

Growth and properties of CuInS₂ thin films

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MS received 12 May 1997; revised 6 January 1998

Abstract. Single phase copper indium disulphide (CuInS₂) thin films of thickness between 60 nm and 650 nm with the chalcopyrite structure are obtained on NaCl and glass substrates by flash evaporation. The films were found to be *n*-type semiconducting. The influence of the substrate temperature on the crystallinity, conductivity, activation energy and optical band gap was studied. An improvement in the film properties could be achieved up to a substrate temperature of 523 K at a molybdenum source temperature of 1873 K.

Keywords. CuInS₂; flash evaporation; substrate temperature.

1. Introduction

Copper indium disulphide (CuInS₂) is one of the I–III–VI₂ ternary chalcopyrite semiconductors which has been attracting considerable interest in recent years. It has some exceptional material characteristics and properties with a potential for effective photovoltaic conversion. In fact, a theoretical calculation by Meese *et al* (1975) predicted solar conversion efficiencies between 27% and 32% for CuInS₂ based homojunctions having a direct band gap of 1.55 eV. An efficiency of 7.3% obtained by using a ZnO/CdS/CuInS₂ solid-state thin film solar cell (Mitchell *et al* 1988) and that of 9.7% by using a CuInS₂-based photochemical cell (Lewerenz *et al* 1986) had been reported. If a material is to attain any large scale and economical device utilization, its production in thin film form is a necessity. Accordingly, several workers have studied the growth and physical properties of CuInS₂ thin films prepared using a variety of methods and modifications (Hodes *et al* 1980; Hwang *et al* 1980; Saman *et al* 1986). It has always been found difficult to obtain single phase films with reproducible results by thermal evaporation methods whereas other methods are complex in nature leading to a large variation in the physical properties of these CuInS₂ films. Since CuInS₂ dissociates incongruently, it was found (Hwang *et al* 1978) very difficult to deposit single phase CuInS₂ thin films by the flash evaporation method which is so successfully used for the growth of a variety of binary and ternary chalcogenides. Recently, Abo El Soud *et al* (1993) reported the transport properties of CuInS₂ thin films prepared by thermal vacuum evaporation of the bulk compound but did not report any structural characterization of the films. This is particularly important as it has been reported earlier (Kazmerski *et al* 1977)

that single source evaporation does not produce good quality single phase CuInS₂ films. Neumann *et al* (1981) reported the optical properties of CuInS₂ thin films prepared by flash evaporation but again without any details of structural properties. In view of the technological importance of the material and dearth of information concerning the growth and characterization of CuInS₂ thin films prepared by flash evaporation, we report here our results on the same which should prove useful in further research work.

2. Experimental

Single phase CuInS₂ bulk compound was synthesized first, by the stoichiometric mixing and fusing of the high purity (99.999%) individual elements. The single phase bulk with a grain size of about 100–150 μm was utilized as the source material for flash evaporation. The distance between the source and the substrate was kept constant at about 12 cm. A molybdenum boat maintained at a sufficiently high temperature of about 1873 K was found to lead to monophasic film formation. Glass slides and freshly cleaved NaCl surfaces were used as the substrates. Substrate temperature, as measured using a chromel–alumel thermocouple, was varied in the range 300–650 K. The film thicknesses (from 60 nm to 650 nm) were measured during the deposition using a quartz crystal monitor. A measured pressure of about 1 × 10⁻³ Pa was maintained during all the evaporations.

The CuInS₂ films formed on glass and NaCl substrates were examined by X-ray and electron diffraction for structural characterization. The chemical composition was confirmed by energy dispersive analysis of X-rays (EDAX). The optical absorption spectra of the film–glass substrate combination were recorded using a Shimadzu-365 UV-VIS-NIR spectrophotometer in the wavelength

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range 200–1500 nm. The substrate contribution to the optical absorption was corrected by introducing an uncoated substrate in the reference beam. The d.c. electrical resistivity was measured using a high impedance electrometer and pre-evaporated silver films provided ohmic contacts.

