

# DEPOSITION OF $\text{CuInAlSe}_2$ FILMS USING CO-SPUTTERED PRECURSORS AND SELENIZATION

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## ABSTRACT

$\text{CuInAl}$  precursor films with varying  $\text{Al}/(\text{Al}+\text{In})$  ratios were co-sputtered onto Mo coated soda-lime glass substrates. Samples were then selenized under high vacuum using thermally evaporated elemental selenium. Single-step and two-step selenization heating profiles were investigated. Single-step samples resulted in better Mo- $\text{CuInAlSe}_2$  adhesion than those selenized using the two-step approach. Precursor and selenized films were characterized for composition, crystalline structure, surface morphology, and composition with depth. The development of a method to co-sputtered  $\text{CuInAl}$  precursors is discussed, as well as the effect of selenization temperature and heating profile on selenized film properties.

## INTRODUCTION

Much of the work on Cu-chalcopyrite absorber materials has been focused on  $\text{CuInGaSe}_2$  (CIGS). In these films Ga is substituted for In in the  $\text{CuInSe}_2$  lattice to increase the band gap ( $E_g$ ) from  $\sim 1$  eV ( $\text{CuInSe}_2$ ) to as high as  $\sim 1.7$  eV ( $\text{CuGaSe}_2$ ). Theoretically an absorber layer with an  $E_g$  of  $\sim 1.4$  eV would give the highest efficiency for a single junction device, however high efficiency CIGS are limited to an  $E_g$  of  $\sim 1.15$  eV [1,2]. This equates to a  $\text{Ga}/(\text{Ga}+\text{In})$  ratio of  $\sim 0.3$ . As more Ga is introduced beyond this point device efficiencies decrease, presumably as a result of defects which degrade the electronic properties of the films [3, 4, 5].

Aluminum can be used as an alternative to gallium to increase the absorber  $E_g$ .  $\text{CuInAlSe}_2$  (CIAS) films have a  $E_g$  range of  $\sim 1$  eV ( $\text{CuInSe}_2$ ) to  $\sim 2.7$  eV ( $\text{CuAlSe}_2$ ). A CIAS film would require less than half the Al substitution for In as Ga would be needed in CIGS to produce the same band gap film. This means reduced lattice deformation in CIAS, which may result in fewer defects associated with higher  $E_g$  films [6].

Record CIAS lab scale efficiency of 16.9% has been obtained using a co-evaporation process [6]. An alternative method to co-evaporation that has produced device quality Cu-chalcopyrite films is sequential or co-sputtering of metal precursors, followed by selenization in a selenium atmosphere [7,8]. Of the two sputtering methods, co-sputtering allows for better compositional depth uniformity through control of metal precursor deposition conditions. This process is believed to be easier to scale up to a high throughput-manufacturing environment where monolithic modules must be uniform

in thickness and composition over large deposition areas.

Potential applications for CIAS include both single and multi-junction devices. A  $\text{CuInSe}_2$  bottom absorber, combined with one or two CIAS absorbers of wider  $E_g$ 's would be ideal for space applications where the inherent radiation resistance of the chalcopyrite structure, along with the high specific power (W/kg) of a thin film multi-junction cell would be desired.

In our approach, precursor films are co-sputtered from Cu, In, and Al targets, and then selenized in a one or two-step heating process using thermally evaporated elemental selenium. This paper will discuss the results of different co-sputtered precursor deposition parameters on their film properties, as well as the characteristics of selenized films under different heating conditions.

## EXPERIMENTAL

### Precursor Deposition

Precursor films for this work were deposited on 1" x 3" Mo coated soda-lime glass substrates. Mo films were deposited by DC magnetron sputtering to a thickness of  $\sim 1$   $\mu\text{m}$ .  $\text{CuInAl}$  films were deposited by co-sputtering from Cu, In, and Al targets in a con-focal arrangement to a thickness range of 1-1.5  $\mu\text{m}$ . The Cu gun was on for the entire deposition, while the In and Al guns were on for varying times depending on the desired film composition. A typical deposition sequence is shown in Fig. 1. Fine-tuning of film composition was accomplished by adjusting the power density ( $\text{W}/\text{cm}^2$ ) of the In and Al targets while maintaining the Cu gun at a fixed setting.

