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Growth and characterization of $CuInSe_2$ thin films

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Films of $CuInSe_2$ have been grown using a technique similar to close-spaced vapour transport. The effect of substrate temperature and the distance of the substrate from the source have been optimised to grow well-oriented chalcopyrite phase of $CuInSe_2$. D.c. conductivity and Hall coefficient studies have been made in the temperature range 77–300 K. The films grown at a substrate temperature of 350 °C have an electron mobility of 3.4×10^3 $cm^2 V^{-1} s^{-1}$ at 77 K.

Introduction

The ternary compound semiconductor $CuInSe_2$ (CIS) which belongs to the family of chalcopyrites, has emerged recently as a promising solar cell material [1]. This is mainly due to the fact that the energy gap observed for this compound, $E_g \approx 1.04$ eV at room temperature [2, 3] is ideal for solar photovoltaic conversion. It also possesses a very high absorption coefficient and can be made n- or p-type conducting. Durable, efficient and low-cost solar cells have been made of it. Shay *et al.* [4] have reported heterojunction solar cells of n-CdS/p-$CuInSe_2$ with an efficiency of 12%. For economic reasons, low-cost production methods are under active study. The possibility of large-scale production makes thin-film approach an effective method for producing durable and highly efficient solar cells [5–7] with low cost.

The structural, electrical and optical properties of $CuInSe_2$ films are influenced greatly by the growth technique. Several techniques have been used to prepare $CuInSe_2$ thin films, e.g. single-source evaporation [8], two-source evaporation [9], flash evaporation [10], molecular beam epitaxy [11], sputtering [8, 12] and spray pyrolysis [13]. Most of these investigations show the production of polycrystalline films. Because the crystallinity of the films affects the efficiency of the photovoltaic device, we have produced well-oriented films of $CuInSe_2$ using a modified single-source evaporation technique. This growth technique is similar to close-spaced vapour transport (CSVT) technique. The effect of growth parameters, i.e. substrate temperature and the distance of the substrate from source, on the structural, optical and electrical properties of $CuInSe_2$ have been studied in detail.

2. Experimental procedure

A large number of rectangular films of $CuInSe_2$ of size 21 mm × 4 mm were grown from a stoichiometric charge prepared using a mixture of high-purity (> 99.999%) elements, copper, indium and selenium, containing 2% excess indium, by a resistive heating technique in different batches using a tantalum boat. Fresh source material was used in each evaporation. The method used to grow the films is very similar to close-spaced vapour transport. In this technique, the distance between the source and the substrate is kept very small compared to the conventional evaporation technique and the evaporation is carried out in a high vacuum $\sim 5 \times 10^{-6}$ torr (1 torr = 133.322 Pa). The utility of this technique has already been established for growing II–VI compound thin films [14, 15]. The films were grown on mica and glass substrates preheated to various temperatures by varying the distance between the source and substrate under the vacuum of 5×10^{-6} torr. The deposition rate was of the order of about 1.5 nm s^{-1} and the thickness of the films was monitored using a quartz crystal thickness monitor. The thickness of the films was in the range of 0.4–1.0 μm. The Van der Pauw method was used to measure the d.c. conductivity and Hall coefficient in the temperature range 77–300 K. The films grown with 2% excess indium were found to be n-type, which was confirmed by the hot-probe method.

3. Results and discussion

3.1. X-ray diffraction

The structures of the films were studied by X-ray diffraction using Philips (PW 1804/01/11) diffractometer and CuK_α radiation. The X-ray diffraction spectrum of $CuInSe_2$ powder with 2% excess indium used to grow the films, is shown in Fig. 1a. The spectrum of the powder is seen to exhibit the sharp peaks at $2\theta = 26.6°$, 35.5°, 44.3° and 50.4°, which correspond to

(1 1 2), (2 1 1), (2 2 0) and (3 1 2) characteristic planes of chalcopyrite phases of $CuInSe_2$. The peak positions are in good agreement with the ASTM X-ray powder file data (23–209) for chalcopyrite phase. It may be mentioned that 2% excess indium over the stoichiometric charge has been taken to have n-type $CuInSe_2$ films [16], and no extra peak was observed due to this excess indium.

