

Optical Constants of CuInSe₂ Thin Films Prepared by Two-Stage Process

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Received October 22, 2003; accepted in revised form May 26, 2004

PACS numbers: 78.66.–w; 78.20.Ci; 78.40.Fy

Abstract

Thin film CuInSe₂ chalcopyrite semiconductors have been prepared on glass substrates by means of two-stage process. The structural properties and atomic compositions of films were determined by energy-dispersive analysis of X-rays (EDAX) and X-ray diffraction (XRD) measurements. Reflectance and transmittance measurements were performed on the films in the photon wavelength range of 300–2200 nm. The samples used in the measurements have different Cu/In ratios. The reflectance and transmittance spectra were analyzed on the basis of multiple reflection model considering the absorbing film on a non-absorbing substrate and then complex refractive-index $n^*(E) = n(E) + ik(E)$ and complex dielectric constant $\epsilon^*(E) = \epsilon_1(E) + i\epsilon_2(E)$ were determined. It has been concluded that the films having higher Cu/In ratios show stronger absorption at low photon energy region than those having lower Cu/In ratios.

1. Introduction

CuInSe₂ thin films are interesting materials used mainly for absorbing layers in solar cell structures. These materials have good chemical stability, high absorption coefficients and suitable band gap energies for photovoltaic conversion [1]. Optical properties of CuInSe₂ have been investigated by various authors [2–5]. Especially, optical anisotropy in bulk samples were analyzed and optical parameters were estimated by modeling the dielectric function [1, 3]. CuInSe₂ thin films have optical band gap energies of about 1 eV and have large absorption coefficients for energies higher than their band gaps. Therefore, even a 2 micron thick CuInSe₂ thin film can absorb more than 90 percent of radiation incident upon it [6–8]. These films can be prepared both in amorphous and polycrystalline forms. The structural difference between them depends mainly on the preparation conditions, especially on the temperature of the substrate during deposition [9]. Electrical properties of the films show stronger dependency on the preparation conditions and the stoichiometry. For example, the resistivity of CuInSe₂ thin films can be varied in the 10^{-2} to 10^4 ohm · cm range depending on the Cu/In ratio [10, 11].

CuInSe₂ thin films can be prepared by different methods. The CuInSe₂ solar cells which have the highest conversion efficiency so far reported have been obtained with the films which prepared by co-evaporation [12]. Evaporation processes can be applied to CuInSe₂ growth using different techniques. As examples to these techniques, evaporation by single-source, evaporation by two sources, evaporation by three-sources, and two-stage process can be mentioned. The two-stage process and evaporation by three sources have apparent advantages over other techniques with respect to stoichiometry control ability.

The aim of this study is to determine the optical constant of various polycrystalline CuInSe₂ thin films, which have different Cu/In ratios, prepared by a two-stage process approach.

2. Experimental Method

The CuInSe₂ thin films used here were prepared by a two-stage technique. At the first stage of this preparation method Cu and In films were sequentially deposited onto a glass substrate (Corning 7059) by e-beam evaporation at a pressure of about 2×10^{-5} Torr. The materials used had 5–9 purity. The thickness of the Cu layer was about 0.2 µm and the thickness of the In layer was adjusted to obtain the desired Cu/In ratios.

During the second stage of the process, to add Se into the Cu-In films, the glass Cu-In structure was placed in a furnace reactor tube containing an atmosphere of 5%–10% H₂Se in Ar for about 1 hour at 400 °C [13]. Temperature was ramped from room temperature to 400 °C in about 10 minutes after the tube was evacuated and re-filled with 10% H₂Se. During the ramp-up and during selenization flow of the gas mixture was kept on at a level of about 100 cc/min. At the end of the reaction step furnace clam-shell was opened to cool down the tube and the sample, which took about 15 minutes.

The samples so prepared were analyzed by a JOEL JSM-840A Scanning Electron Microscope (SEM) combined with EDAX. The atomic composition (amounts of Cu, In and Se) of films were determined from these measurements. Furthermore, X-Ray Diffraction (XRD) Patterns of samples were taken using a Philips PW3710 X-Ray Diffractometer having $\lambda = 1.5418$ Å wavelength.

In addition to these measurements, transmittance and reflectance measurements were also performed by Jasco Model V-570 UV/VIS/NIR spectrophotometer, in the wavelength range of 300–2200 nm.

