ISSN 1330–0008
CODEN FIZAE4

PROPERTIES OF AMORPHOUS AND CRYSTALLINE p-$CuInSe_2$ THIN FILMS

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Received 11 May 1992
UDC 538.95

Original scientific paper

Structural and optical properties of amorphous and crystalline p-$CuInSe_2$ thin films of different thicknesses were studied. The effect of annealing temperature on these properties were investigated. The thin films were prepared by thermal vacuum evaporation of the bulk. The films were investigated by X-ray diffraction and electron microscope technique. The lattice constants for p-$CuInSe_2$ in powder form were found to be $a = 0.5766$ nm and $c = 1.1329$ nm. The optical constants (refractive index n, absorption index k and absorption coefficient α, valence band density of states g_i and dielectric constants ε', ε'') were determined. The analysis of the optical absorption spectra revealed the exsistence of three optical transition mechanisms: allowed direct transition with $E_g^{d_1} = 1.014$ eV, forbidden direct transition with $E_g^{d_2} = 1.14$ eV and indirect transition with $E_g^i = 1.082$ eV. The optical constants n, k, ε', ε'' and g_i found to depend on the annealing temperature. The d.c. conductivity was measured as a function of the temperature and the data were analysed in order to establish he conduction mechanism in the measured temperature range.

1. Introduction

In recent years the ternary chalcopyrite semiconductor $CuInSe_2$ has been received considerable attention to gain a better and deeper understanding of the structural, optical and electrical properties of this material, since it shows promis-

ing properties for practical use as an effective absorber-generator material in thin film solar cells[1)].

$CuInSe_2$ crystallizes in the chalcopyrite structure which is closely related to that of zinc blende with lattice parameters $a = 0.5785$ nm and $c = 1.157$ nm at room temperature[2)]. This ternary material is a direct band gap semiconductor with a fundamental absorption edge between 0.94 and 1.06 eV[3−5)] which is close to optimum for terrestial photovoltaics[6)]. The electronic behaviour including the type (n or p) can be controlled with small variation in stoichiometry of the constituent elements (Cu, In, Se), which can be achieved through simple annealing treatments[7−10)]. Heterojunction solar cells of $CdS/CuInSe_2$ single crystal[8)] and $CuInSe_2$ thin film solar cell[11)] with efficiencies greater than 10% after post-deposition heat treatment have been reported. Mirovsky et al.[12)] found that single crystal of n-$CuInSe_2$ in aqueous polysulfide solution exibit a quantum efficiencies of 0.8 – 0.9 in the wavelenght region between 600 – 1150 nm when used as photoanodes in photoelectrochemical cells. In the present work an attempt was made to study the effect of the annealing temperature on the structure and the optical properties of $CuInSe_2$ thin films, and also on the mechanism of conduction in this material.

2. Experimental

$CuInSe_2$ was prepared by direct fusion of spec-pure Cu, In and Se in sealed evacuated silica tube. The mixture was heated at 850 °C for 20 hours. The tube was shaken through the melting operation to ensure the mixing of the elements. The temperature was then reduced to 300 °C over a period of 6 hours.

Thin films were prepared by thermal evaporation of the fine grain powder from a tantalum boat on clean glass substrates under vacuum of 10^{-3} Pa at deposition rate of 10 nm s^{-1} using Leybold Univex 300 coating unit. The X-ray diffraction patterns were obtained for samples in the powder and thin films by X-ray diffractometer (Philips, P.W. 1373) with a Ni filter and Cu target. Films of about 150 nm thick were used for the investigation.

To study some morphological features of the thin films under test diffraction electron microscopy was carried out using Siemens (West Germany) TEM type.

The transmittance T and the reflectance R at normal incidence for p-$CuInSe_2$ films were recorded using PMQ III Carl Zeiss spectrophotometer in the spectral range from 500 to 2000 nm. The optical absorption coefficient (α) of the films heat treated in vacuum (0.1 Pa) at 373, 423, 473 and 523 K were calculated. The electrical conductivity was measured over the temperature range between 190 ° to 200 °C, using the conventional four-probe method.

