

Post-Deposition Sulfur Incorporation into CuInSe₂ Thin Films

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ABSTRACT

The effect of initial film composition and substrate in the sulfurization of CuInSe₂ was investigated. CuInSe₂ films deposited on either soda-lime glass (SL) or Corning 7059[®] borosilicate glass (7059) substrates were reacted in flowing H₂S for times from 1 to 8 hours. Films with Cu-rich composition, Cu/In > 1, reacted for 1 hour had nearly all the Se replaced by S. For Cu-poor films the incorporation of S was significantly reduced. In addition, in Cu-poor films on SL glass CuInS₂ and NaInS₂ were found at the film surface. These phases were not detected in films on 7059 substrates or in Cu-rich films. A phenomenological model is proposed to explain the formation of segregated surface phases in Cu-poor films on SL substrates.

INTRODUCTION

A graded band gap absorber layer could be used to increase the voltage obtained with Cu(In,Ga)Se₂ based solar cells by reducing the recombination current in the space charge region while leaving carrier generation and collection relatively unaffected [1,2]. A Cu(In,Ga)(Se,S)₂ film that has a higher S content near its surface is such a structure.

The incorporation of S in a Cu(In,Ga)Se₂ film has been shown to depend on the composition and structure of the film. With greater than 25% Cu in the film, the rate of S incorporation increases during co-evaporation of the elements [3] or post-deposition sulfurization of Cu(In,Ga)Se₂ [4]. In addition, films with small grains take up S faster than films with large grains [4,5]. In Cu-rich CuInSe₂ films on SL substrates, S incorporation has been quantitatively described as a combination of bulk and grain boundary diffusion [6]. On CuGaSe₂ and Cu(In,Ga)Se₂ films, post-deposition sulfurization produces a completely sulfurized surface layer that has been correlated with a structure visible in scanning electron microscope (SEM) cross-sectional images [7]. In the same reference, it was observed that in sulfurized CuInSe₂ films a Na compound tends to segregate at the surface.

In this paper, the effect of variations in the ratio of atomic concentrations of Cu and In (Cu/In) and substrate material on the sulfurization of CuInSe₂ films is investigated. The results are explained on the basis of diffusion and reaction mechanisms.

EXPERIMENT

Films of CuInSe₂ with an approximate thickness of 2 μm were made by co-evaporation of the elements in a bilayer process, with initially Cu-rich and subsequently Cu-poor film growth [8]. The substrates used were Mo covered SL and 7059 glass, and the substrate temperature during CuInSe₂ deposition was 550°C. Energy dispersive x-ray spectroscopy (EDS) and Auger

electron spectroscopy depth profiling confirmed good lateral and vertical uniformity of the composition, respectively.

The films were sulfurized in an atmospheric pressure reactor under constant flow of 2% H₂S diluted in Ar, at a gas flow velocity of 3.7 cm/sec across the film surface. During a standard sulfurization run the samples were introduced into the reaction zone while the reactor was cold and remained there while the reactor was heated to 575°C. To ensure thermal stabilization, the samples were preannealed for a period of 30 min in flowing Ar prior to the start of the H₂S flow. The samples were sulfurized for, typically, 1 hour before they were extracted from the reaction zone and the H₂S flow was terminated. These conditions are referred to as standard sulfurization conditions in the discussion below.

The composition of the films was determined by EDS at 20 kV with a vertically incident beam on an Oxford INCA system in an Amray 1810 T SEM. Phase identification and S distribution information was obtained by XRD using a Philips/Norelco Bragg-Brentano focusing diffractometer with a Cu tube at 35 kV. Surface analysis of the films was carried out by glancing incident angle XRD (GIXRD) on a Phillips X'pert PW3040-MPD system with a Cu tube at 40 kV. The XRD spectra shown in the following were smoothed and normalized to the same peak area. Standard peak positions were obtained from JCPDS files. Mo was used as an internal standard.

Non-uniformities in film composition were observed along the plane of Cu-poor CuInSe₂ films on SL substrates after sulfurization. The edge region of the films showed increased values of Na by EDS. The cause of this effect is not clear at this point. The data presented in the following was taken at the center of the samples in order to exclude edge effects.