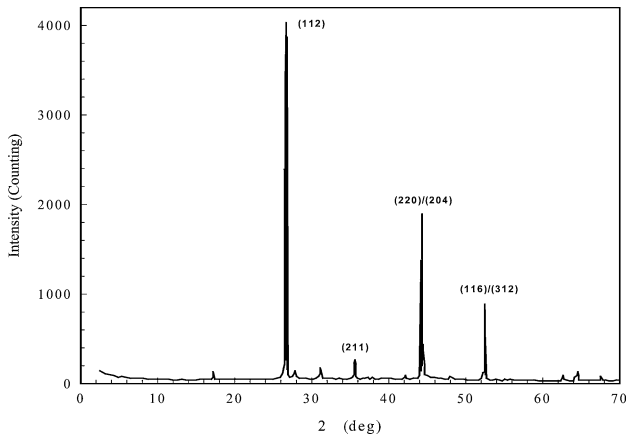
3. Results and Discussion

The atomic composition of films used in this study were determined by L_α transitions at energy distribution spectra, and

Table I. Atomic compositions and Cu/In ratios of CuInSe₂ thin films.

Sample	Cu (%)	In (%)	Se (%)	Cu/In
S1	18.99	33.44	47.57	0.5679
S2	18.03	34.22	47.75	0.5269
S3	16.61	34.70	48.69	0.4786
S4	15.68	36.15	48.17	0.4337

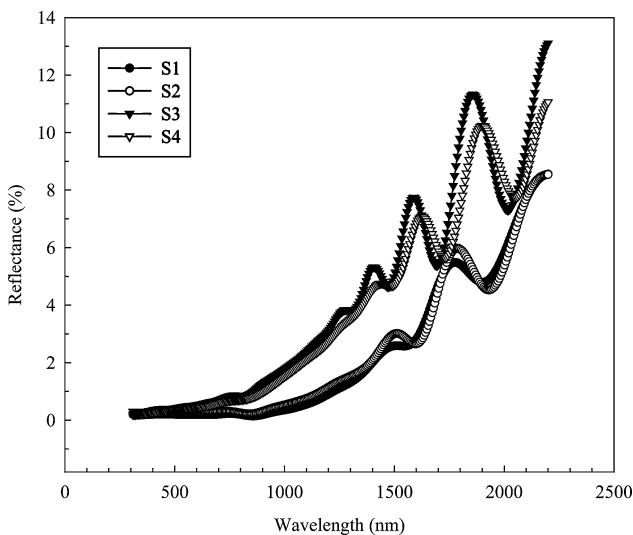
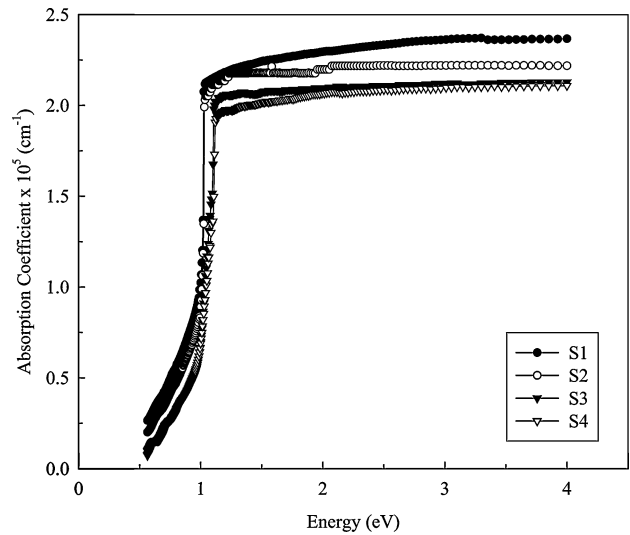
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Fig. 1. XRD pattern of CuInSe₂ thin film (S1).

the results are given in Table I. The samples in the Table are labeled as S1, S2, S3 and S4 with respect to decreasing order of Cu/In ratios.

Since all the samples were prepared by the same method and under equivalent preparation conditions, only three XRD spectra belonging to S1, S2, and S4 samples were recorded and only one of them, which belongs to S1, is shown in Figure 1. By inspection of the XRD spectrum of S1, it can be seen that the main major peaks observed are (211), (112)/(103) and (105)/(203), which are characteristic peaks associated with the chalcopyrite structure of CuInSe₂ thin films [13]. Peak intensity ratio of (112) to (220) was found to be approximately 2.12. The lattice parameters of the films were found to vary roughly 5.78 and 5.80 Å range for *a*, and between 11.56 and 11.62 for *c*, depending on the Cu/In ratios. Namely, as the Cu/In ratios increase, the lattice parameters also stretch out.

