

Preparation and characterization of flash-evaporated CuInSe₂ thin films

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Abstract. Thin films of CuInSe₂ have been evaporated onto glass substrates by flash evaporation. The as-deposited films are amorphous and annealing in selenium atmosphere produces polycrystalline films. The films were characterized by TEM and x-ray diffraction techniques. The optical absorption of the films shows three energy gaps of 1.03, 1.07 and 1.22 eV. The crystal field and spin-orbit splitting are thus found to be 0.04 eV and 0.16 eV respectively. The percentage *d*-character of the valence band states is ~ 35%. The Arrhenius plot of electrical conductivity of films showed impurity ionization of $E_A = 75$ meV.

Keywords. Thin films; chalcopyrites; optical absorption; electrical conductivity.

1. Introduction

The semiconductor CuInSe₂ belongs to the I-III-VI₂ group of compounds with the chalcopyrite structure. This compound has attracted considerable interest in the last decade after the demonstration of 12.5% efficiency of *p*-CuInSe₂/*n*-CdS heterojunction solar cells (Shay *et al* 1975). Thin film *p*-CuInSe₂/CdS cells have given > 10% efficiency (Mickelson *et al* 1984). Garcia and Tomar (1983) recently reported screen-printed CuInSe₂/CdS thin film cells of 3% efficiency. Although research on these solar cells is only of recent origin, it has already warranted a review (Herman and Zweibel 1983). Various methods of preparing thin films of CuInSe₂ have been investigated to make these solar cells economically viable. Pamplin and Feigelson (1979) developed a spray-pyrolysis technique for the preparation of CuInSe₂ thin films. R.F. sputtered films have been characterized by Krishnaswamy *et al* (1983). Loferski (1981) reviewed the performance of CuInSe₂/CdS thin film solar cells prepared by various techniques and concluded that flash-evaporated and R.F. sputtered films were more nearly stoichiometric and of more reproducible compositions.

In this paper we report the characterization of flash-evaporated CuInSe₂ thin films using optical and electrical characterization techniques. Structural characterization of the films was done by TEM and x-ray diffraction techniques.

2. Experimental

The polycrystalline bulk CuInSe₂ was prepared by melting the stoichiometric mixture of 99.999% pure Cu, In and Se at 1050°C in evacuated quartz ampoules. The charge was powdered and remelted two or three times to ensure thorough mixing and reaction of the components. The formation of single-phase, chalcopyrite CuInSe₂ was verified by x-ray diffraction and the exact composition verified by EPMA. The CuInSe₂ so prepared is powdered finely and used in the flash evaporation.

A simple flash deposition technique developed in our laboratory was employed for coating CuInSe_2 thin films. A calling-bell type plunger was used as the vibrator, the frequency of which was varied using a variac. The hopper was filled with finely powdered CuInSe_2 and a tantalum boat at 1300°C evaporated the powder instantaneously. The evaporation was carried out using a vacuum coating unit (Hind High Vacuum Co.) under a vacuum of 10^{-5} torr. Thin films of thickness in the range $0.1\ \mu\text{m}$ to $0.3\ \mu\text{m}$ were coated on glass substrates.

The glancing angle x-ray diffractogram of the films showed all the prominent reflections of the chalcopyrite structure. Films with minimum thickness were used for TEM. The TEM analysis of as-deposited films showed them to be amorphous in nature. A 45 min anneal in Se atmosphere at 250°C converted the films to polycrystalline. A typical SAD of selenium-annealed films is shown in figure 1. From this, the values of the lattice parameters were calculated as $a = 5.85\ \text{\AA}$ and $C = 11.76\ \text{\AA}$ which are in good agreement with previously reported values (Shay and Wernick 1975). Only selenium annealed films were used throughout the study.

The optical absorption spectrum of CuInSe_2 thin films was recorded in the spectral range $800\text{--}1300\ \text{nm}$ using spectrophotometer (Cary 2300), and shown in figure 2. It was analyzed by the usual procedures. The electrical conductivity of the films was measured by a four-probe technique in the temperature range $400\text{--}77\ \text{K}$. The films were evaporated through a special contact mask, which gave films with four specific contact geometries. The steady state electrical conductivity measurements were in argon atmosphere. Indium pressure contacts gave good ohmic contacts. Figure 3 shows the Arrhenius plot of conductivity of CuInSe_2 films.

3. Results and analysis

The optical absorption spectrum shown in figure 2 shows three distinct regions of absorption. The absorption coefficient α rises sharply initially, then becomes rather flat and again increases sharply. This may be considered as due to a direct transition in the



Figure 1. SAD of selenium annealed CuInSe_2 thin films.