3. Results and discussion

3.1. Structural properties of $CuInSe_2$ thin films

X-ray diffraction pattern of the prepared p-$CuInSe_2$ in powder form was recorded using X-ray diffractometer as shovn in Fig. 1. Analysis of this pattern

shows that the powder is polycrystalline chalcopyrite of tetragonal structure phase with the following lattice parameters, $a = 0.5766$ nm and $c = 1.132$ nm, which are in good agreement with the results reported earlier[2,13)].

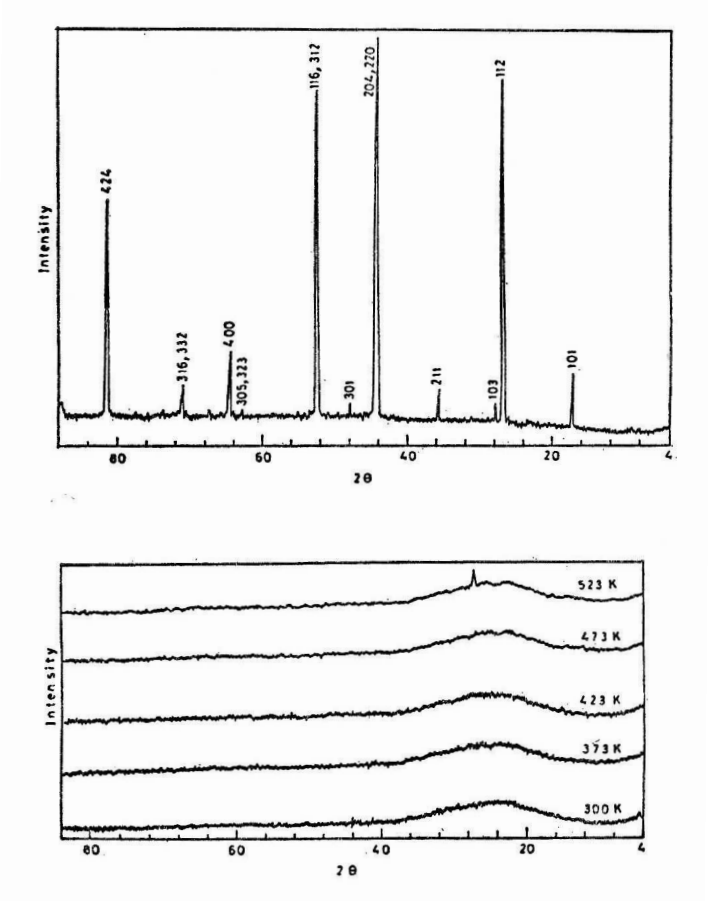

Fig. 1. X-ray diffraction patterns of p-$CuInSe_2$ (a) powder sample, (b) thin films of 170 nm *thickness annealed in vacuum at different temperatures.*

Fig. 1b shows that the thin films of p-$CuInSe_2$ of thickness 150 nm, both as-deposited and annealed in vacuum (0.1 Pa) for 1 hr, at annealing temperature ≤ 473 K are amorphous in nature, while those annealed at 523 K show polycrystalline structure, with preferred orientation about (112) plane. The electron microscope diffraction patterns carried out for films of thickness 75 nm, both as deposited and annealed in vacuum (0.1 Pa) at 423 and 523 K, are illustrated in Fig. 2a, b and c. As observed, for the as-deposited film Fig. 2a and that annealed at 423 K Fig. 2b the rings are diffused indicating that these films have a nature showing amorphous structure, but for those annealed at 523 K (Fig. 2c) the pattern is composed of well defined rings, indicating polycrystalline structure.

