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High-Resolution AES Mapping and TEM Study of Cu(In,Ga)Se₂ Thin Film Growth

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ABSTRACT

The chalcopyrite Cu(In,Ga)Se₂ (CIGS) shows promise as an absorber layer in thin polycrystalline solar cells, however, details of the PVD growth of this complicated material remain in a developing stage. Previous workers have postulated the existence of a thin film of liquid Cu_xSe on the growing CIGS film, and that this layer acts as a reservoir of copper as well as a layer in which rapid mass transport is possible. In this paper we present transmission electron microscopy (TEM) and high resolution Auger electron spectroscopy (AES) mapping data taken on samples that had their growth interrupted at a stage when Cu_xSe was expected to be present. The AES maps show CIGS grains which are highly enriched in copper relative to the rest of the CIGS film, and that these same areas contain almost no indium, results consistent with the presence of Cu_xSe. Small-area diffraction analysis and energy dispersive spectroscopy (EDS) performed on these same samples independently confirm the presence of Cu_xSe at the surface of growing CIGS films.

1. Introduction

Of the several methods available for the deposition of CIGS thin films, physical evaporation of the elemental precursors in the “three-stage” process has yielded the most efficient devices to date [1]. The first stage of this process involves the coevaporation of gallium and indium in a selenium ambient. Next, the film is made copper-rich by stopping the In and Ga fluxes and ramping up the copper source. The third stage is typified by a short exposure to In and Ga fluxes without copper.

Previous workers have proposed on the basis of phase diagrams and the relevant growth conditions a growth model in which there is a thin film of liquid copper selenide on the surface of the solid film during the time that the film is copper rich [2,3]. There has so far been little experimental evidence to support this model, in part because X-ray diffraction cannot distinguish between the similar structures of copper selenide phases and CIGS. In this paper, we use the techniques of SEM, AES, TEM, electron diffraction, and energy dispersive spectroscopy to identify different selenide phases that were present during CIGS thin film growth.

2. Experimental

Thin films of (In,Ga)₂Se₃ precursors were deposited in “stage 1” on heated, Mo-coated soda-lime glass substrates by coevaporation of the pure elements. The second stage in which a copper flux is provided to the growing films was completed, and the films were allowed to cool to room temperature (“quenched”) without proceeding through the usual third stage.

The AES experiments were conducted on quenched films that were transferred through air to the UHV chamber of a Physical Electronics 670 field emission scanning Auger spectrometer. Best elemental contrast was obtained on

samples that had been subjected to just enough sputtering with 3 keV Ar⁺ ions to remove the oxygen and carbon containing overlayers contaminating the samples. A typical sputtering time for this process was 30 s at a current density of 20 μA/cm². SEM and AES imaging was carried out using a 10 kV, 10 nA primary beam and with standard sensitivity factors [4]. TEM, small area diffraction, and energy dispersive spectroscopic measurements were performed in a Phillips CM30 TEM operating at 300 keV.

3. Results and Discussion

Figure 1 is comprised of SEM and Auger images of the same area of a CIGS surface. The SEM image is taken by collecting all secondary electrons excited by the primary 10 keV electron beam, whereas the Auger images are maps of the intensities of electrons with particular kinetic energies. The copper and indium AES maps in Fig. 1 show that the distribution of these elements on the film’s surface is not uniform, in contrast to the selenium distribution. Furthermore, one can see that the indium and copper concentrations are inversely correlated spatially, i.e. the crystallites that are rich in copper contain almost no indium, and likewise, those that are rich in indium are poor in copper. This stands as the first piece of evidence that a Cu_xSe phase was present in the quenched CIGS film.

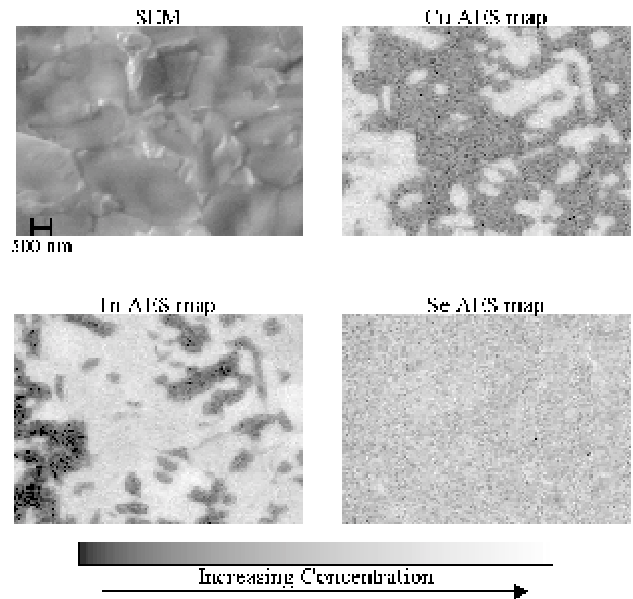


Figure 1. SEM image and Auger maps of copper, indium, and selenium.