RESULTS

CuInSe₂ films coevaporated onto SL and 7059 substrates with Cu/In ratios of 0.90 (Cu-poor) and 1.35 (Cu-rich) were reacted under the standard sulfurization conditions listed above. The XRD [112] peaks of these films after sulfurization are shown in figure 1. The peaks of the Cu-rich films are narrow and are located close to the standard peak position of CuInS₂, which indicates that, in the entire volume, almost all the Se was replaced with S. In contrast, for Cu-poor films only very little Se was replaced with S, as indicated by the position of the main peak close to the standard position of CuInSe₂. There is only a small tail due to film volume with higher concentrations of S, which extends all the way to the peak position of CuInS₂.

Cu-rich films

For Cu/In ratios of 1 or greater, Cu₂Se is assumed to be present in the film. Engelmann, et al. [6] described the S incorporation into CuInSe₂ films as a 2-step process. The first step is the chalcogen exchange reaction at the solid-gas interface, and the second step is the diffusion of S into the film and of Se out of the film. They were able to extract values for the bulk and the grain boundary diffusion coefficients from the XRD peaks of films with Cu/In greater than but close to 1. They sulfurized one film under the same conditions that were used for the films shown in figure 1, and the XRD peak of that film closely matches the peaks of the Cu-rich films shown here.

To understand the role of Cu₂Se, a film on SL substrate was etched with KCN prior to sulfurization. EDS showed that the KCN reduced the Cu/In ratio from 1.45 to 1.05 by etching

away excess Cu_2Se . However, this compositional value indicates that some Cu_2Se remained in the film. Figure 2 shows the [112] XRD peaks of the etched film compared to an unetched film on SL substrate after sulfurization. From the peak shape and position it can be concluded that S diffusion is reduced when most of the Cu_2Se has been removed. This indicates that the Cu_2Se phase enhances diffusion in Cu-rich films as compared to Cu-poor films.

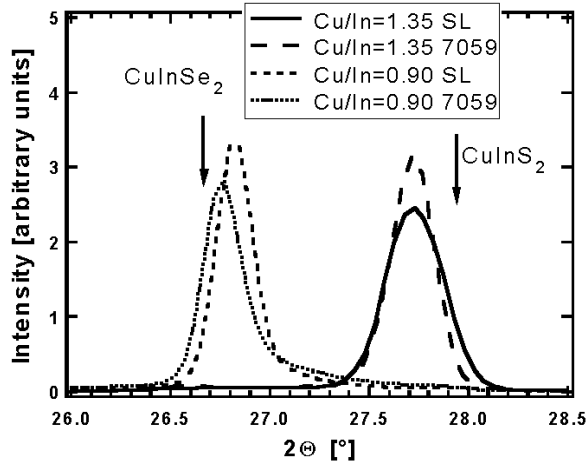


Figure 1. XRD spectra of Cu-rich and Cu-poor CuInSe_2 films on SL and 7059 substrates, after 1 hour of sulfurization. The arrows represent the [112] peak position in the standard XRD patterns.

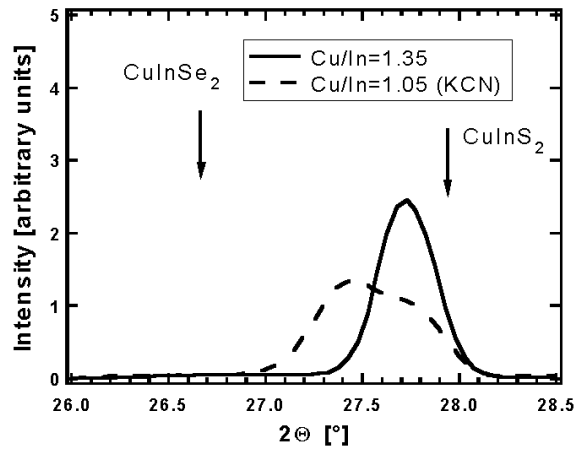


Figure 2. XRD spectra of KCN etched and unetched Cu-rich CuInSe_2 films on SL substrates after 1 hour of sulfurization.

Cu-poor Films

CuInSe_2 films with $\text{Cu/In} \approx 0.9$ were reacted for times from 1 hour to 8 hours. Figure 3 shows the XRD [112] peaks of films on SL and 7059 substrates that were sulfurized for 4 hours. The spectra are similar except that the film on SL substrate has a small [112] CuInS_2 peak. In addition, NaInS_2 was detected on the film on the SL substrate. This suggests that the incorporation/diffusion of S into the CuInSe_2 films is independent of substrate, and in the films on SL substrates there are additional reactions occurring due to the presence of Na.