3. Results and discussion

3.1 Structural properties

The CuInS_2 deposits formed on cleaved surfaces of NaCl at room temperature (303 K) were always amorphous or had fine grained structure as the electron diffraction patterns were diffuse (figure 1a). When the substrate temperature was raised to about 423 K the films became polycrystalline as shown in figure 1b. The selected area electron diffraction (SAED) pattern could be indexed on the basis of the chalcopyrite structure of CuInS_2 films. The values of the crystallographic parameters obtained are $a = 0.5498$ nm and $c = 1.1095$ nm in close agreement with those reported by Hwang *et al* (1978). The energy

dispersive analysis of X-rays indicated the atomic percentage ratio of Cu : In : S as 24.8 : 26.0 : 49.2. A further raise of substrate temperature to about 523 K caused an improvement in the crystallite size and crystallinity (figure 1c). The average grain size was found to be about 80 nm. An increased $\langle 001 \rangle$ type orientation could be observed. Still higher substrate temperature was found to lead to the dissociation of the single phase and the films exhibited deficiency in sulphur content. Annealing in a sulphur atmosphere at this stage may compensate the deficiency which, however, could not be carried out in the present case.

The CuInS_2 films formed on glass substrates at room temperature (303 K) were found to be poorly crystalline as indicated by the X-ray diffraction (figure 2a). At a substrate temperature of 523 K the diffraction peak corresponding to the (112) reflection of the chalcopyrite structure became sharper and stronger indicating an improvement in the single-crystallinity of the films (figure 2b). A preferential orientation of the (112) axis compared with the (220) orientation could be observed. A further rise in the substrate temperature led to sulphur deficient

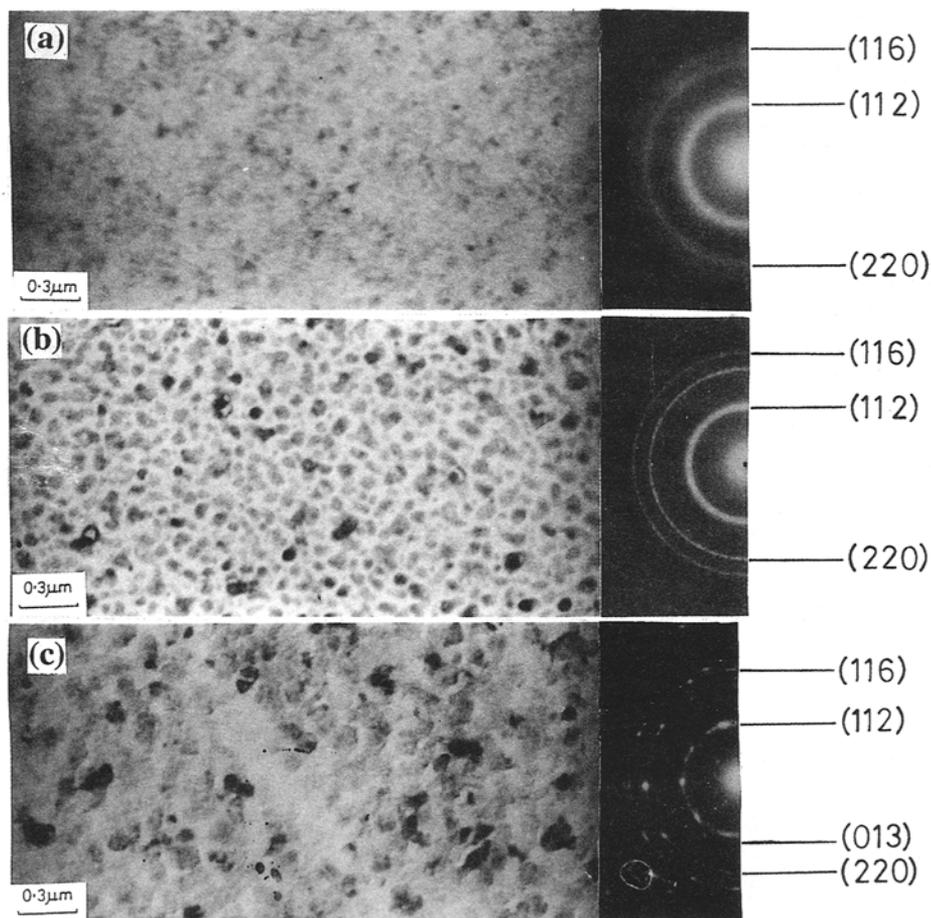


Figure 1. Transmission electron micrograph and the corresponding SAED pattern of CuInS_2 films formed on NaCl substrate at (a) 303 K, (b) 423 K and (c) 523 K (film thickness, 60 nm).

films. Also, when the source temperature was increased beyond 1873 K multiphase films resulted with CuInS_2 , InS and In being the dominant ones, as observed both in electron and X-ray diffractions. It is to be noted here that the (112) orientation observed in our flash evaporated films was also observed in the CuInS_2 films prepared by various other techniques (Nishitani *et al* 1992; Takahiro Wada *et al* 1993).