The fact that the selenium concentrations do not vary substantially across the surface of the film is consistent with prior studies on similar materials [3], and indicates that the Cu_xSe phase has a stoichiometry that results in a selenium

concentration the same as the surrounding phase, Cu(In,Ga)Se_2 . Matrix effects are assumed to be negligible.

Small-area electron diffraction patterns and a TEM image are shown in Figure 2. An electron diffraction pattern from the lighter area of the TEM image labeled “a” is shown in the first panel of the figure and has the symmetry and spot spacing appropriate for chalcopyrite Cu(In,Ga)Se_2 . A diffraction pattern from one of the small dark crystallites observed in the TEM image is displayed in panel (b) of the figure. As expected from the similar lattice constants and structure of CIGS and Cu_xSe , the diffraction patterns are similar, and differ mainly by the more intense third order spots exhibited by the “b” crystallites. The origin of these higher order spots is not fully understood at this time and is the subject of continuing investigations. In any case, distinguishing between Cu_xSe and CIGS cannot be done on the basis of the diffraction patterns alone.

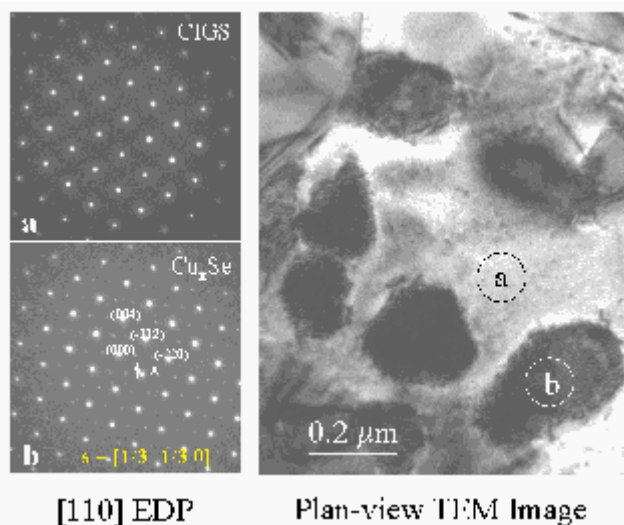


Figure 2. Small area diffraction patterns and TEM image of Cu_xSe and CIGS.

Figure 3 shows energy-dispersive spectra of the same two areas of the CIGS film shown in Figure 2. It can be seen from the two spectra that crystallite “b” has a much higher ratio of copper to selenium than area “a”. It is also apparent that area “b” is devoid of gallium and indium, whereas area “a” contains these elements in proportions consistent with the CIGS stoichiometry. Taken together with the Auger mapping data, there is a consistent picture of these CIGS films being partially covered with particulates of a solid copper selenide phase.

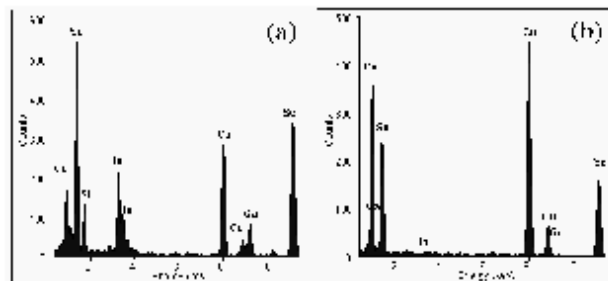


Figure 3. Energy dispersive spectra of the two areas of Figure 2.

4. Summary

Thin films of copper rich CIGS were grown on Mo coated glass substrates. High resolution Auger elemental mapping data showed portions of the films that were rich in copper and devoid of gallium and indium. Although electron diffraction data did not allow the unambiguous identification of the two different materials, the diffraction patterns did differ in that the copper selenide phase showed intense third order spots. Energy-dispersive spectra confirmed the AES mapping data: the CIGS film was at least partially coated with a layer of solid copper selenide that under the growth conditions is a liquid. During PVD growth, this liquid layer is expected to serve as a layer in which rapid mass transport if able to occur, and function as a reservoir of copper for further film growth.

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