The thickness measurements of samples were performed using a Tencor profilometer and the values of 2.4, 2.5, 2.5 and 2.6 micron are found for the samples S1, S2, S3 and S4 respectively. The measured optical reflectance spectra of samples are shown in Figure 2. The interference effects are quite apparent in the reflectance curves of all samples, especially for those having lower Cu/In ratios, namely S3 and S4. At long wavelengths, this interference effect becomes more dominant. As the Cu/In ratios

Fig. 2. Measured reflectance spectra of CuInSe₂ thin films having different stoichiometric ratios.Fig. 3. Variations of calculated absorption coefficients of CuInSe₂ thin films with energy.

decreases, not only the interference effects gain more importance, but also the reflectance intensity itself has a higher value. It can be concluded from this observation that, the reflectance intensity depends strongly on the Cu/In ratios, especially at long wavelengths, and shows an increasing trend as this ratio decreases, at least in the Cu/In range between 0.56 and 0.43 investigated here. On the other hand, at the short wavelengths, the reflectance is very small.

The measured transmittance spectra are converted to the absorption coefficient, by considering the reflectivity dispersion and the interference effects in thin films by using the following relationship [14, 15]

$$\alpha = -\frac{1}{d} \ln \frac{-(1-R)^4 + \sqrt{(1-R)^4 + 4T^2R^2}}{2TR^2} \quad (1)$$

where *d* is the thickness of film, *R* is the reflectance and *T* is transmittance measured. The results obtained for the four samples are drawn in Figure 3. Absorption coefficients of the films are shown as a function of energy, instead of wavelength. As shown in the Figure, the CuInSe₂ thin films demonstrate very high absorptivity for energies higher than roughly 1 eV. Absorption coefficient shows a sharp rise nearly at the forbidden band edge and reaches to a value of approximately $2.2 \times 10^4 \text{ cm}^{-1}$. Therefore, even a CuInSe₂ thin film of 2.5 micron thickness can absorb almost all the photons having energies higher than the band gap. Owing to this property, the CuInSe₂ thin films have a very distinctive status in solar cell applications as an absorber layer [16].

The extinction coefficient *k*₁ of films can be calculated by using the $\alpha_1 = \frac{4\pi k_1}{\lambda}$ relationship. Results are shown as a function of wavelength in Figure 4 for all four samples. Similar to the absorption coefficient, the extinction coefficient curves also show very sharp rises at around the forbidden band gap energies for each film. The samples having higher Cu/In ratios have demonstrated stronger absorptivity at long wavelengths. Pal *et al.* [19] have found similar results for extinction coefficients of CuInSe₂ films which were prepared by three-source evaporation technique.

The transmittance and reflectance spectra of films were analyzed on the basis of model of multiple reflection system given by Heavens [17]. According to this model, transmittance and reflectance can be expressed in terms of both material and system parameters, for absorbing films on non-absorbing

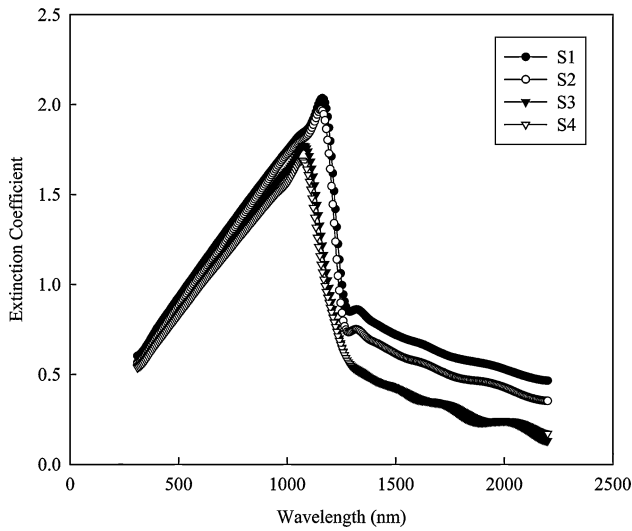


Fig. 4. Extinction coefficient variations of CuInSe₂ thin films with wavelengths calculated by using the absorption coefficient.