3.2. XRD studies on film grown at near normal incidence ($< 30°$)

Fig. 1b–g show the X-ray spectra of the films grown at different substrate temperatures, T_s, between 100 and 350 °C and by varying the distance, D between substrate and source, 3–15 cm. The films grown at 100 °C with a separation of 3 cm between source and substrate have a peak at $2\theta = 21.0°$, as shown in Fig. 1b. This peak does not correspond to any binary or ternary phase of $CuInSe_2$. A similar type of peak at $2\theta = 21.0°$ has also been observed by other workers [3, 17] for spray-deposited and vacuum-evaporated films. Gorska *et al.* [17] have assigned this peak to the In_2O_3 phase in the films. When the distance between source and substrate was increased from 5 cm to 15 cm the films were amorphous in nature, showing no peak corresponding to any plane as shown in Fig. 1c.

The films grown at 250 °C substrate temperature with a separation of 3 cm between source and substrate have two peaks at 21.0° and 26.6°, as shown in Fig. 1d. The peak at $2\theta = 26.6°$ corresponds to the (1 1 2) plane of $CuInSe_2$. No peak corresponding to other planes of CIS at 35.5° and 44.3° were observed, which indicates the sphalerite structure of the films [18]. However, the films grown with a separation of 5–15 cm were also found to have sphalerite structure of CIS, but in these films no peak at 21.0° was observed, as shown in Fig. 1e.

Fig. 1f shows the X-ray diffraction spectrum of films grown at a substrate temperature of 350 °C with a distance between source and substrate of 3 cm. The peaks at 26.6°, 35.5° and 44.3° correspond to (1 1 2), (2 1 1) and (2 0 4) (2 2 0) planes of $CuInSe_2$, respectively, confirming the chalcopyrite structure of the films. However, in these films a peak at $2\theta = 21.0°$ is also observed [3]. In the films grown with a separation of 5–15 cm at this substrate temperature, peaks at 26.6°, 35.5° and 44.3° were observed showing chalcopyrite structure of $CuInSe_2$ [18, 19]. No peak at $2\theta = 21.0°$ was observed in these films. A typical spectrum of the film grown at 350 °C with a separation of 5 cm is shown in Fig. 1g.

