. For example, it may be desirable to have type inversion of the CIS near the heteroface for enhanced device performance.⁶ This can be accomplished by creating a layer that is very In-rich. Also, alloyed films have been made

with metals such as Ga, Al, or Zn to form a higher band-gap material within the space charge region, which may increase the open-circuit voltage.⁷ If the depth of the alloyed region can be limited, then the rest of the film will remain at a lower band gap and will be able to absorb lower energy photons.

Deposition processes or post-deposition treatments that involve long annealing periods at high temperatures will tend to result in diffusion toward an equilibrium state where any concentration gradients in the film are smoothed out. Rapid thermal annealing (RTA) is a technique developed in the semiconductor wafer processing industry, where annealing is desired without significant diffusion.⁸ Our goal is to form high-quality CIS and alloyed CIS with concentration gradients using RTA.

The current work entails forming the CIS from a precursor containing Cu, In, and Se. Later work will involve taking an already crystallized CIS film, depositing a thin layer of an alloying metal on top, and then using RTA to alloy the metal with the CIS with minimal diffusion. Before intentionally introducing compositional gradients into the films, we chose to look at the CIS formation from a precursor that was deposited with a constant Cu-to-In flux ratio throughout the deposition.

Although the technique of coevaporation may not be desirable on an industrial scale, it is convenient at the experimental level, and we chose this method to form the precursors as a proof of principal. Slow coevaporation upon a high temperature substrate is another primary method of forming high quality CIS, and previous work has been done with rapid annealing a precursor coevaporated at an intermediate substrate temperature.⁹ For this work, we chose to evaporate on an unheated substrate to minimize binary and ternary crystalline formation during deposition so that the overall technique would be more applicable to a general type of precursor.

EXPERIMENTAL PROCEDURE

Two different substrates were tried: soda-lime-silica (SLS) glass and alumina (Al_2O_3), both coated with Mo as a back contact. The elements were evaporated onto these substrates from separate, resistively heated boats within a bell jar vacuum system. The resulting films were generally $>2 \mu\text{m}$ thick. The Cu and In rates were monitored using electron impact emission spectroscopy (EIES), and the Se rate was monitored using a quartz-crystal oscillator. Each elemental rate was kept constant throughout a specific deposition, with a typical In rate of $4.4 \text{ \AA}/\text{s}$. Cu rates were varied for different films to give $0.87 < X < 1.01$ for the precursors.

Excess Se was incorporated into the precursor films to allow for Se evaporation during annealing. A measure of the excess or deficiency of anions to cations in the films is usually examined by means of the *valence*

stoichiometry variable: $Z = \frac{2[\text{Se}]}{[\text{Cu}] + 3[\text{In}]}$, and in our case the excess Se typically resulted in precursors with $Z > 1.2$.

Following the deposition, the precursors were exposed to air and were placed in an *AET Addax RX* rapid thermal processor for annealing. The samples were placed on a silicon wafer, film side up, and a thermocouple was placed on the film. The chamber was then purged with Ar. The sample was heated from below by infrared lamps that were computer controlled by feedback from the thermocouple.

Annealing parameters that could be varied include the temperature ramp rate, the final annealing temperature, and the annealing time at the final temperature. Ramp rates were varied from 100° to 1°C/s, the final anneal temperature was typically around 500°C, and the final annealing time varied from 30 s to several minutes.

The films were examined using scanning electron microscopy (SEM) for structural characterization, X-ray diffractometry for crystalline characterization, and electron microprobe spectroscopy for compositional analysis.

Devices were made from some annealed samples by evaporating 0.4 μm of intrinsic CdS onto the CIS, followed by 1.25 μm of In-doped CdS. Top aluminum contacts were deposited using physical vapor deposition through a mask. Separate devices were defined on each sample using photolithography.

RESULTS

Films deposited on Mo-coated SLS glass substrates peeled or bubbled upon annealing. The films adhered much better to Mo-coated alumina, and therefore we chose to deposit most of the films on these substrates. Alumina can withstand much higher temperatures than can glass, but we chose to keep the processing temperature below the strain point of the glass so that a modified process could later be applied to glass, which is significantly cheaper than alumina. Bubbling still persisted with the alumina in many cases, although on a much smaller scale. In general, the bubbling was worse with higher Cu contents (higher X) and with faster ramp rates.