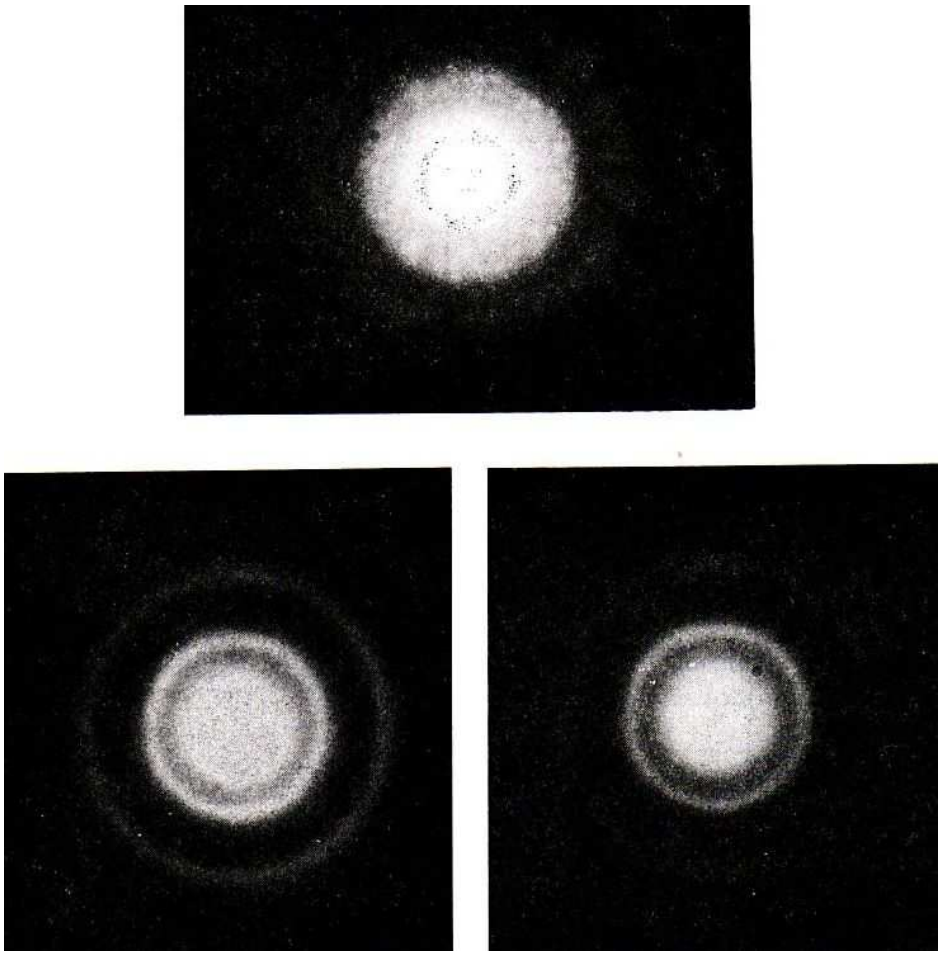

Fig. 2. Electron microscope diffraction patterns of p-$CuInSe_2$ of 75 nm *thickness, for: (a) as-deposited, and for different annealing temperatures, (b) 423 K and (c) 523 K.*

3.2. Optical properties

To investigate the effect of the annealing temperature on the energy gap of *p*-$CuInSe_2$ thin films, the transmission (T) and the reflection (R) at normal incidence in the spectral range 500 – 2000 nm were measured for thin film of thickness 250 nm subjected to different annealing temperature, and the absorption coefficient α was calculated. Taking into consideration that the fundamental absorption edge of *p*-$CuInSe_2$ is due to direct allowed transitions between parabolic bands[14], the energy gap was determined by plotting $(\alpha h\nu)^2$ as a function of the photon energy

($h\nu$) in the range from 1 to 1.25 eV, which is shown in Fig. 3. So the calculated allowed direct gap of the as-deposited film was found to be 1.014 eV.