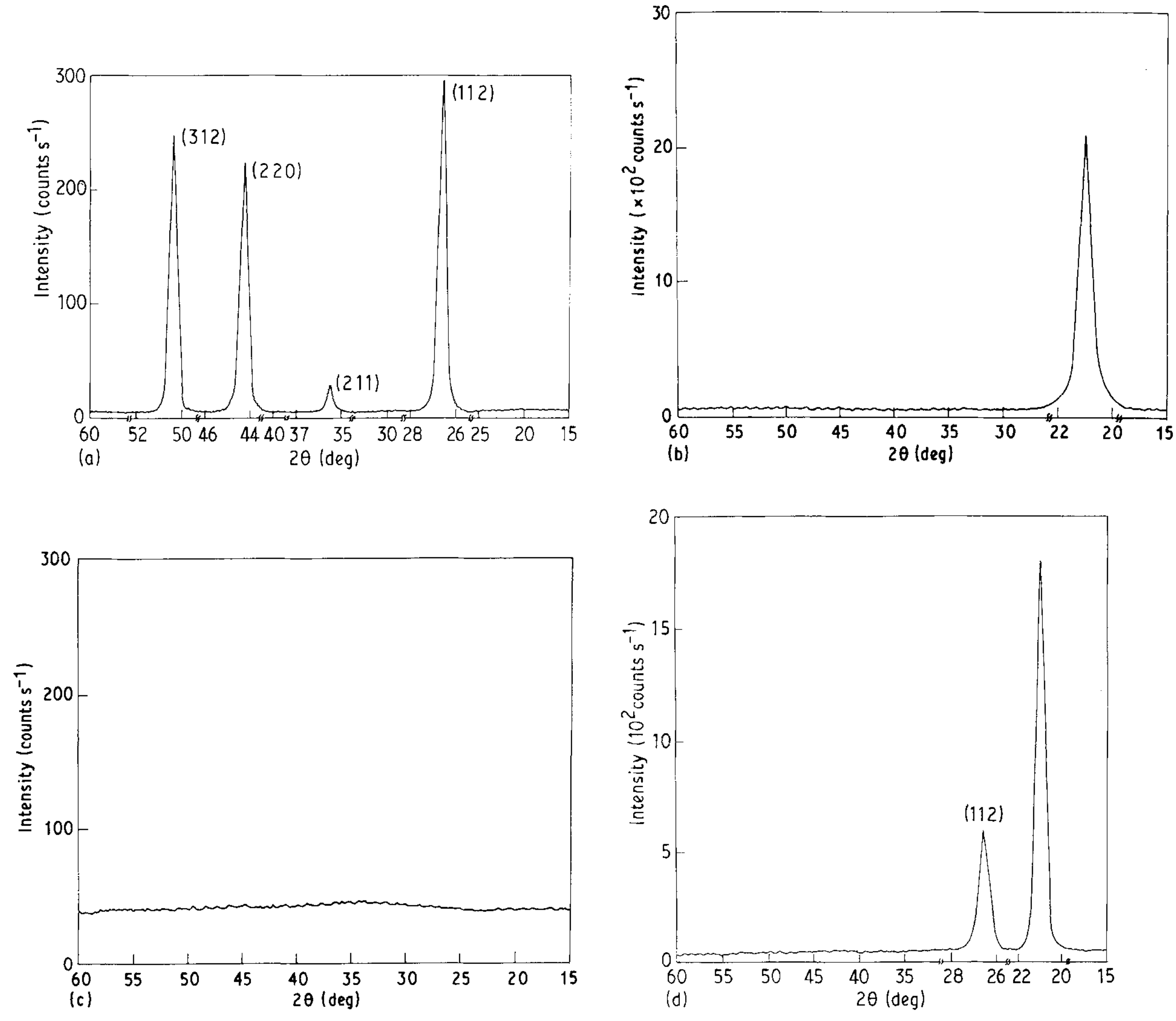
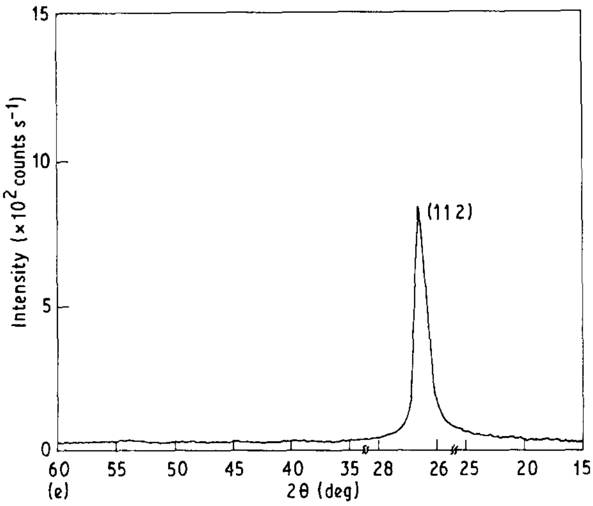
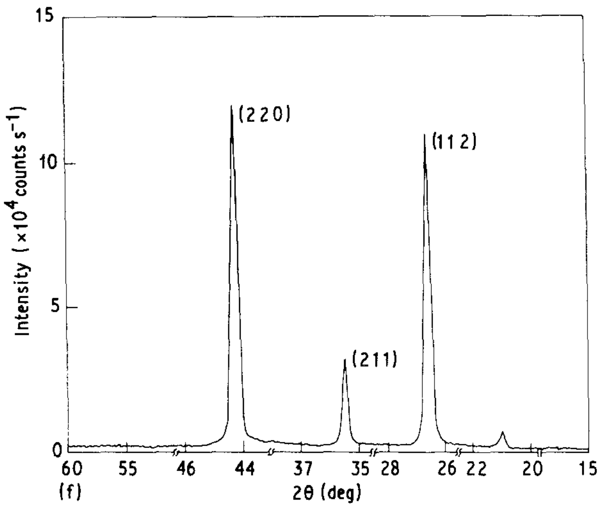