Figure 1 shows SEM cross-section micrographs of annealed films with three different molecularities: $X \approx 0.87$, 0.94, and 1.01 for samples (a), (b), and (c), respectively. These films were ramped at 100°C/s to 500°C, where they remained for two minutes. Sample (a) exhibited no apparent adhesion problems, while the other two films both showed bubbling. The sample with $X \approx 0.94$ was also annealed with a ramp rate of 10°C/s, and Fig. 2 clearly shows the reduced bubbling resulting from this slower ramp rate.

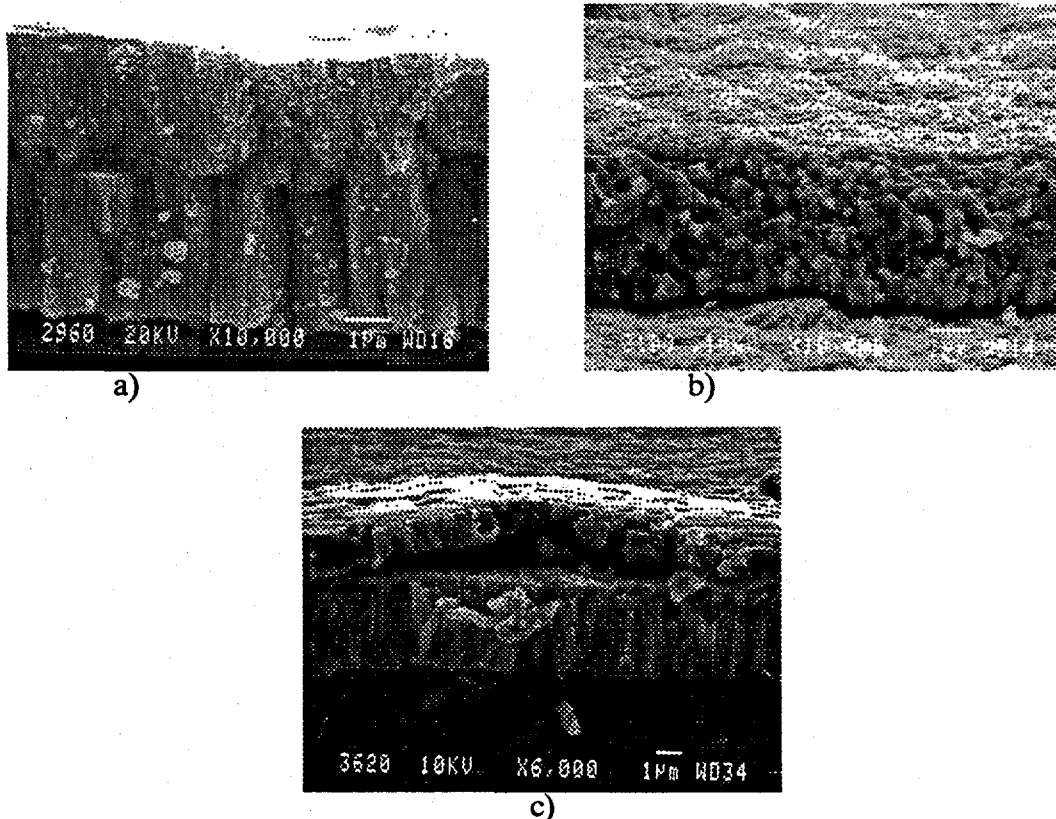


Fig. 1. SEM micrographs of the film cross-sections. (a) x10k, $X=0.87$: both Mo and CIS are visible, with the CIS on top. (b) x10k, $X=0.94$: just the CIS cross-section is visible. (c) x6k, $X=1.01$: an example of a bubble in the CIS film on top of the Mo.

