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The optical properties of $CuGa_{0.5}In_{0.5}Se_2$ thin films

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$CuGa_{0.5}In_{0.5}Se_2$ thin films with thickness in the range 50 to 280 nm were deposited by thermal evaporation of prereacted material on glass substrates. The films were found to be polycrystalline with single phase having chalcopyrite structure as that of bulk material. The optical constants of these films were determined by transmittance and reflectance measurements at normal incidence for light in the wavelength range 400 to 1200 nm. Three characteristic energy gaps of 1.30, 1.55 and 2.46 eV were obtained from an analysis of the optical absorption spectrum. The optical constants of the films appear to be independent of the substrate temperature.

1. Introduction

Several members of the I-III-VI_2 ternary semiconducting compounds, which crystallize in the chalcopyrite structure ($I\bar{4}2d$) and are electronic analogues of the $A^{II}B^{VI}$ binary compounds, have recently received considerable interest because of their potential application in photovoltaic devices, light emitting diodes and non-linear optics [1]. Particularly, $CuInSe_2$ and $CuGaSe_2$ have received more attention since they show promise as effective absorber–generator materials in thin film solar cells. In this connection the energy gap and absorption coefficients are essential characteristics of the material. $CuInSe_2$ is a direct band gap semiconductor with an optical absorption coefficient greater than $10^5\ cm^{-1}$ over most of the solar spectrum, and an approximately 14% efficient thin film $CuInSe_2$/(Cd, Zn)S heterojunction solar cell has been reported recently [2].

The band gap energy of $CuInSe_2$ ($\sim$ 1.04 eV) is too small to allow much higher photovoltaic conversion efficiencies despite the excellent absorption characteristics. $CuGaSe_2$ thin films, however, although not as promising a material in a stand alone device with a band gap of about 1.67 eV, have exhibited potential as a co-constituent with $CuInSe_2$ in either a quaternary alloy system, $CuGa_xIn_{1-x}Se_2$, or as a series component in a tandem cell arrangement. The former has exhibited efficiencies approaching 11% [3] whereas the latter has a calculated theoretical efficiency of 33% [4]. The $CuGa_xIn_{1-x}Se_2$ solid solutions can have an energy gap between 1.0 eV and 1.7 eV dependent on x and this suggests that the selenide film can be made as an optimum absorber by choosing the approximate value of x so that the band gap matches the solar spectrum [5]. Photovoltaic devices consisting of a polycrystalline $CuGa_xIn_{1-x}Se_2$ based absorber are quickly proving to be the most economical in high-efficiency thin film solar cell technology. Keeping this in view, we have studied the optical constants of equimolar per cent $CuGa_{0.5}In_{0.5}Se_2$ thin films.

Thin films of $CuInSe_2$ and $CuGaSe_2$ have been prepared by several techniques by several research workers and extensive literature data are available on their optical transition energies near and above the fundamental absorption edge [6–16]. These ternary compounds show a three fold optical structure near the fundamental edge due to crystal field and spin orbit splitting of the uppermost valence bands. These valence band-to-conduction band transitions are conventionally labelled A, B, C in terms of increasing energy and correspond to transitions $\Gamma^4_{7v} - \Gamma^1_{6c}$, $\Gamma^5_{6v} - \Gamma^1_{6c}$ and $\Gamma^5_{7v} - \Gamma^1_{6c}$. However, the literature data on optical properties of $CuGa_{0.5}In_{0.5}Se_2$ compound are scarce. Pamplin and Feigelson [17] used spray pyrolysis to prepare and study thin films of $CuGa_xIn_{1-x}Se_2$ solid solutions and verified that the band gap energy does increase as x increases from 0 to 1. The quadratic dependence of energy gap on x was found by Bodnar *et al.* [18]. The energy gap of $CuGa_{0.5}In_{0.5}Se_2$ thin films, prepared by flash evaporation, was found to be about 1.29 eV [19] which is in between the energy gap for $CuInSe_2$ (1.04 eV) and $CuGaSe_2$ (1.67 eV), and the photovoltaic conversion is optimum in this range. The same transition energy was also observed by Stewart *et al.* [20] in studying thin film polycrystalline solar cells based on $CuGa_{0.5}In_{0.5}Se_2$ compound.

The aim of the present paper is to elucidate the structure of the fundamental absorption edge in very thin films of $CuGa_{0.5}In_{0.5}Se_2$ by determining the optical constants from measured transmittance and reflectance up to energies well above the edge. The

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analysis of the optical absorption near and above the fundamental absorption edge is given. The structure of thin films and the effect of substrate temperature have also been studied. Our observations are concurrent with the results obtained by Soliman *et al.* [11] on $CuInSe_2$ thin films.