Figure 1 a–d.





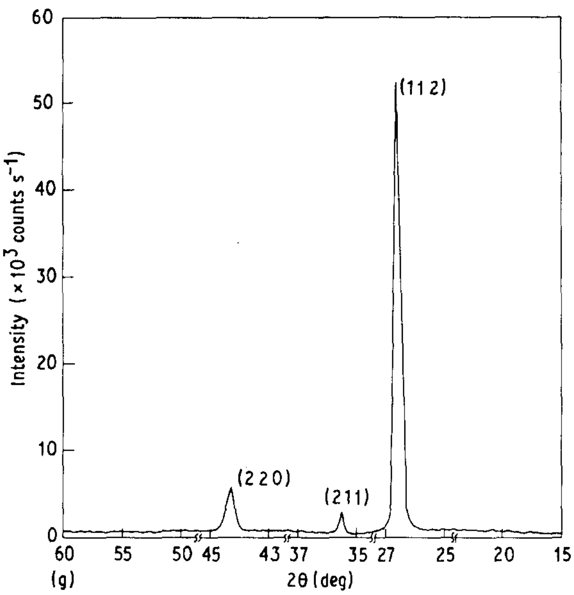


Figure 1 X-ray diffraction spectra of (a) $CuInSe_2$ powder with 2% excess indium; (b–g) films grown at substrate temperature and source–substrate separation of $T_s = 100\,°C$, $D = 3$ cm; (c) $T_s = 100\,°C$, $D = 5$–15 cm; (d) $T_s = 250\,°C$, $D = 3$ cm; (e) $T_s = 250\,°C$, $D = 5$–15 cm; (f) $T_s = 350\,°C$, $D = 3$ cm; (g) $T_s = 350\,°C$, $D = 5$–15 cm.

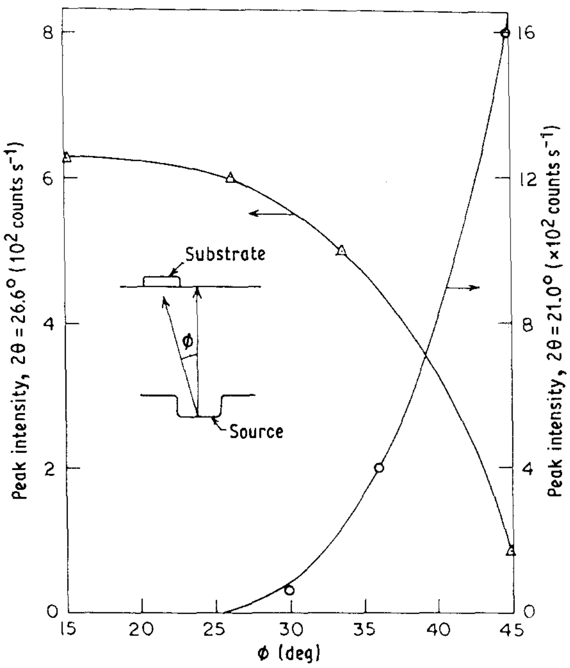


Figure 2 Variation of peak intensity at $2\theta = 21.0°$ and $26.6°$ with ϕ, for films at $T_s = 350\,°C$.