3.2 Electrical properties

The CuInS_2 deposits formed on glass substrates at room temperature that were found to be poorly crystalline by X-ray diffraction exhibited a high d.c. electrical resistivity. The resistivity, however, decreased with an increase in the substrate temperature owing to the improvement in grain size and single crystallinity of the films. This behaviour can easily be explained on the basis of the well known Petritz's (1956) barrier model. The CuInS_2 films exhibited *n*-type conductivity as determined by hot probe and Hall effect methods. The d.c. resistivity was then measured as a function of temperature in the range 300–423 K for the CuInS_2 films deposited at different substrate temperatures (figure 3). The variation of resistivity (ρ) with temperature (T) could be expressed in the well known form

$$\rho = \rho_0 \exp(\Delta E/kT), \quad (1)$$

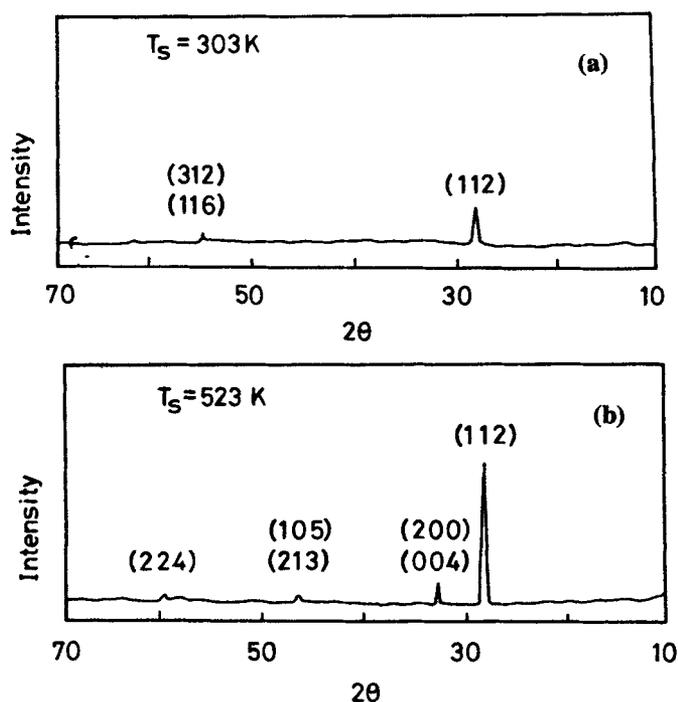


Figure 2. X-ray diffraction patterns of CuInS_2 films formed on glass substrate at (a) 303 K and (b) 523 K (film thickness, 600 nm).

where ρ_0 represents the pre-exponential factor, ΔE the activation energy for electrical conduction and k the Boltzmann constant. The values of conductivity activation energy, ΔE , obtained from the slopes of figure 3 were 0.280, 0.530, 0.570, 0.795 and 0.890 eV for the substrate temperatures of 303, 373, 423, 473, and 523 K, respectively. These values of activation energy are lower compared to the reported intrinsic band gap value of 1.55 eV. Hence, in the observed temperature range 300–423 K the activation energy values may indicate the position of localized gap states below the conduction band edge in these *n*-type CuInS_2 thin films. The increase in the conductivity activation energy with the increase of substrate temperature can be due to the improvement in the crystallite size and crystallinity. The dependence of grain size and orientation upon substrate temperature has been reported for CuInS_2 thin films by Kazmerski *et al* (1975, 1976). Also, as the substrate temperature increases, the impurity content of the film decreases, resulting in activation energy values becoming closer to the single crystalline value.