substrates, simply as

$$\frac{1-R}{T} = \frac{1}{2n_2(n_1^2 + k_1^2)} \times \left[n_1 \{ (n_1^2 + n_2^2 + k_1^2) \sinh(2\alpha_1) + 2n_1n_2 \cosh(2\alpha_1) \} + k_1 \{ (n_1^2 - n_2^2 + k_1^2) \sin(2\gamma_1) + 2n_2k_1 \cos(2\gamma_1) \} \right] \quad (2)$$

where n_1 and n_2 are the refractive indices of film and the substrate respectively, k_1 is the extinction coefficient of the film, d is the film thickness and λ is the light wavelength. The other two quantities used in the above expression defined as in reference [18].

$$\alpha_1 = \frac{2\pi k_1 d}{\lambda} \quad \text{and} \quad \gamma_1 = \frac{2\pi n_1 d}{\lambda}.$$

We have calculated the refractive indices of samples by solving Eq. (2) numerically for each wavelength (λ) and found the results shown in Figure 5 for four samples. In this figure, it is seen that, the refractive indices of all samples have the same behavior until approximately 1000 nm in the high energy region and in this region they show a smooth increase from 2.2 to 3.4, with

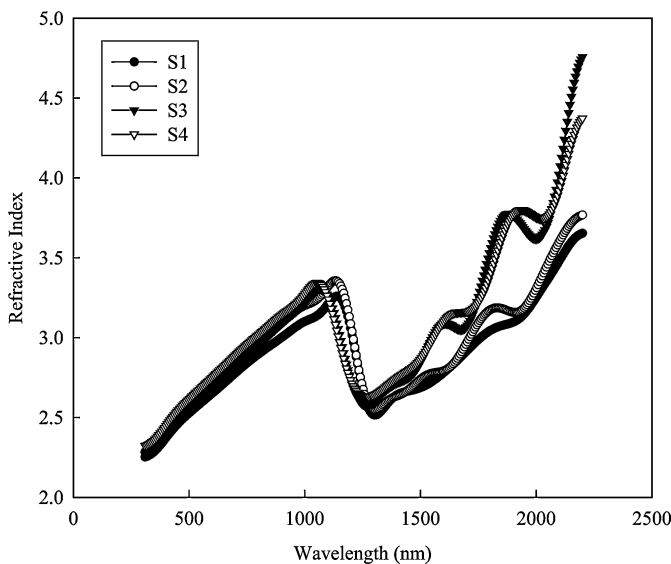


Fig. 5. Refractive indices of CuInSe₂ thin films computed by solving numerically Eq. (2).

wavelength of light. But, at larger wavelengths (over 1000 nm) the differences in refractive indices become more significant. It is very understandable that the CuInSe₂ films have not demonstrated any interference effect in most of their optical constants over the high energy region (at energies greater than the forbidden band gap) because of their extremely high absorptivity. The refractive index shows an interesting behavior for the wavelengths higher than 1000 nm. Within the 1000 nm to 1250 nm range, the samples with higher Cu/In ratios have higher values of refractive index. When the wavelength increases beyond 1250 nm the situation is just the opposite, that is those samples with lower Cu/In ratios have higher values of refractive index. For instance, in case of S3, the value of refractive index approaches to 5 at 2200 nm. As the wavelength increases, the absorbance of films become weaker and interference effects become more apparent.

In Figures 6 and 7, real part ϵ_1 and imaginary part ϵ_2 of the complex dielectric constants of samples are given respectively. The ϵ_1 and ϵ_2 variations are calculated by using the n_1 and k_1 values.

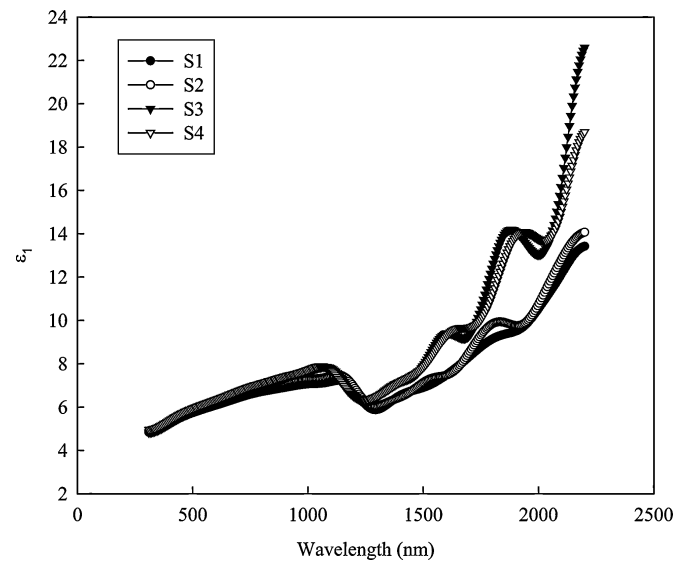


Fig. 6. Real part of complex dielectric constant CuInSe₂ thin films.