3.3. XRD studies of films grown at an oblique angle (> 30°)

For the films grown at substrate temperatures of 250 and 350 °C, a peak at $2\theta = 21.0°$ is always present, irrespective of the distance between source and substrate. It is also observed that the height of the peak at 21.0° increases with increase in the oblique angle, ϕ, whereas the height of CIS peak at 26.6° continues to decrease with increasing oblique angle. The variation of peak intensity at $2\theta = 21.0°$ and 26.6° with oblique angle, ϕ, for the films grown at 350 °C is shown in Fig. 2.

Thus the films grown at a substrate temperature of 350 °C with a separation of 5–15 cm and $\phi < 30°$ were found to have a chalcopyrite structure of $CuInSe_2$. However, the crystallinity of the films improves as the distance decreases. The optimum distance between source and substrate was found to be 5–7 cm. XRD results, i.e. peak position and the nature of the $CuInSe_2$ phase in the films grown on glass were similar to those grown on mica substrates. However, the peak height was slightly less. The optical and electrical results reported here are for the films grown on mica substrates under optimum condition.

3.4. Optical band gap

Optical transmission measurements were performed on $CuInSe_2$ films grown at 350 °C substrate temperature. The optical band gap and absorption coefficient, α, in the region of the fundamental absorption edge were determined at various photon energies from the transmission spectra using the relation

$$\alpha = \frac{1}{d} \ln \left(\frac{1}{T} \right) \qquad (1)$$

where d is the thickness of the film and T is the observed transmittance. The results were replotted according to the direct transition

$$\alpha = \frac{B}{h\nu}(h\nu - E_0)^{1/2} \qquad (2)$$

where E_0 is the optical band gap and B is a constant. A typical plot of $(\alpha h\nu)^2$ with photon energy ($h\nu$) for a 0.4 μm thick $CuInSe_2$ film is shown in Fig. 3. Extrapolation of the linear portion of the curve to $(\alpha h\nu)^2 = 0$ gives the optical band gap, which is about 1.1 eV. The value is in good agreement with the standard band gap of 1.04 eV [2, 3].

3.5. Electrical properties

Electrical measurements were carried out on various $CuInSe_2$ films grown at 350 °C. Typical results of Hall coefficient and Hall mobility taken on a film of 0.6 μm thickness are reported. The measurements were made in the temperature range 77–300 K. The observed variation of Hall coefficient, R_H, as a function of temperature (log R_H versus $10^3/T$), is shown in Fig. 4 for CIS film. It is evident from the figure that the Hall coefficient decreases slowly in the temperature range 125 K and above. The value of carrier concentration at 300 K is found to be 1.36×10^{15} cm^{-3} for CIS film grown on a mica substrate. The carrier activation energy, E_n, in these film can be estimated using the relation

$$R_H \propto \exp(E_n/K_B T) \qquad (3)$$

The carrier activation energy was found to be 9.5 meV in the lower temperature region (77–90 K) and 194 meV in the higher temperature region (230–300 K). This suggests that there exist two donor levels at 9.5 and 194 meV below the conduction band. Such type of donor levels at 8 ± 2 and 180 meV have also been reported by other workers [20, 21]. The shallow donor level (10 meV) has been reported to be due to defects originating from the presence of indium in the copper site (In_{Cu}), whereas the donor level corresponding to 180 meV is due to the interstitial indium as may be expected from the sample grown from a charge with excess indium.

The variation of observed Hall mobility, μ_H, of $CuInSe_2$ film on mica is shown in Fig. 5 as a function of temperature in the temperature range 77–300 K. Typically, the mobility of the CIS film is 3.4×10^3 $cm^2 V^{-1} s^{-1}$ at 77 K and 20 $cm^2 V^{-1} s^{-1}$ at 300 K. The mobility is found to decrease with increasing temperature. It may be observed that the mobility, μ_H, decreases with increasing temperature above 100 K, suggesting the observed mobility in the films is limited by lattice scattering in this temperature region. The mobility variation in the lower temperature region (77–100 K) shows weak dependence on the temperature suggesting that the mobility of the charge carriers is limited by neutral and ionized impurity scatterings. Such a type of mobility variation has also been reported for $CuInSe_2$ films [20].