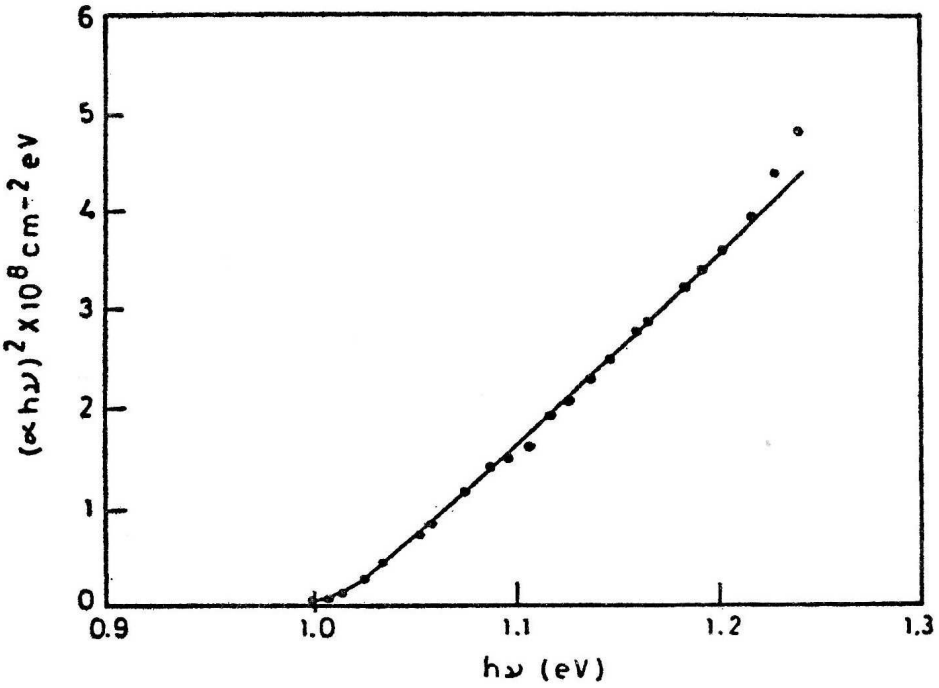

Fig. 3. $(\alpha h\nu)^2$ *as a function of photon energy* $h\nu$ *for the as-deposited* p-$CuInSe_2$ *films of thickness 250* nm.

In the strong absorption region ($h\nu = 1.16 - 1.35$ eV) it was found that the dependence of $(\alpha h\nu)^{2/3}$ and $(\alpha h\nu)^{1/2}$ on $h\nu$ are practicaly linear (Fig. 4). This indicates that the absorption can be due as much to a forbidden direct transition ($E_g^{d_2} = 1.14$ eV) as to an indirect transition $E_g^i = 1.082$ eV). The energy band structure of p-$CuInSe_2$ predicts forbidden direct transition caused by transitions between the copper d-state in the valence bands and the s-type conduction band. These results are in good agreement with those obtained by Varela et al.[15]. The presence of such a forbidden direct transition in p-$CuInSe_2$ has also been detected in thin films prepared by flash evaporation[16] and D.C sputtering techniques[17].

To investigate the effect of annealing temperature on the allowed direct energy gap $E_g^{d_1}$, the calculated absorption coefficient $(\alpha h\nu)^2$ has been represented in Fig. 5 as a function of $h\nu$ for the as-deposited p-$CuInSe_2$ films and those annealed in vacuum (0.1 Pa) at different temperatures (423, 473 and 523 K). It was found that $E_g^{d_1}$ of the as-deposited films and annealed at moderate temperatures (373, 423 and 473 K) were constant (1.014 eV), while it increased to 1.04 eV for films annealed at

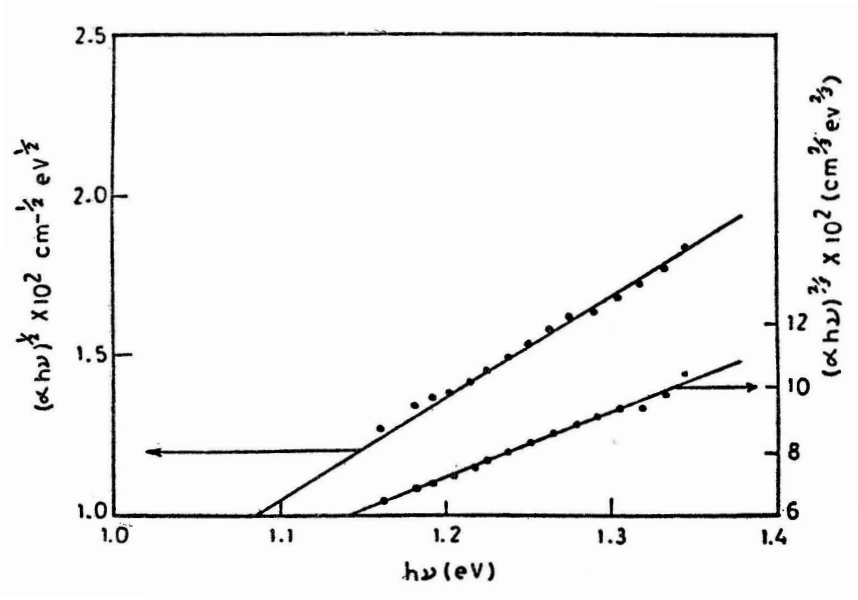

Fig. 4. $(\alpha h\nu)^{1/2}$ *and* $(\alpha h\nu)^{2/3}$ *as a function of photon energy* $h\nu$ *for the as-deposited* p-$CuInSe_2$ *films of thickness 250* nm.