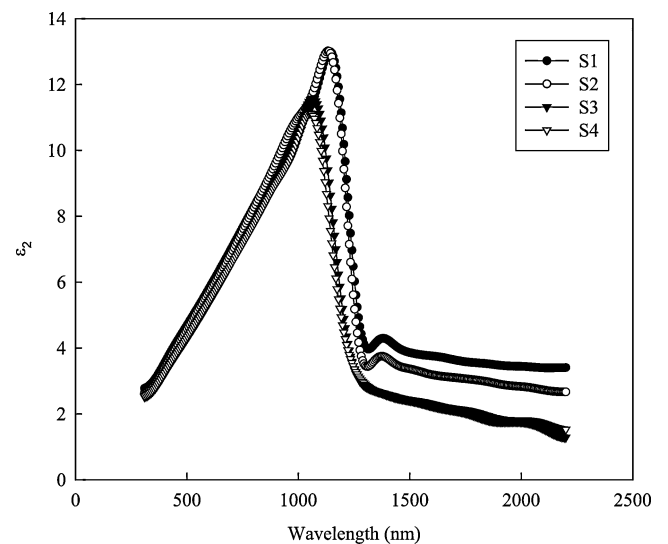


Fig. 7. Imaginary part of complex dielectric constant of CuInSe₂ thin films.

4. Conclusions

The chalcopyrite CuInSe₂ thin films prepared by the two-stage process utilizing e-beam evaporation have very useful properties for solar cell applications. They have forbidden band gap energies of about 1 eV, depending weakly on the Cu/In ratios, and have high absorption coefficients [16]. Stoichiometric ratios seem not to affect the band gap energies very strongly but they have more influence on the optical constants of the films at energies lower than the band gap edge. Also, in this lower energy region interference effects are more apparent. Therefore, at high energy regime (until the band edge), the CuInSe₂ thin films having Cu/In ratios between about 0.56–0.43 range can be assumed to have nearly the same optical behavior.

References

1. Djuricic, A. B. and Li, E. H., Appl. Phys. A **73**, 189 (2001).
2. Bottomley, D. J., Mito, A., Niki, S. and Yamada, A., J. Appl. Phys. **82**, 817 (1997).
3. Kawashima, T., Adachi, T., Miyake, H. and Sugiyama, K., Appl. Phys. **84**, 5202 (1998).
4. Sobotta, H., *et al.*, Phys. Status Solidi A **60**, 531 (1980).
5. Hidalgo, M. L., *et al.*, Physica Status Solidi B **200**, 297 (1997).
6. Başol, B. M., Tr. J. Phys. **17**, 294 (1993).
7. Oktik, Ş., Prog. Crystal Growth Charac. **17**, 171 (1998).
8. Kapur, V. K., Başol, B. M. and Tseng, E. S., Solar Cells **16**, 289 (1987).
9. Chopra, K. L., Das, S. R., "Thin Film Solar Cells" (Plenum Press, New York 1983).
10. Neumann, H., Nowak, E., Kühn, G. and Heise, B., Thin Solid Films **102**, 201 (1983).
11. Naufi, R. and Dick, J., J. Appl. Phys. **58**, 3384 (1985).
12. Contreras, M., *et al.*, Progress in PV **7**, 311 (1999).
13. Başol, B. M. and Kapur, V. K., IEEE Trans. Elect. Devices **37**, 418 (1990).
14. Chichibu, S., *et al.*, J. Appl. Phys. **83**, 3678 (1998).
15. Huang, C. H., *et al.*, Opt. Laser Tech. **34**, 209 (2002).
16. Yüksel, Ö. F., Başol, B. M., Şafak, H. and Karabıyık, H., Appl. Phys. A **73**, 387 (2001).
17. Heavens, O. S., "Optical Properties of Thin Solid Films" (Butterworth, London 1955).
18. Tomlin, S. G., Brit. J. Appl. Phys. **1**, 1667 (1968).
19. Pal, R., Chattopadhyay, K. K., Chaudhuri, S. and Pal, A. K., Thin Solid Films **247**, 8 (1994).