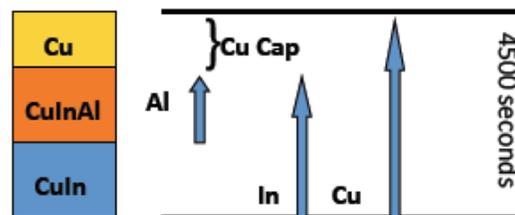


Fig. 1. Schematic of a typical precursor deposition

It has been shown previously that indium tends to be mobile during sputtering, depositing in a vapor $\rightarrow$ liquid $\rightarrow$ crystalline sequence at or above room temperature forming indium rich islands at the surface of films [7]. It is also known that In-Se reactions occur at

much lower temperatures than any Al-Se reaction [9]. To counteract early In-Se/CIS formation which would phase separate the film a deposition scheme was created to favor an Al rich surface, and minimize the diffusion of In towards that surface. Also, due to the presence of Al a capping layer of Cu was used to avoid the formation of Al<sub>2</sub>O<sub>3</sub>. Depositions began with Cu and In to create an In-rich base. The Al gun was then turned on part way through the process, and films were finished by turning both In and Al guns off and sputtering a Cu capping layer to a thickness of ~20 nm or ~ 100nm.

Table 1 shows the desired precursor film compositions. A slightly Cu poor film is needed for p-type conductivity [5]. The Al/(Al+In) ratio was varied in order to study the effect of increasing Al content on selenized film properties. The approximate E<sub>g</sub> of each film was calculated assuming a linear relationship between Al/(Al+In) ratio and E<sub>g</sub>.

	E <sub>g</sub>	Cu (at. %)	In (at. %)	Al (at. %)
<b>Target 1</b>	~1.15	46-49	46-49	3-5
<b>Target 2</b>	~1.4	46-49	38-41	11-13
<b>Target 3</b>	~1.7	46-49	30-33	19-21

Table 1. Target precursor film compositions.

### Selenization of Co-sputtered Precursors

Selenization of precursor films was performed in a thermal evaporation chamber with a based pressure of 1 x 10<sup>-6</sup> Torr. Elemental selenium was provided from a box source, and the deposition rate was held constant at 4 Å/sec through closed-loop feedback with a quartz crystal monitor. The temperature ramp rate was maintained at ~50°C/min for all heating steps.

Two different selenization heating profiles were used. In the one-step procedure only a high temperature step was used at either 450°C or 500°C for 40 minutes. The two-step heating profile consisted of a low-temperature step at 350°C for 20 minutes to partially react the film, followed by a high temperature step at either 450°C or 500°C for 20 minutes.

Precursor and selenized films were characterized for surface and cross-sectional morphology using a Carl Zeiss 1550 Schottky source electron microscope (SEM) operating at 15 KV. A Scintag x-ray diffractometer (XRD) with a Cu K $\alpha$  source, and the JCPDS database were used to determine crystalline phases in the selenized films. Bulk film composition was determined using electron probe microanalysis (EPMA) in a JEOL 8600 Superprobe. Accelerating voltages of 15 KV and 20 KV were used for precursor and selenized films respectively. A Physical Electronics 15-100B Auger electron microscope (AES) operating at 5 KV was used to measure compositional depth profiles.

## RESULTS AND DISCUSSION

### Precursor Films

Table 2 shows the average composition of deposited precursors measured by EPMA. All films were within the error ( $\pm$  5%) of the desired composition.

	Cu (at. %)	In (at. %)	Al (at. %)
<b>Target 1</b>	48	49	3
<b>Target 2</b>	48	40	12
<b>Target 3</b>	49	33	18

Table 2. Average precursor composition.

SEM images and AES depth profiles of two Target 3 films, with different thickness Cu capping layers can be seen in Fig. 2. Films with a thinner capping layer consistently showed small agglomerations uniformly distributed over the surface of the film. This was found in all films regardless of composition. AES depth profiles confirmed this material to be a Cu-In rich surface. AES also shows that Al diffuses towards the Mo as In diffuses towards the top surface. A small amount of Al appears to be very close to the surface in these films as well, which may have resulted in oxidation.