Preliminary investigations on the Hall effect in these films deposited at 473 K indicated the values of electron mobility and concentration as $5 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{sec}^{-1}$ and $2 \times 10^{18} \text{ cm}^{-3}$, respectively. These values appear to be

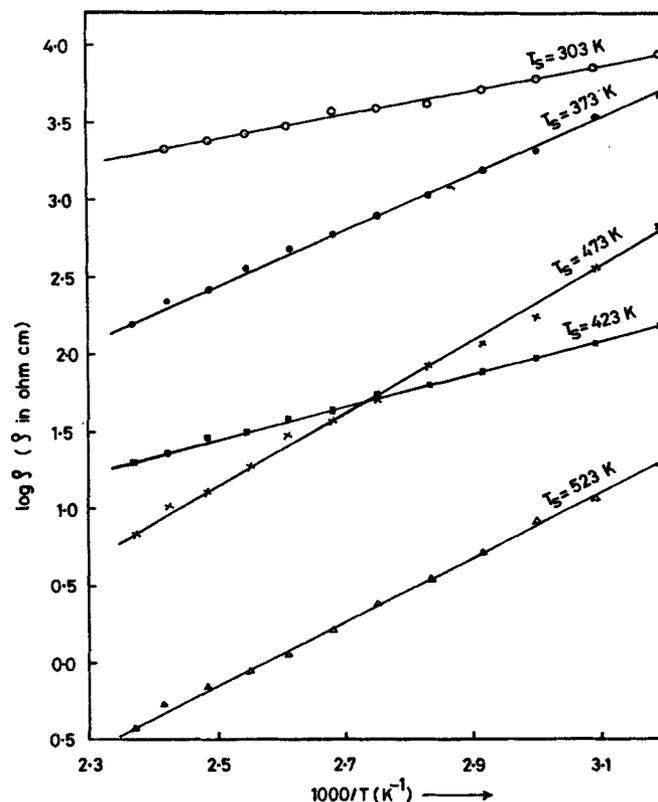


Figure 3. Variation of electrical resistivity with temperature of CuInS_2 films formed on glass substrate at different temperatures (film thickness, 650 nm).

attractive at this stage, considering the polycrystalline nature of the films and simple deposition process without any pre and post-deposition treatment. At still higher substrate temperature (> 523 K) dissociation of the CuInS_2 single phase was observed. Kazmerski *et al* (1975) reported an electron mobility range of $1\text{--}10 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{sec}^{-1}$ for their single and double source deposited $n\text{-CuInS}_2$ thin films. It is to be mentioned here that most of the recent reports (Abo El Soud *et al* 1993) dealt with only p -type CuInS_2 thin films with extremely poor values of hole mobility. Hence our work attains significance and further work is in progress for obtaining high mobility thin films.

3.3 Optical properties

The intrinsic absorption edge of the flash evaporated CuInS_2 thin films was examined using the relation given by Bardeen *et al* (1956) which states that the absorption coefficient α is related to the incident photon energy ($h\nu$) as

$$\alpha h\nu = \beta(h\nu - E_g)^x, \quad (2)$$

where E_g is the energy gap and $x = 1/2$ for a direct allowed transition. β is the parameter that depends on the transition probability. A plot of the average value of $(\alpha h\nu)^2$ against $h\nu$ was found to be a straight line for the films deposited at different substrate temperatures (figures 4a and b). The intercepts of these linear plots on the energy axis at $(\alpha h\nu)^2 = 0$ gave the band gap energies at different substrate temperatures. These direct optical band gap energy values were found to be 1.16, 1.20, 1.26 and 1.31 eV at glass substrate temperatures of 303, 373, 473, and 523 K, respectively. Thus, we found that the optical band gaps increased with increasing substrate temperature in CuInS_2 thin films. At lower substrate temperatures the presence of localized states leads to lower band gap values. Higher substrate temperatures reduce the density of band tail states i.e. localized disordered regions. As mentioned earlier, substrate temperature could not be increased beyond 523 K in the present studies.

It is to be observed here that the optical band gap energy values, obtained as above, are smaller than the reported (Rocket and Birkmire 1991) single crystal value of 1.55 eV. It is known that in the case of CuInS_2 the thin films show band gaps less than the single crystal value (Gupta and Murthy 1991; Takahiro Wada *et al* 1993). Neumann *et al* (1981) reported a direct optical gap of 1.524 ± 0.005 eV in their CuInS_2 thin films obtained by a flash evaporation technique at a substrate temperature of 720 K. In addition to this, an indirect allowed transition was also observed at 1.565 ± 0.005 eV by them. It is known (Kazmerski and Juang 1977) that

CuInS_2 films with excess of sulphur are p -type and with deficiency of sulphur are n -type. Hence, such higher substrate temperatures are not feasible in our already n -type CuInS_2 films, which would otherwise lead to a further deficiency of sulphur and disturb the single phase nature.