Figure 4 shows GIXRD data for films on SL and 7059 substrates that were sulfurized for 1 hour. In this method, decreasing values of the incident angle result in a decreasing penetration depth of the x-ray beam, which is indicated in the figure. Therefore, spectra at lower incident angles represent more of the surface of the films. For the film on SL substrate, the GIXRD spectrum contains the CuInS_2 peak, which is stronger at $0.2 \mu\text{m}$ penetration depth than at $0.9 \mu\text{m}$. On the other hand, a similar peak was not detected in films on 7059 substrates. Therefore, in films on SL substrates under sulfurization, CuInS_2 accumulates in a surface layer, while no such accumulation occurs in films on 7059 substrates.

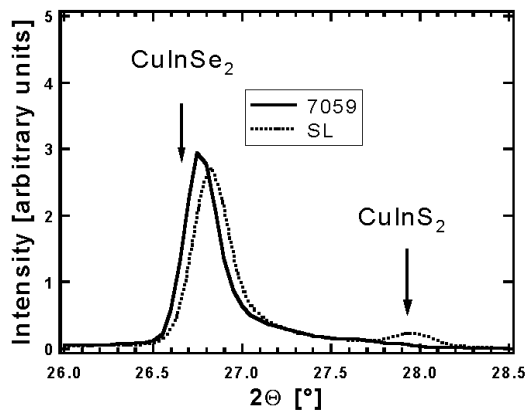


Figure 3. XRD spectra taken on Cu-poor CuInSe_2 films on SL and 7059 substrates after 4 hours of sulfurization.

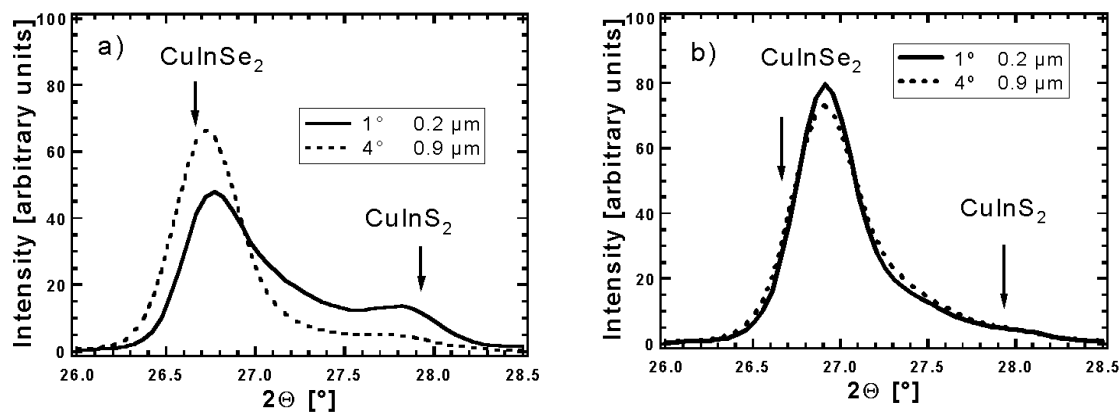


Figure 4. GIXRD spectra of Cu-poor CuInSe_2 films on a) SL and b) 7059 substrates after 1 hour of sulfurization.

Figure 5 shows GIXRD spectra at 1° and at 8° incident angle for a film on SL glass sulfurized for 1 hour, showing the presence of NaInS_2 . At both penetration depths, NaInS_2 and $\text{CuIn}(\text{Se},\text{S})_2$ peaks are observed, and Mo peaks are visible in the 8° scan since the entire film is sampled. The NaInS_2 peaks are much stronger in the spectrum taken at 1° incident angle, indicating the NaInS_2 is at or near the surface. Additionally, Na was detected by EDS, with its concentration increasing towards the film edge. Values as high as 11 atomic % were measured by EDS after 8 hours of sulfurization, even though no Na was detected by EDS in the as deposited films. Also, no Na was detected by EDS in Cu-rich films.