Thicker Cu capping layers resulted in a large decrease in surface indium for the majority of samples. Islands were found to be In-rich, consistent with previous CIGS work, whereas the smooth background is Cu [10]. The data shows the combination of a thicker Cu cap and the earlier Al deposition seem to limit the diffusion of indium towards the surface, as well as minimize the chance of Al being exposed to atmosphere. This effect was most pronounced in Target 3 films where In is sputtered for a shorter time period, making the cap a combination of Cu-Al followed by Cu.

### Selenized Films

#### Adhesion Issues

Both the one and two-step selenizations produced CIAS films according to XRD results (Fig. 3). However, the adhesion to the Mo back contact was found to be much worse with the two-step process for all but the lowest Al content films. For the two-step samples pits or flaking occurred during the selenization process, during cleaving for sample analysis, or during the CdS chemical bath used post-selenization. Although the 2-step approach has been used successfully for the depositions of CIS and CIGS films, it appears that the formation mechanism is not ideal for CIAS [8,11]. The incorporation of Al into films does not occur until temperatures greater than 400°C, whereas CIS should begin forming slightly above the melting point of Se [9]. This likely resulted in a top layer of CIS completely separated from the Al. As In diffused towards the surface, Al would have been forced towards the Mo back contact during the low temperature step. The limited time period for the high temperature step would have resulted in little Al diffusing into the CIS structure. Resulting films are either highly phase segregated, or have an un-reacted Al layer underlying the

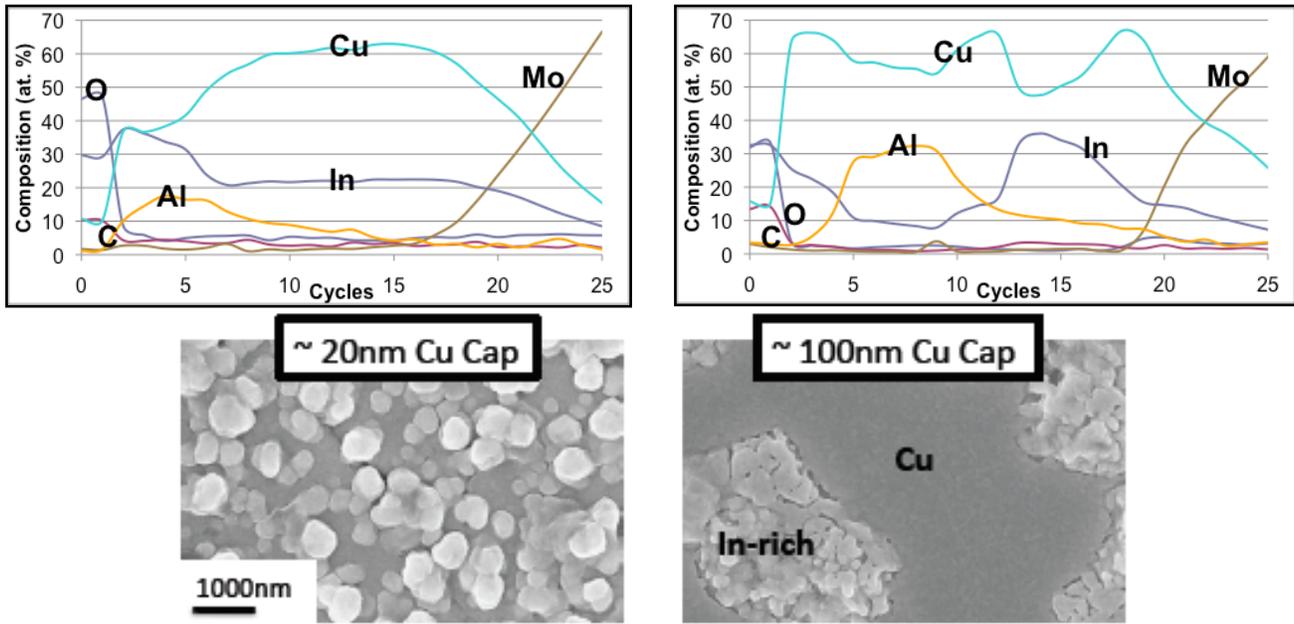


Fig. 2. AES depth profiles and SEM top-view images of Target 3 precursor films with different thickness Cu capping layers.