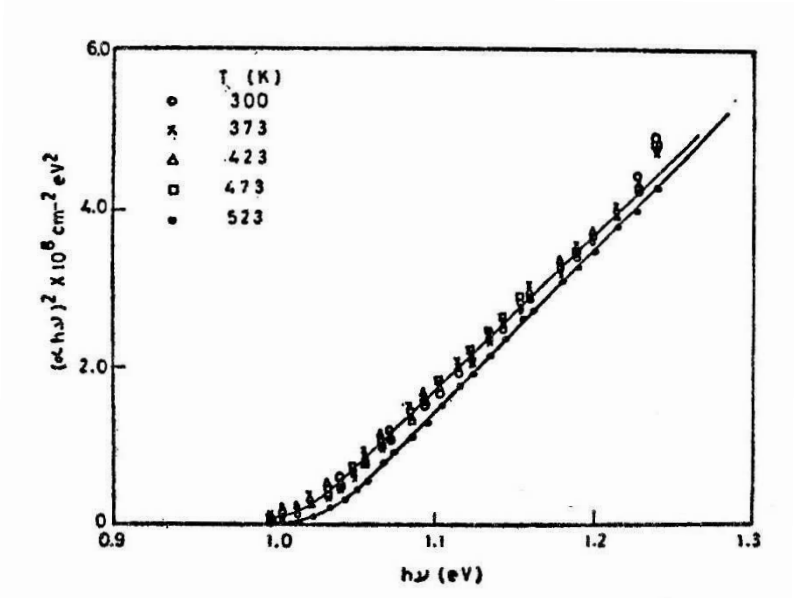

Fig. 5. $(\alpha h\nu)^{1/2}$ *as a function of photon energy* $h\nu$ *for* p-$CuInSe_2$ *films of thickness 250* nm*, for different annealing temperatures.*

523 K. This can be explained by the variation of the disorder and defects present in the amorphous structure with heat treatment. The diminution of disorder and defects in the structural bonding is known to increase the optical gap $E_g^{d_1}$ according to the model of Mott and Davis[18].

As given by Biswas et al.[19] the valence band density of states g_i may be estimated from the following relation

$$g_i(E_g^i - \hbar\omega) = \left(\frac{const \cdot nc}{k_f h^2 \omega_g^2}\right)\left[2\omega(\hbar\omega\,\alpha(\omega)) + \omega\hbar\omega\frac{\mathrm{d}(\hbar\omega\alpha)}{\mathrm{d}(\hbar\omega)}\right] \tag{1}$$

which can be written in a more convenient form

$$g_i(E_g^i - h\nu) = const \cdot n\left[4\pi\nu h\alpha(\nu) + 2\pi\nu h\nu\frac{\mathrm{d}(h\nu\alpha)}{\mathrm{d}(h\nu)}\right] \tag{2}$$

where n is the refractive index.

Representing $\alpha h\nu$ as a function of $h\nu$, the valence band density of states was estimated for different photon energies for p-$CuInSe_2$ thin films annealed at different temperatures and the results are shown in Fig. 6. It was found that g_i decreases only at temperature of annealing equal to 523 K.

The refractive index (n) and the absorption index (k) of films of thickness 250 nm annealed in vacuum at different temperatures were determined from reflection and transmission measurements. The curves of the optical constants n, k and dielectric constants as a function of wavelength are shown in Figs. 7 and 8, respectively. It is clear that the general behaviour of these constants is the same, since they have decreased by increasing the wavelength. It is also clear from the relations that the values of n, k, ε' and ε'' decrease only when the film was annealed at 523 K. The accuracy in the determination of n and k was about $\pm 2\%$.