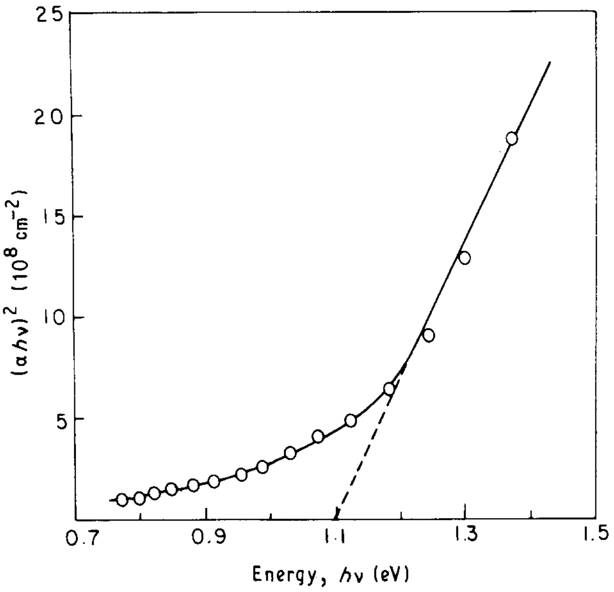


Figure 3 Variation of $(\alpha h\nu)^2$ with photon energy ($h\nu$).

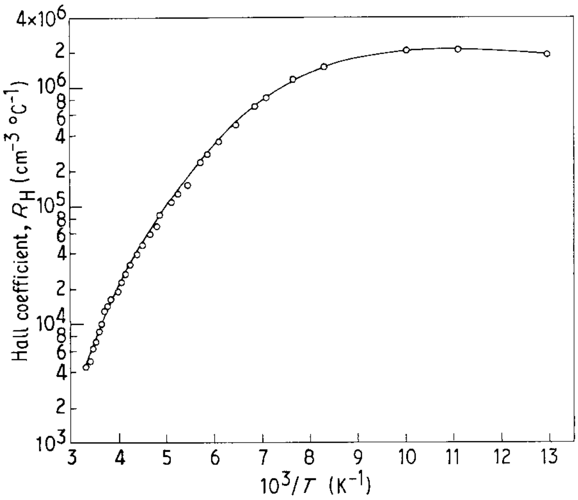


Figure 4 Variation of Hall coefficient R_H, with $10^3/T$.

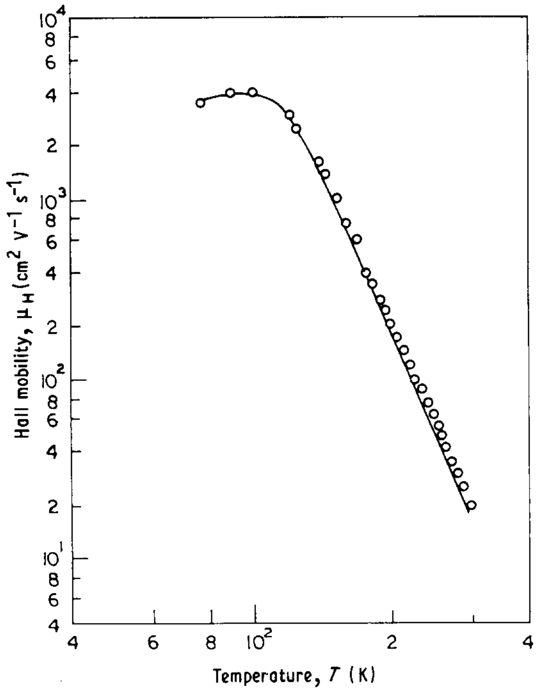


Figure 5 Variation of Hall mobility, μ_H, with temperature.

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