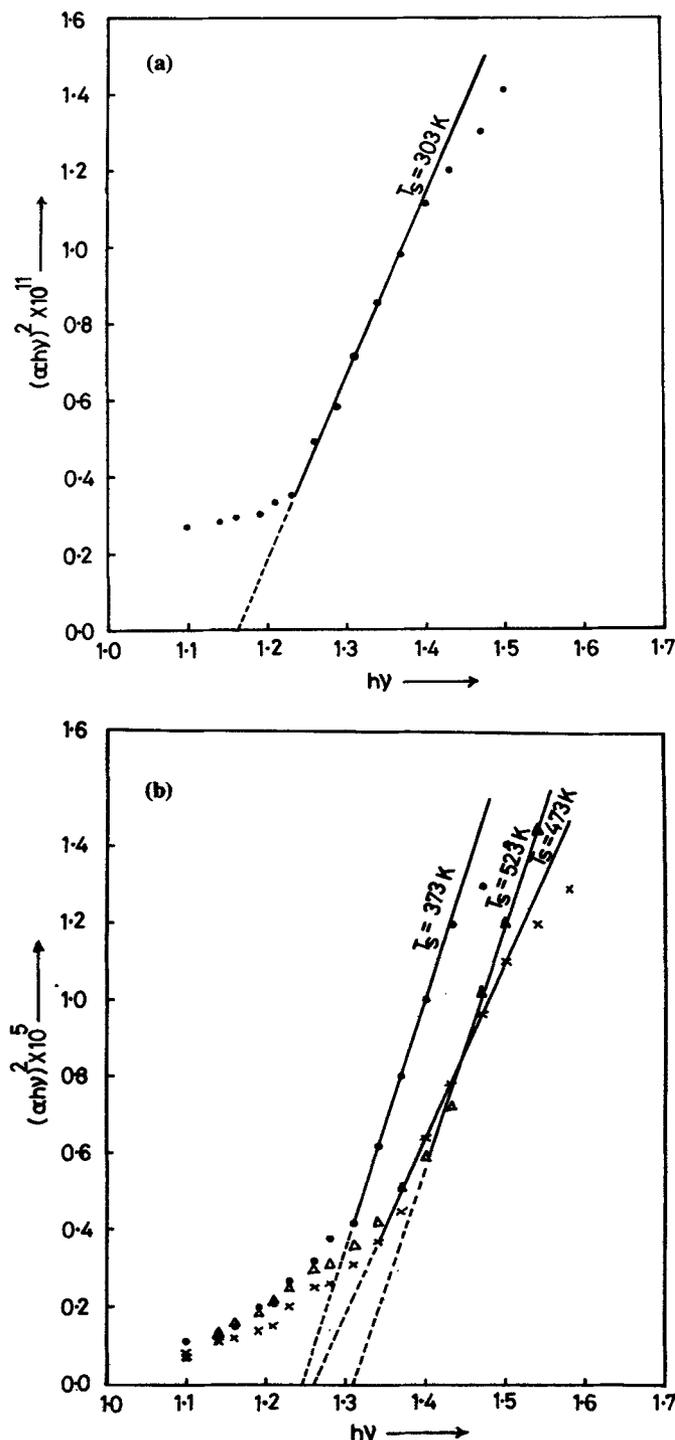


Figure 4. Variation of $(\alpha h\nu)^2$ vs photon energy ($h\nu$) for films formed on glass substrates at (a) 303 K and (b) $\bullet = 373$ K, $\times = 473$ K, $\Delta = 523$ K (film thickness, 60 nm).

4. Conclusions

Single phase CuInS₂ thin films with chalcopyrite structure could successfully be grown by the flash evaporation method. The films were found to be *n*-type semi-conducting in nature. The influence of substrate temperature on the crystallinity, conductivity activation energy and optical band gap was investigated. A molybdenum source temperature of 1873 K and a substrate temperature of 523 K were found to be the upper limits for obtaining reproducible results and single phase *n*-type CuInS₂ thin films in our flash evaporation process.

Acknowledgement

One of the authors (SHC) is grateful to the Council of Scientific and Industrial Research (CSIR), New Delhi for the award of a Senior Research Fellowship for carrying out this work.

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