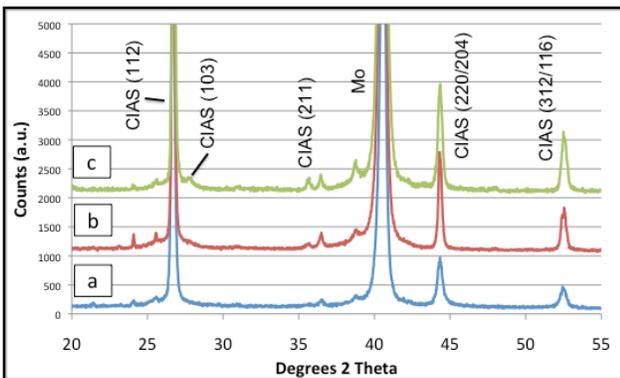


Fig. 3. XRD spectra of selenized Target 3 films. Selenization conditions are; 450°C two-step (a), 450°C one-step (b), 500°C one-step (c).

top CIS layer resulting in poor film adhesion.

The following characterization was obtained from single heating step selenized films.

### Characterization of Selenized Films

SEM top-view images are shown in Fig. 4. There appears to be a variation in grain size between samples, which is most likely due to small variations of Cu in the films, or degree of selenization. Films selenized at 500°C also appear less dense than those selenized at 450°C. When films were analyzed for composition it was found that samples selenized at 450°C had ~46-48% Se, while those heated at 500°C were only ~45-46% Se. This is likely a result of increased selenium re-evaporation from

the surface at higher temperature before incorporation into the film. The dependence of Se on film density has been observed in previous studies of CIGS as well [12]. Both films require either a faster Se evaporation rate, or longer reaction time.

AES data of a Target 2 film (Fig. 5) reveals that the Al appears to have moved towards the back contact as well as oxidized to a degree. This is seen in all samples at both temperatures, and both capping layer thicknesses. This explains the apparent lack of Al, and abundance of In in EPMA composition measurements in Fig. 4. The Al-K $\alpha$  x-ray has an energy of ~1.49 eV. These x-rays are only capable of escaping from a depth of ~500 nm, while the actual depth in the sample is > 1000nm. Since none of the Al is being measured the composition is biased towards the In-rich surface.

The source of this oxygen in the film is still under investigation. Since only surface oxidation is seen in the precursor films with thicker capping layers it is unlikely the Al was oxidized pre-selenization. The XRD results in Figure 3 show additional unlabeled peaks in selenized films. These were found to be Al and Cu-Al phases. This was only observed in Target 2 and 3 films, indicating unreacted film remained post-selenization at the higher Al compositions. If Al has all separated towards the back contact, and XRD results indicate not all Al has incorporated into the stable chalcopyrite structure, it is likely this oxygen could have incorporated post deposition. Either upon initial exposure to atmosphere, during characterization, or possibly during depth profile sputtering. The third seems less likely as the AES system is kept at  $10^{-8}$  -  $10^{-9}$  Torr, and oxygen is the first element scanned after sputtering. Another possible source is the selenization process itself, where during heating all surfaces in the chamber outgas water. Oxygen would