3.3. Electrical conductivity

The electrical conductivity σ of the prepared thin film ($CuInSe_2$) was measured over the temperature range betwen 80 and 473 K. It can be seen from Fig. 9, that the conductivity increases with increasing temperature. However, the increase is smaller in the low temperature region 80 – 200 K.

In the high temperature region, above 200 K, the conductivity increases exponentially and can be represented by the relation

$$\sigma \sim \frac{1}{T^{1/2}} \exp\left(\frac{-E_\sigma}{KT}\right) \tag{3}$$

where E_σ is the activation energy.

The plot of $\ln \rho T^{1/2}$ versus $1/T$ for the film is shown in Fig. 10. It is clear from this figure that the activation energy in the low temperature range (0.01 eV) is much smaller than that in the high temperature region. The small value at low

temperatures is possibly due to the dominant variable-range hopping mechanism in this temperature range[29]. This can be verified in accordance with the relation

$$\sigma \sim (T_0/T)^{1/4} \tag{4}$$

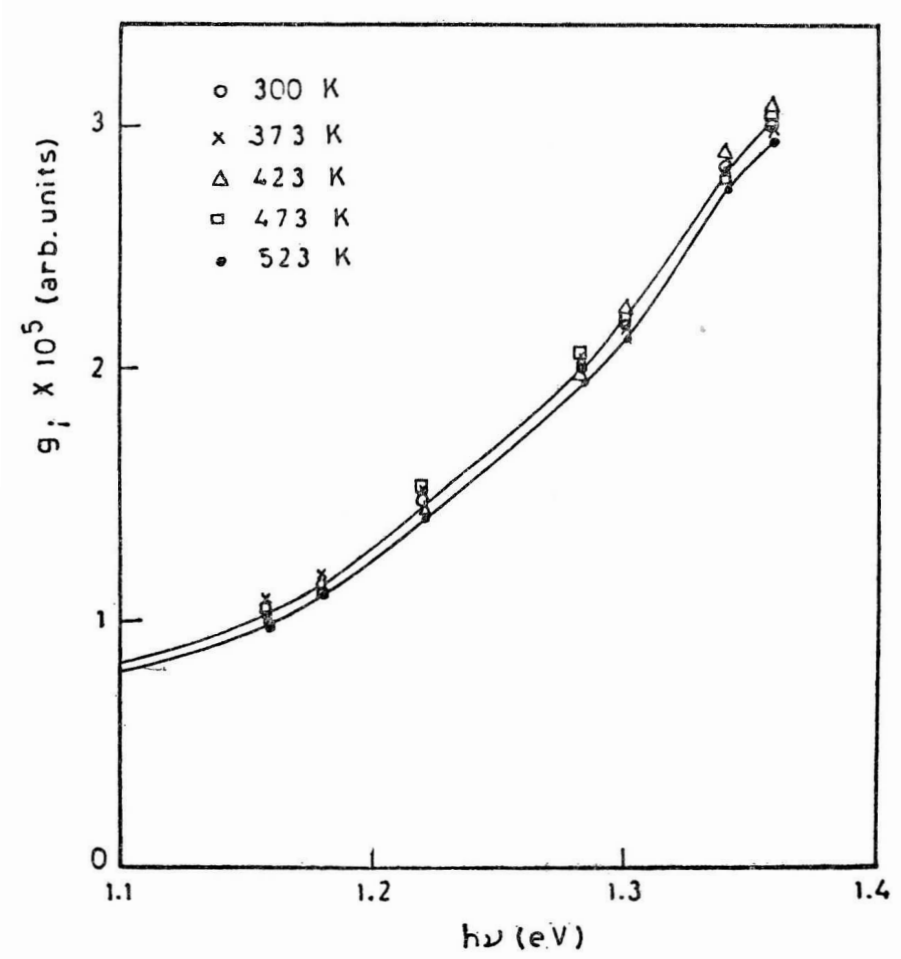

Fig. 6. Density of states g_i as a function of $h\nu$ for p-$CuInSe_2$ *thin films of 250* nm *thickness, for different annealing temperatures.*

By plotting $\ln\sigma$ against $(1/T)^{1/4}$ as shown in Fig. 11, it is clear that the obtained relation is a linear one, which indicates the occurence of a variable-range hopping conduction mechanism. The existence of the localized states necessary for such a conduction process is a consequence of imperfections associated with the polycrystalline nature of the film[21].