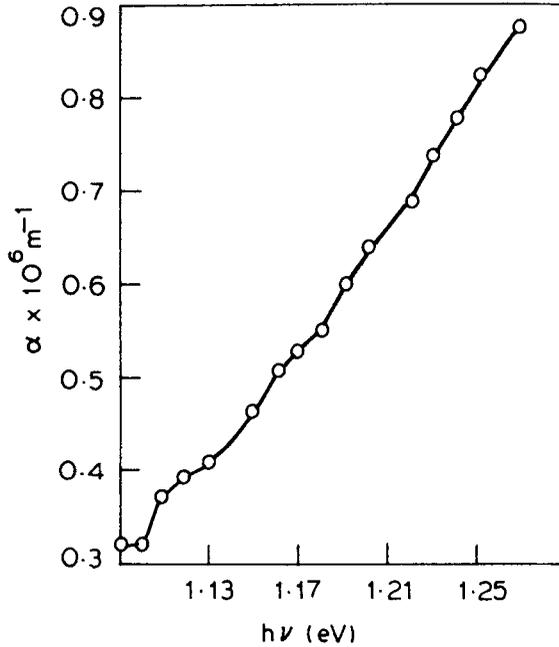


Figure 2. Absorption spectrum of CuInSe₂.

low energy regions. The flat portion at 1.15 eV is due to the onset of a forbidden transition, the absorption of which is much less than that due to a direct transition. The increase of α beyond 1.2 eV is due to the onset of another allowed transition. The absorption spectrum was analyzed following Neumann *et al* (1979).

The initial rise of α below the photon energy $h\nu \leq 1.15$ eV was a direct allowed transition given by

$$\alpha = \frac{A_1}{h\nu} (h\nu - E_{g1})^{1/2}, \quad (1)$$

with $E_{g1} = 1.03$ eV and $A_1 = 1.45 \times 10^6 \text{ cm eV}^{1/2}$. This value of the energy gap compares well with the reported direct band gap of 1.04 eV (Shay *et al* 1973) for this material.

For energies greater than 1.15 eV, if we calculate α using equation (1) and the observed values of E_{g1} and A_1 , we find that the calculated α_1 is always less than the experimental values. This is due to the onset of additional absorption mechanisms. Hence, the additional absorption coefficient, $\alpha_2 = \alpha - \alpha_1$ was analyzed for $h\nu \geq 1.15$ eV. It was found that α_2 satisfies quite well the relation,

$$\alpha_2 = \frac{A_2}{h\nu} (h\nu - E_{g2})^{3/2}, \quad (2)$$

for $1.15 \leq h\nu \leq 1.20$ eV, with $E_{g2} = 1.07$ eV, which corresponds to a direct forbidden transition.

Once again, the values of α_2 calculated using (2) beyond $h\nu = 1.2$ eV were always less than the experimental values. This is due to the onset of a third interband transition. Therefore, now $\alpha_3 = \alpha - \alpha_1 - \alpha_2$ was analyzed and it was found that α_3 can also be described by equation (1) with $E_{g3} = 1.22$ eV.