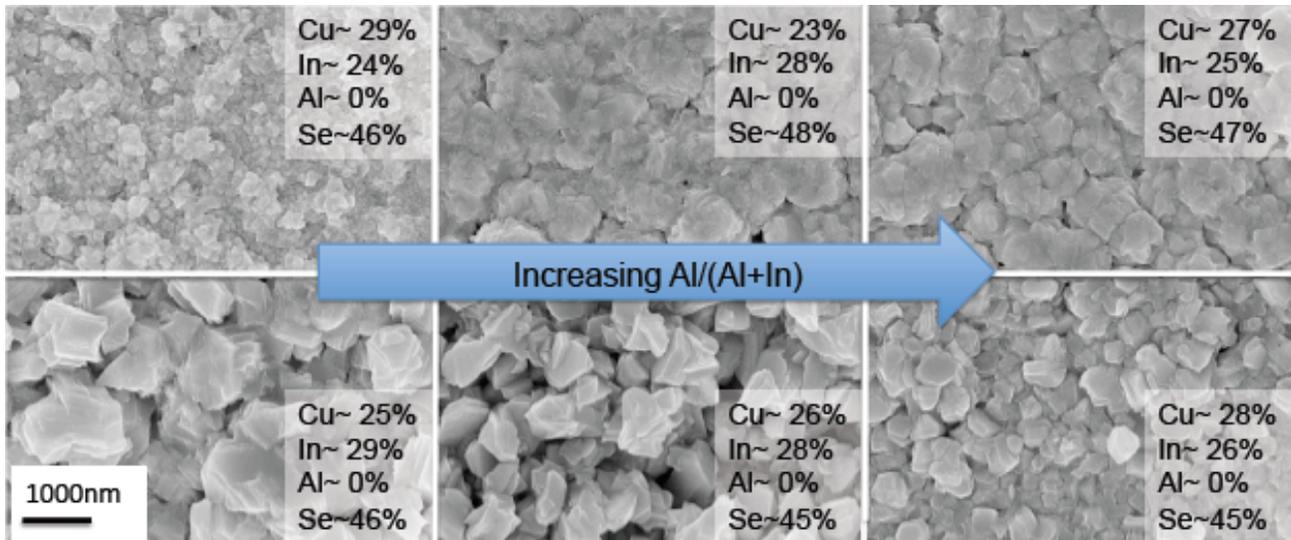


Fig. 4: Top-view SEM images of selenized films and their corresponding compositions. Film thicknesses are all in the range of 1.5-2.5  $\mu\text{m}$ .

then have to diffuse through the film to interact with the Al. It is also possible there is oxygen diffusion up through the Mo layer [13]. The Mo is kept under vacuum post-deposition so  $\text{MoO}_x$  is unlikely to be the source.

The above results suggest there are still improvements to be made to the selenization process before device quality films are produced. More experiments are being performed to determine if Al can be incorporated into the film without oxidation through a higher temperature or longer anneal, and how film properties are affected by higher Se evaporation rate.

Devices have been finished with CdS,  $\text{i-ZnO}$ ,  $\text{ZnO:Al}$ , Ni/Al grids. For the Target 1 CIAS film composition, 5.2 % device efficiency has been recorded under AM1.5 illumination. More work is underway to correlate film properties to device performance.

## CONCLUSIONS

$\text{CuInAlSe}_2$  films have been deposited through a two-step process using co-sputtered precursors followed by selenization. The co-sputtering process has been developed to produce slightly Cu poor precursors, limit Al exposure to atmosphere, as well as allow control over the compositional depth uniformity of metal precursor films.

These precursors have been selenized using elemental selenium vapor in a single-step and a two-step selenization procedure. Results indicate CIAS films can be produced with both methods, however adhesive losses occur with the two-step approach due to the separation of CIS and Al during the selenization process.

Analysis of the one-step selenized CIAS films indicates compositions become more Se poor as reaction temperature is increased indicating the need for longer selenization time, or increased Se evaporation rate. AES depth profiles show Al grading towards the back contact

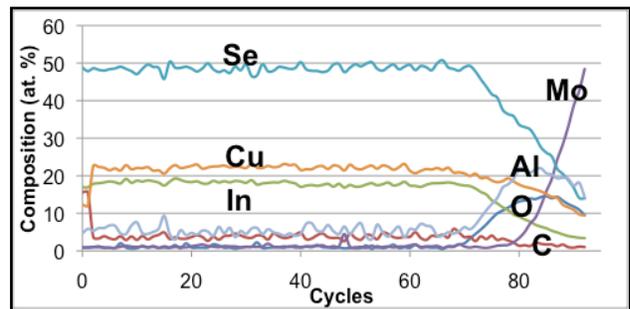


Fig. 5. AES depth profile of a Target 2 film.

as well partial oxidation of the Al.

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