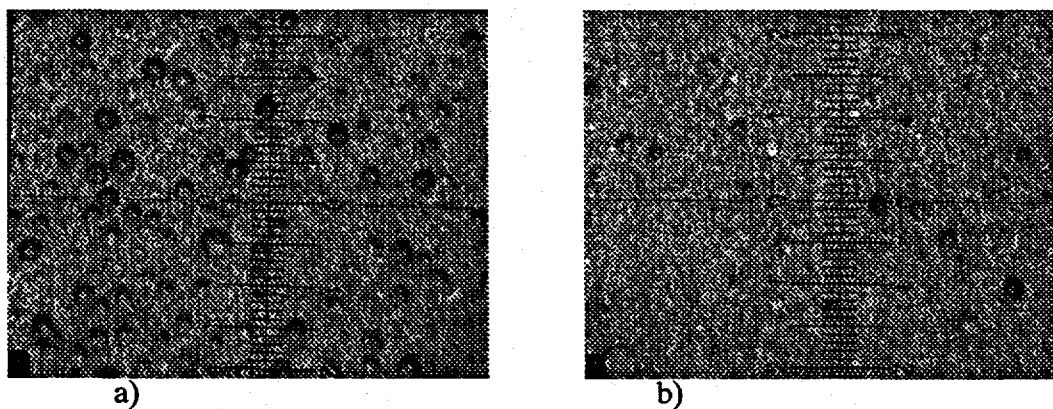


Fig. 2. Optical micrographs of the film surface for $X=0.94$. Each small tick=5 µm. (a) ramped at 100°C/s, (b) ramped at 10°C/s

Figure 3 shows the X-ray diffraction pattern of a precursor and an annealed sample with $X=0.87$. The precursor exhibits no crystalline peaks other than those for the substrate and back contact. However, upon annealing, the crystalline CIS peaks emerge.

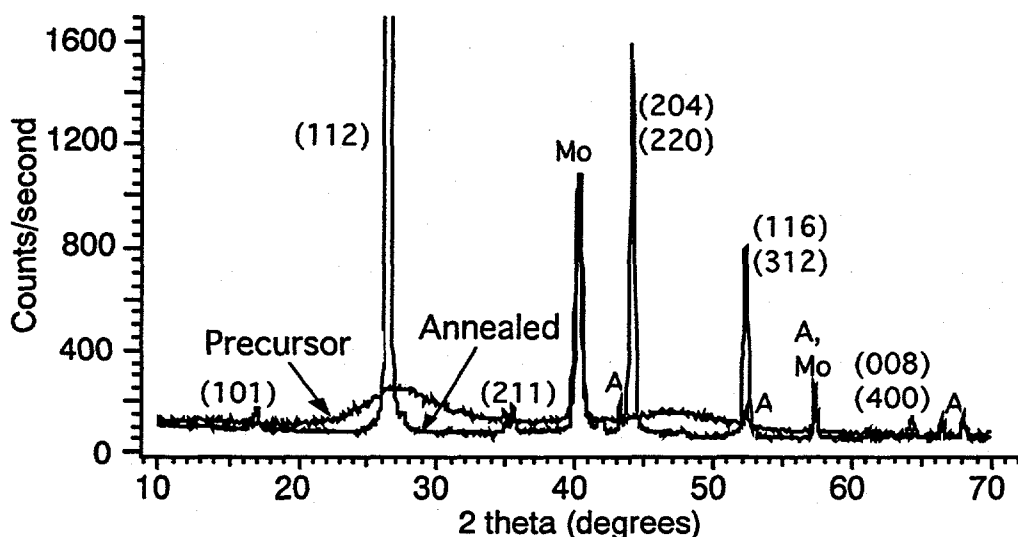


Fig. 3. X-ray diffraction pattern of a film as-deposited and annealed. The alumina peaks are labeled with an "A".

A current vs. voltage (I-V) curve of the best device is shown in Fig. 4. This device was made from sample (a) of Fig. 1. As fabricated, the device had an efficiency of <1% and a very low open-circuit voltage and shunt resistance; however, after annealing the device in air at 200°C for two hours, the device efficiency increased to the shown value. Further air annealing caused a slight decrease in the short-circuit current, which resulted in a slightly lower efficiency. Devices made from films with higher values of X were of poorer quality and had very low shunt resistances, even after an air anneal. This shunting was most likely related

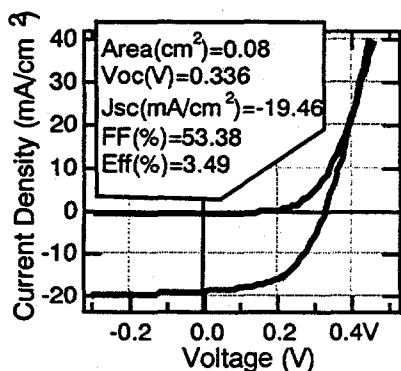


Fig. 4. I-V curve for a device made from a film with $X \approx 0.87$. The device was annealed in air at 200°C for two hours.

to cracking in the films from adhesion problems.