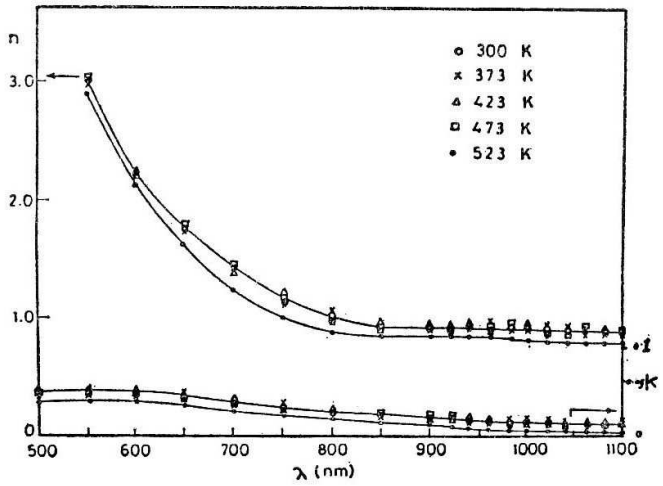

Fig. 7. Dispersion curves of both n and k for p-$CuInSe_2$ thin films of 250 nm *thickness, for different annealing temperatures.*

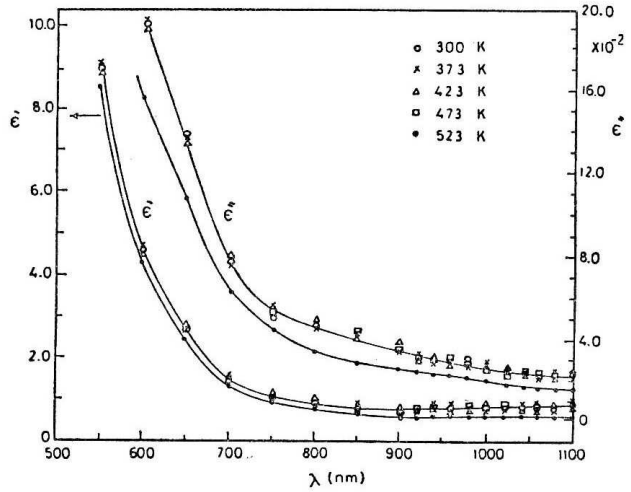

Fig. 8. ε' and ε'' as a function of λ for p-$CuInSe_2$ thin films of 250 nm *thickness, for different annealing temperatures.*

The value of T_0 calculated from Fig. 1 is equal to 6.58×10^2 K. T_0 is related to the density of the localized state $N(E)$ by the relation

$$N(E) = \frac{16\alpha_0^3}{KT_0} \tag{5}$$

Taking the value of $\alpha = 10^7$ cm^{-1}, the value of $N(E)$ calculated using Eq. (5) was found to be 2.82×10^{23} eV^{-1} cm^{-3}.

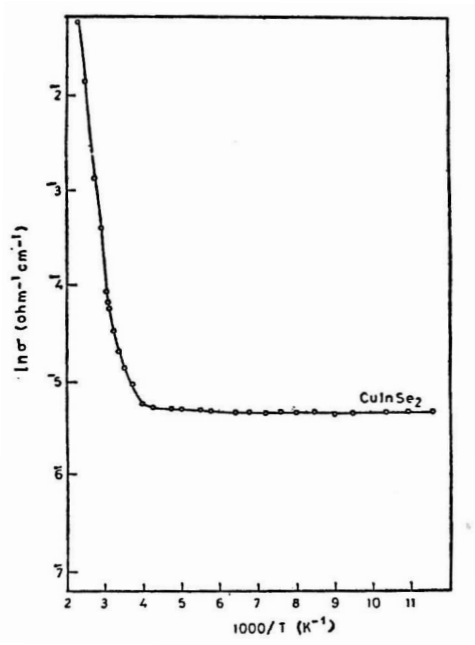

Fig. 9. Variation of d. c. conductivity σ with temperature for p-$CuInSe_2$.

