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Structural and optical properties of $\text{CuIn}_{1-x}\text{Al}_x\text{Se}_2$ thin films prepared by four-source elemental evaporation

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Abstract

$\text{CuIn}_{1-x}\text{Al}_x\text{Se}_2$ (CIASe) thin films with $x = 0.25, 0.5$ and 0.65 were prepared by four-source elemental evaporation. The structural and optical properties were investigated by X-ray diffraction, scanning electron microscopy, energy dispersive analysis, and optical transmission. The results showed that these films contain chalcopyrite structure with preferred orientation along (112) direction. The morphology, grain distribution and composition of CIASe films were studied and compared for different Al content. The optical studies revealed that the films were highly absorbing and the energy band gap calculated from transmission spectra for $x = 0.25, 0.5$ and 0.65 were 1.2, 1.51 and 1.73 eV, respectively. The variation of Al content in the CIASe composition offered a very effective change in the optical band gap.

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1. Introduction

Ternary I–III–VI₂ chalcopyrite semiconductors have received considerable attention in recent years because of their applications in photovoltaic devices [1,2]. As thin film solar cells based on CuInSe_2 and related polycrystalline chalcopyrite materials move towards commercialization, a key area for ongoing research is the development of wider band gap alloys for high efficiency devices. Substantial efforts have been done on CuInSe_2 alloys using gallium and/or sulfur to enhance the band gap, but the efficiency of the devices with $E_g > 1.3$ is reduced by degradation of electronic properties of the absorber leading to losses in fill factor and open circuit voltage [3,4]. Alternatively, performance of thin film CuInSe_2 based solar cells can be improved by the addition of Al to form CuInAlSe_2 absorber

layers with increased band gap, which matches closely with the solar spectrum [5].

It has been reported that optical band gap of CuInSe_2 and CuAlSe_2 were 1.07 [6] and 2.7 eV [7], respectively. Therefore it can be expected that the partial replacement of In by Al controls the optical band gap energy and serves as another candidate of solar cell material. The aim of this work was to prepare CIASe thin films by four-source elemental evaporation and to study the microstructure and the optical properties.

2. Experimental procedure

Polycrystalline chalcopyrite compounds $\text{CuIn}_{1-x}\text{Al}_x\text{Se}_2$ with $x = 0.25, 0.5$ and 0.65 were deposited on glass (corning 7059) by vacuum evaporation method. The multilayer film of Cu, In, Al and Se was deposited sequentially under a vacuum of 2×10^{-6} Torr. The substrate temperature was varied from room temperature to 100 °C. The substrate

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temperature was measured by a chromel–alumel thermocouple placed near the substrate. It is worth noting that no elements remained in molybdenum boats after the deposition, as it is crucial to maintain the stoichiometry in the final film. Thin films of $\text{CuIn}_{1-x}\text{Al}_x\text{Se}_2$ with thickness 0.5–2.0 μm were prepared by the above method. The atomic ratio of the elements were designed so as to become $\text{Cu}:(\text{In} + \text{Al}):\text{Se} = 1:1:2$ assuming that atoms are isotopically emitted from the source in the evaporation process. The films, grown at lower substrate temperatures, were kept in a graphite box and were conventionally annealed in a tube furnace at 500 $^\circ\text{C}$ for 60 min under a dynamic Ar flow. The graphite box reduced the reevaporation of Se during annealing.

The structural properties of the films were studied by X-ray diffraction using $\text{Cu K}\alpha$ radiation. The composition of the films was determined by using energy dispersive X-ray analysis (EDAX), while the grain morphology was studied with a scanning electron microscope (SEM). A Hitachi spectrophotometer was used to record the transmission spectra in the near-infrared (NIR) and visible wavelength range.

3. Results

The structural properties of $\text{CuIn}_{1-x}\text{Al}_x\text{Se}_2$ films were studied by SEM, EDAX and XRD measurements. The XRD spectrum of the films is shown in Fig. 1. All the peaks shown correspond to CIASe film. It was found that (112) diffraction intensity in all the thin films was strong, indicating that the films produced by four-source elemental evaporation in the present work assumed a preferred orientation along the (112) plane parallel to the substrate. The intensity of (112) reflections are shown in Fig. 2 for films with $x = 0.25, 0.5$ and 0.65 . It is seen that the peaks shifts to higher 2θ values as the Al content is increased. This is mainly due to decrease in d spacing in accordance with Vagard's law.