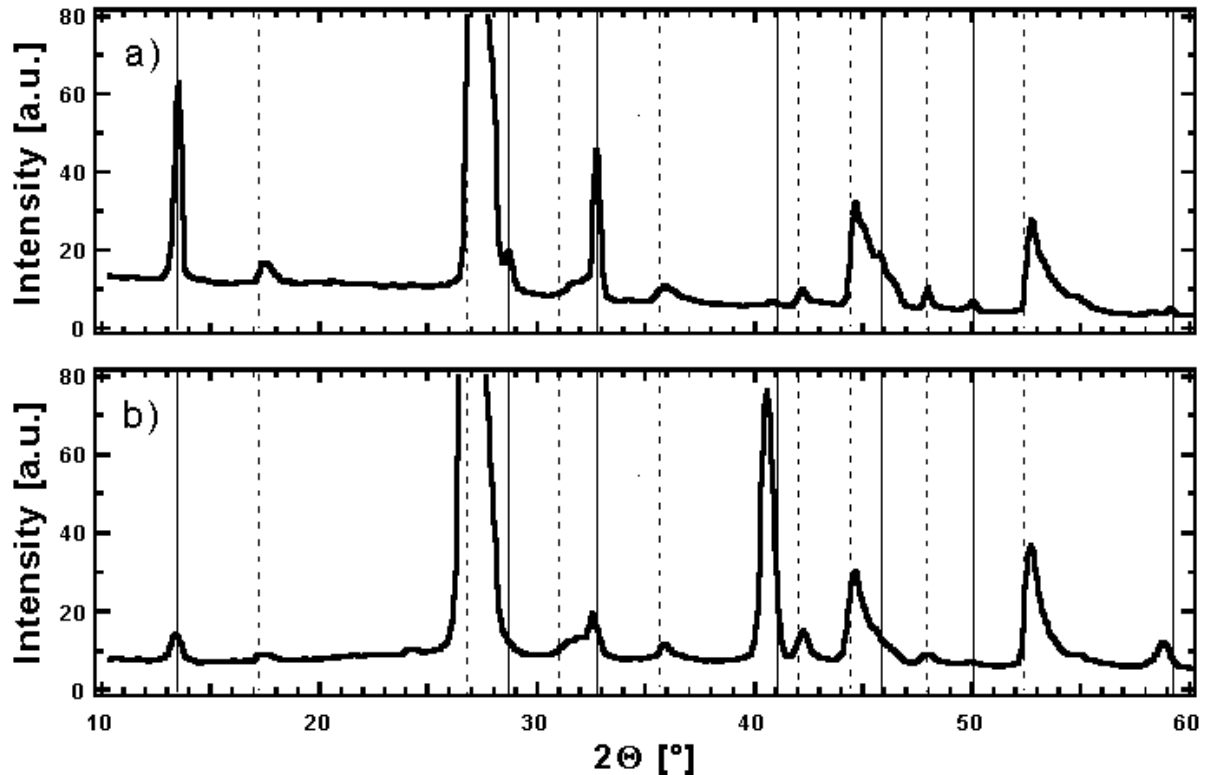


Figure 5. GIXRD spectra taken on a Cu-poor CuInSe_2 film on SL glass sulfurized for 1 hour at a) 1° and b) 8° incident angle. Solid lines represent the primary standard peak positions of NaInS_2 , dashed lines represent those of CuInSe_2 . In the spectrum taken at 8° incident angle, the peaks at 40.6° and at 58.7° are due to Mo.

DISCUSSION AND CONCLUSIONS

The Na is assumed to originate from the substrate in the form of Na_2O and to diffuse through the Mo to the grain boundaries and surfaces of the CuInSe_2 film. It is proposed that Na reacts with CuInSe_2 and H_2S to form NaInS_2 , and that, at the same time, CuInS_2 is formed. This causes an increase in the Cu/In ratio of the unreacted CuInSe_2 . The reaction of Na and H_2S with CuInSe_2 may be possible only when the CuInSe_2 is Cu-poor, such that there is excess In available. In this case, a self-limiting mechanism is implied for the formation of NaInS_2 . With sufficient Na available, the process will stop once $\text{Cu/In} = 1$ in the remaining $\text{CuIn}(\text{Se,S})_2$ phase. This is supported by a study on the preparation of CuInS_2 by sulfurization finding that the amount of NaInS_2 formed increased with a decrease in the Cu/In ratio of the precursors [11]. For the case of $\text{Cu/In} > 1$, the supply of Na to the surface may be restricted by the presence of Cu_2Se in the grain boundaries.

To summarize:

- 1) For $\text{Cu/In} > 1$, the presence of Cu_2Se enhances S diffusion in Cu-rich films, compared to Cu-poor films.
- 2) S diffusion is independent of the presence of Na in the substrate material in both Cu-rich and Cu-poor films.

- 3) In Cu-poor films, when Na is supplied from the substrate it moves through the film and reacts with H₂S and CuInSe₂ to form CuInS₂ and NaInS₂. This reaction may be self-limiting with regard to In, and it does not occur on Cu-rich films.

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