To see whether the annealed sample had uniform composition as a function of depth in the film, we had a depth profile performed on a precursor and an annealed sample using Auger electron spectroscopy in combination with ion beam sputtering. We were surprised to find that the precursor was far from uniform. As shown in Fig. 5, significantly more In than Cu is found in the front of the film, while

the reverse is true in the back. This was quite unexpected because each elemental rate was held constant during the deposition process. Upon annealing for two minutes, the film became fairly uniform.

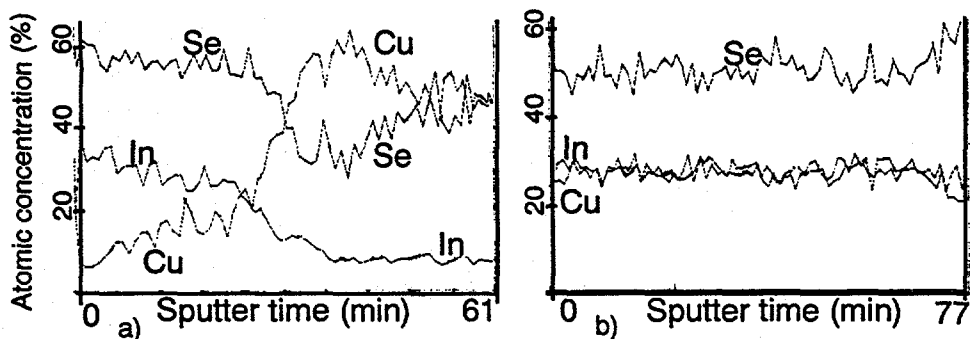


Fig. 5. Depth profiles of (a) precursor and (b) annealed samples. The horizontal axis is sputter time or, equivalently, depth in the film. The vertical scale is approximate atomic concentration and is meant to give a qualitative indication of composition.

DISCUSSION

The better film adhesion to alumina than to SLS glass upon annealing cannot be explained in terms of differences in coefficients of thermal expansion (CTE) because these two materials have very similar CTE values. The main factor is most likely the roughness of the substrate, for the alumina is much rougher than the glass. Thus, it may be possible to texture the glass surface and achieve better adhesion with this cheaper substrate material.

In a process like heated three-source evaporation, where the CIS formation occurs upon deposition at high temperature, the CIS and substrate shrink at about the same rate during cooling because they have very similar CTEs. In our process we deposit at room temperature and then raise the temperature during the post deposition anneal. Cu has a much higher CTE than that of the substrate; therefore, heating a film of Cu would result in much compressional stress in the film. In has a very low melting temperature and consequently can readily deform and contribute to stress relief during the anneal. This is consistent with the better adhesion found upon annealing precursors with lower X . Perhaps, if the precursors exhibited less separation of the Cu and In, good adhesion would result even in films with higher X . Also, better adhesion might result from incorporating an interfacial metal layer between the Mo and CIS.¹⁰

Other CIS formation techniques generally achieve better device efficiencies at values of X around 0.95.¹¹ If we can solve the adhesion problems at such higher values of X , we may expect to see higher efficiencies than those achieved so far with the lower X values.

Future work will include attempts to make a more uniform precursor using coevaporation. Variables to explore include substrate temperature during deposition, overall deposition rates, and individual elemental fluxes as a function of time during the deposition. Another important

parameter to explore is the effect of precursor Se content on final film quality. In addition, we plan to look at annealing precursor films deposited by sputtering, which is a more scalable deposition technique and may not produce the Cu and In separation.

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16. Abstract (Limit: 200 words) This report describes work to form thin films of CuInSe ₂ (CIS) by annealing precursor films containing Cu, In, and Se in a rapid thermal processor. This involves two steps: (1) a precursor containing Cu, In, and Se is deposited on unheated substrates such that CIS does not form during this deposition step, and (2) the precursor is annealed in a rapid thermal processor to crystallize the CIS. Advantages of this process are that (1) no H ₂ Se is used; (2) concentration gradients can potentially be built into the film due to the rapid anneal; and (3) the precursor can potentially be deposited using scalable methods such as sputtering, solution growth, and electrodeposition. The deposition method used was three-source, elemental physical vapor deposition. At room temperature, such a method was considered to be a flexible way to deposit a precursor that would be fairly typical of precursors deposited by more scalable techniques. Precursors were made both by the stacked elemental layer approach, where one element at a time was evaporated, as well as by a co-evaporation method. Adhesion problems limited device performance, and the co-evaporated precursors displayed unintended segregation of Cu and In in a direction normal to the film plane. The best cell efficiency was 3.5%.			
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