Fig. 1. X-ray diffraction pattern of CIASe films deposited on corning glass.

Fig. 2. Plot of (112) peak intensity vs. 2θ .

Fig. 3. (a) Scanning electron microscopy images of CIASe films with $x = 0.25$; (b) scanning electron microscopy images of CIASe films with $x = 0.5$.

Fig. 3a and b shows SEM photographs of the surface morphology of the CIASe films for $x = 0.25$ and 0.5 , respectively. It can be observed that these films present a rough surface morphology with a certain degree of non-uniformity in the grain size. The pictures show the co-existence of small and relatively large grains on the film surface. The EDAX studies on both small and bigger grains indicated that the composition of the small grains does not differ from that of the larger grains and ruled out the segregation of any specific element.

Table 1 shows the compositions of the films, which were deposited by EDAX analysis in the SEM. It is seen that the ratio of Cu/(In + Al) is about 0.59 – 0.72 , i.e. Cu atoms are relatively poor compared to (In + Al), while the ratio of (Cu + In + Al)/Se is close to unity.

Fig. 4 shows the variation of the transmittance (T) with wavelength (λ) of incident photons for three CIASe films with varied Al content. The absorption coefficient (α) was calculated using the relation $T = (1 - R)^2 \exp(-A) = (1 - R)^2 \exp(-\alpha d)$ where R is the reflectance, T is the transmittance, A is the absorbance and d is the film thickness. For an absorbing material, the absorption coefficient, is given by Refs. [8,9]

$$\alpha = \left(\frac{1}{d}\right) \ln\left(\frac{T}{(1 - R)^2}\right)$$

where T is transmittance is reflectance and d is the film thickness. The absorption coefficient, α , for a direct transition is related to the band gap of a semiconductor and is given by Ref. [10]

$$\alpha h\nu = \frac{A}{h\nu} (h\nu - E_g)^{1/2}$$

where A is a constant, $h\nu$ is the photon energy, and E_g is the energy gap.

Fig. 5 shows the variation of $(\alpha h\nu)^2$ with photon energy for CIASe films with $x = 0.25$, 0.5 and 0.65 , respectively. The energy gap, E_g , estimated from the intercept of the linear portion of the curve found to be 1.2 , 1.51 and 1.73 eV for $x = 0.25$, 0.5 and 0.65 , respectively. These films could absorb almost all the photons having energies higher than the forbidden bandgap. This property of CIASe thin films may be considered the primary reason for their preferential status as an absorber layer in solar cell application.

Table 1
Quantitative analysis of $\text{CuIn}_{1-x}\text{Al}_x\text{Se}_2$ thin films

Sample	Composition (at %)			
	Cu	In	Al	Se
$\text{CuIn}_{0.75}\text{Al}_{0.25}\text{Se}_2$	20.14	18.92	9.08	51.86
$\text{CuIn}_{0.50}\text{Al}_{0.50}\text{Se}_2$	19.78	14.81	18.19	47.22
$\text{CuIn}_{0.35}\text{Al}_{0.65}\text{Se}_2$	20.07	10.72	18.89	50.32

Fig. 4. Transmission spectra of CIASe films with $x = 0.25$, 0.5 and 0.65 .

4. Conclusions

CIASe thin films were deposited on corning glass (7059) substrates by four-source elemental evaporation. X-ray diffraction analysis had shown preferred (112) orientation and confirmed the chalcopyrite structure. The composition of the smaller grain does not differ from that of the large grains, ruling out the segregation of any specific element. It is found that absorption edge shifts to higher photon energy with increasing Al concentration. The optical band gaps of the films were 1.2 , 1.51 and 1.73 eV for $x = 0.25$, 0.5 and 0.65 , respectively, which are near optimum values for photovoltaic applications.

Fig. 5. $(\alpha h\nu)^2$ vs. $h\nu$ plot for three different compositions.

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