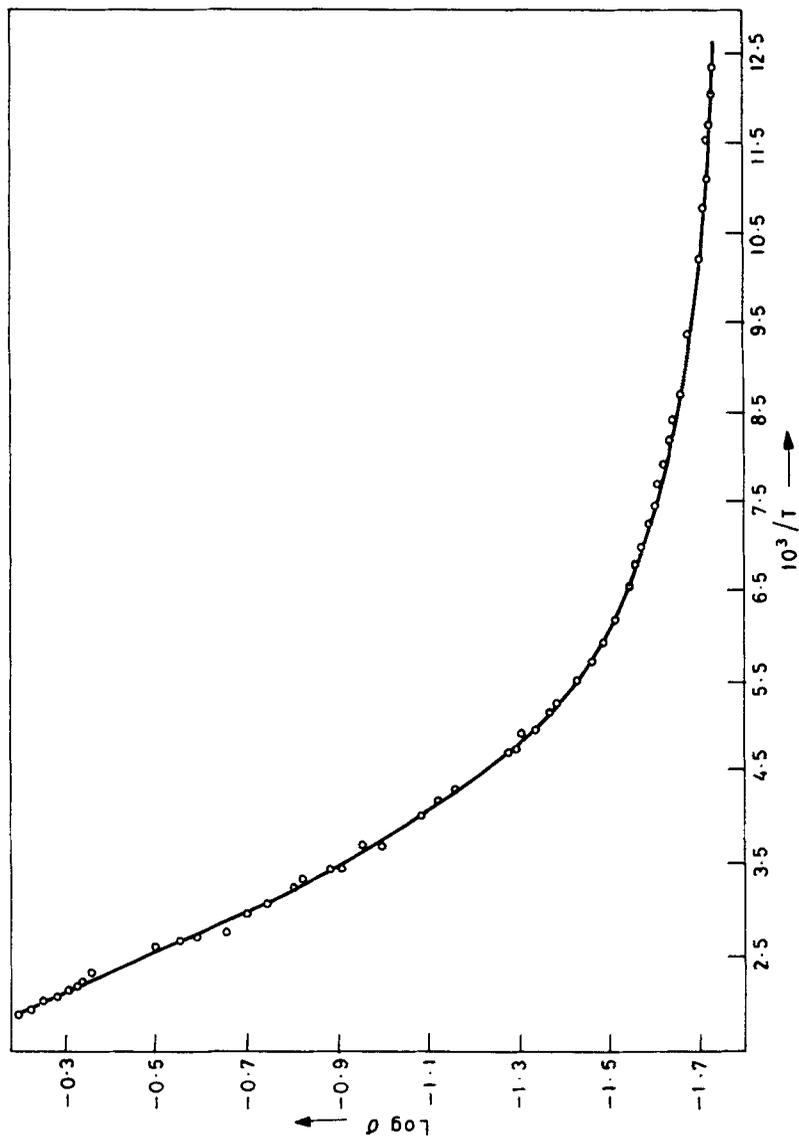


Figure 3. Arrhenius plot of conductivity of CuInSe₂ thin films.

4. Discussion

From the above analysis, three characteristic band gaps for CuInSe₂ were found as $E_{g1} = 1.03$ eV, $E_{g2} = 1.07$ eV and $E_{g3} = 1.22$ eV. These are in good agreement with previously reported values for this material both by optical absorption studies (Neumann *et al* 1982) and by modulation spectroscopic techniques (Shay and Wernick 1975). From the above results, we may draw the zone-centre valence band structure of CuInSe₂ as in figure 4. The three transitions *A*, *B* and *C* correspond to E_{g1} , E_{g2} and E_{g3} respectively. The values of the crystal field splitting and the spin orbit splitting were calculated using the method of Rowe and Shay (1971) to be $\Delta_{cf} = -0.05$ eV and $\Delta_{so} = 0.16$ eV. The percentage *d*-character of the uppermost valence band level was calculated by the procedure of Shay *et al* (1973) to be approximately 35%.

The Arrhenius plot of conductivity in the temperature region 400–77 K is shown in figure 3. Near the room temperature the activation energy is 80 meV and in the temperature range 120–77 K, the activation energy is a few meV. All the films were found to be *p*-type with a hot probe test. Hence the activation energy of 80 meV is attributed to shallow acceptors. Within the hydrogenic approximation of shallow acceptors, the acceptor ionization energy is given by

$$E_A = 13.6(m_p^*/m_0)/\epsilon^2, \tag{3}$$

where ϵ is the static dielectric constant of CuInSe₂ and the hole effective mass $m_p^* = 0.73 m_0$. This gives a calculated value of $E_A = 110$ meV which agrees quite well with that observed here. The low temperature activation energy is probably due to surface or grain boundary migration energy.

5. Conclusions

From the analysis of the optical absorption spectrum of thin films of CuInSe₂ near the band edge, the zone centre valence band structure has been determined. The

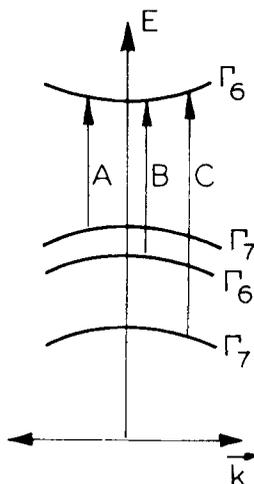


Figure 4. Zone centre band structure of CuInSe₂.

electrical conduction in thin film is dominated by impurity levels of activation energy $E_A = 80$ meV above 200 K and by grain boundary scattering below 200 K.

References

- Garcia F J and Tomar M S 1983 *Jpn. J. Appl. Phys. Suppl.* **53**
Herman A and Zweibel K 1983 *Proc. SPIE Int. Soc. Opt. Eng.* **407** 96
Krishnaswamy S V, Manocha A S and Szedon J R 1983 *J. Vac. Sci. Technol.* **A1** 510
Loferski J J 1981 *Proc. International workshop on physics and semiconductor devices, India*, pp 408
Mickelsen R A, Chen W S, Hsiao Y R and Lowe V E 1984 *IEEE Trans. Electron Devices* **31** 542
Neumann H, Horig W, Reccius E, Sobotta H, Schumann B and Kuhn G 1979 *Thin Solid Films* **61** 13
Neumann H, Perl B, Abdul Hussein N A K, Tomlinson R D and Hill A E 1982 *Crystal Res. Technol.* **17** 469
Pamplin B and Feigelson R S 1979 *Thin Solid Films* **60** 141
Rowe J E and Shay J L 1971 *Phys. Rev.* **B3** 451
Shay J L, Tell B, Kasper H M and Schiavone L M 1973 *Phys. Rev.* **B7** 4485
Shay J L, Wagner S and Kasper H M 1975 *Appl. Phys. Lett.* **27** 89
Shay J L and Wernick J H 1975 Ternary chalcopyrite semiconductors: Growth, electronic properties and applications (New York: Pergamon)