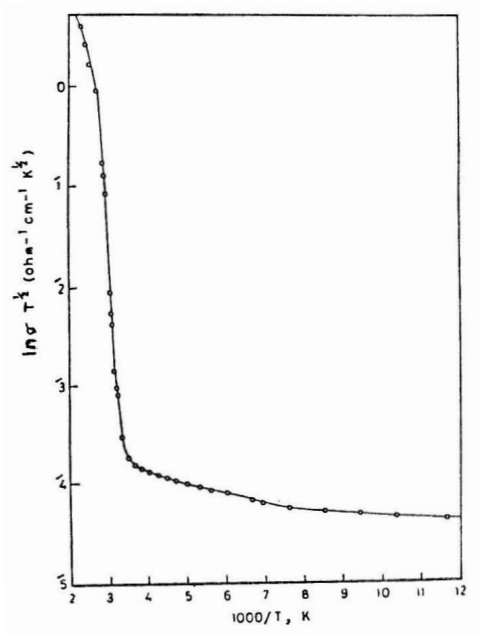

Fig. 10. Variation of $\ln(\sigma T^{1/2}$ *vs.* $1/T$ *for p-*$CuInSe_2$ *films.*

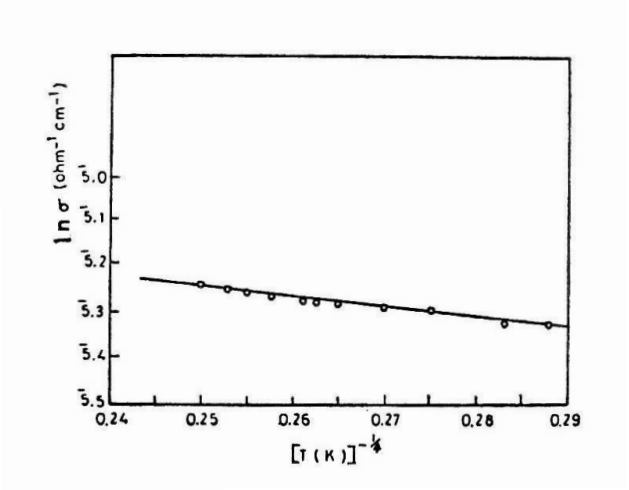

Fig. 11. Variation of d. c. conductivity σ with temperature vs. $T^{-1/4}$ for $CuInSe_2$ *films.*

4. Conclusion

It is concluded that the thin films of $CuInSe_2$ are amorphous in structure at room temperature and up to 473 K. By heat treatment at 523 K of such amorphous films they are transformed to a crystalline one. From the optical absorption spectra follows that there are allowed direct, forbidden direct and indirect transitions with energy gaps 1.014 eV, 1.14 eV and 1.08 eV, respectively. To explain the appearance of indirect transition as a third one, more detailed study on the band structure of this material would be needed. The valence band density of state was found to be constant for the amorphous thin films and decreases at annealing temperature equal to 523 K.

The electrical conductivity increases with temperature. The variable-range hopping conduction mechanism dominates at low temperature. The density of the localized state was found to be 2.82×10^{23} eV^{-1} cm^{-3}.

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SVOJSTVA AMORFNIH I KRISTALININIH TANKIH FILMOVA p-$CuInSe_2$

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UDK 538.95

Originalni znanstveni rad

Utvrđeno je da tanki filmovi $CuInSe_2$ imaju amorfnu strukturu na sobnoj temperaturi, sve do 473 K. Zagrijavanjem do 523 K struktura se mijenja u kristalnu. Iz optičkih apsorpcionih spektara slijedi da postoje dozvoljeni direktni, zabranjeni direktni i indirektni prijelazi sa energijama od 1,014 eV, 1,14 eV odnosno 1,08 eV. Da bi se objasnila pojava indirektnih prijelaza, potrebno je mnogo detaljnije proučavanje energetske strukture ovog materijala. Nađeno je da je valentna gustoća stanja konstantna za amorfne filmove, a da se smanjuje zagrijavanjem do 523 K. Električna vodljivost se povećava s temperaturom. Gustoća lokaliziranih stanja iznosi 2.82×10^{23} eV^{-1} cm^{-3}.