2. Experimental procedure

Polycrystalline ingots of $CuGa_{0.5}In_{0.5}Se_2$ were prepared by fusion of the constituent elements in the stoichiometric ratio in vacuum sealed quartz ampoules. The details of the synthesis and X-ray powder data of $CuGa_{0.5}In_{0.5}Se_2$ along with its structure have been published in our recent paper [21]. Thin films were prepared with material from these ingots by a single source thermal evaporation method using a Hind Hivac evaporation unit with resistively heated molybdenum boat. Excess Se (approximately 3 mol %) was included in the starting composition to compensate for any potential loss of Se vapour during evaporation and to favour p-type electrical conductivity in these films. The films were deposited on glass substrates held at constant temperature in the range 303 to 723 K. The substrates were held directly above the boat at a distance of about 18 cm and the rate of deposition was maintained at about $10\,\mathrm{nm\,min^{-1}}$. The boat temperature was about 1650 K and the vacuum during evaporation was $\sim 2 \times 10^{-6}$ Pa. The film thickness was monitored by a quartz crystal thickness monitor *in situ* and was also determined by the Fizeau fringes technique of multiple beam interference. Films in the range 50 to 280 nm were obtained and used for electron microscopy and optical studies.

A Philips EM-200 electron microscope was used for electron microscopy and transmission electron diffraction analysis of these films. The films were removed from the substrates by etching in 40 vol % HF acid. However, in some cases the films were thinned by etching in HCl before removing from the substrates. The interplanar spacings d in the electron diffraction patterns of the films were determined from the relation $dr = K$, where r is the radius of the diffraction ring and K is camera constant which was calculated by taking a standard gold film pattern.

For optical characterization the transmittance and reflectance of the films at normal incidence were recorded at room temperature with unpolarized light in the wavelength range 400 to 1200 nm using Cary 17D spectrophotometer. To eliminate substrate effects and interface reflections and hence to obtain the transmittance, T_f, and reflectance, R_f of the film the following relations were used [22].

$$T_f = \frac{T_{obs}(1 - R_{obs}R'_s)}{1 + R'_s} \tag{1}$$

and

$$R_f = R_{obs} - \frac{T_f^2 R'_s}{1 - R_{obs}R'_s} \tag{2}$$

where $R'_s = (n_s - 1)^2/(n_s + 1)^2$, n_s is the refractive index of the glass (1.52), and T_{obs} and R_{obs} are the observed transmittance and reflectance of the film deposited on glass substrate.

3. Results and discussion

The films deposited at room temperature (303 K) were found to be polycrystalline and homogeneous. The d values measured from the diameter of the rings matches well with our powder data for bulk material [21], indicating the formation of single phase polycrystalline $CuGa_{0.5}In_{0.5}Se_2$ film of the chalcopyrite structure. A typical electron micrograph and corresponding electron diffraction pattern of the film deposited at room temperature are shown in Fig. 1. The calculated lattice constants, $a = 0.569$ (1) and $c = 1.132$ (1) nm, are in good agreement with the bulk values reported earlier [21]. The average grain size is of the order of 300 to 500 nm. Similar patterns were obtained for the higher substrate temperature films (Fig. 2). The structure in all the specimens was found to be single phase, however, it was observed that the grain size decreased as the substrate temperature was increased and the grains were extremely fine for films

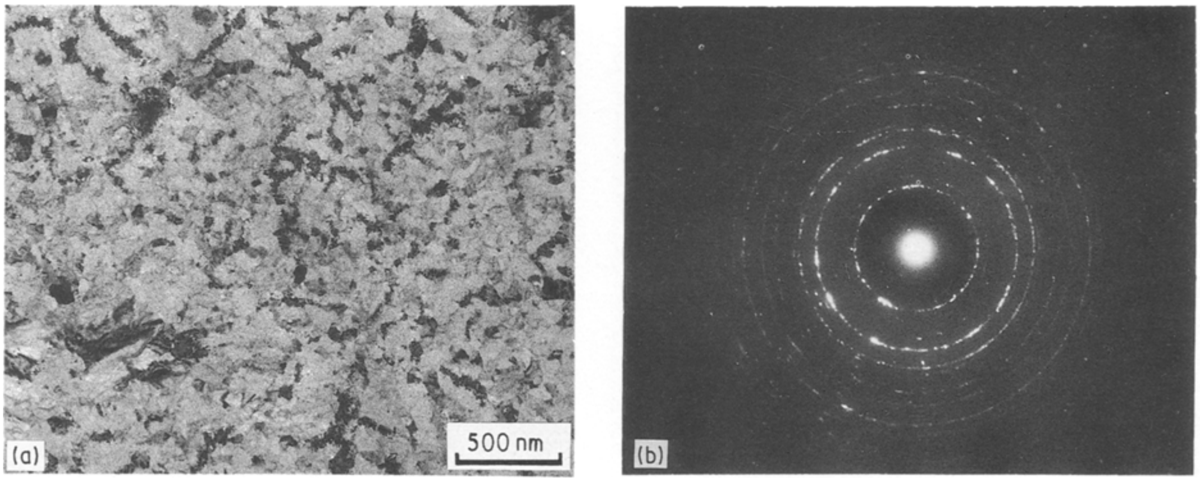

Figure 1 (a) A typical electron micrograph of $CuGa_{0.5}In_{0.5}Se_2$ thin film deposited at 303 K, and (b) its corresponding transmission electron diffraction pattern (voltage 80 kV).

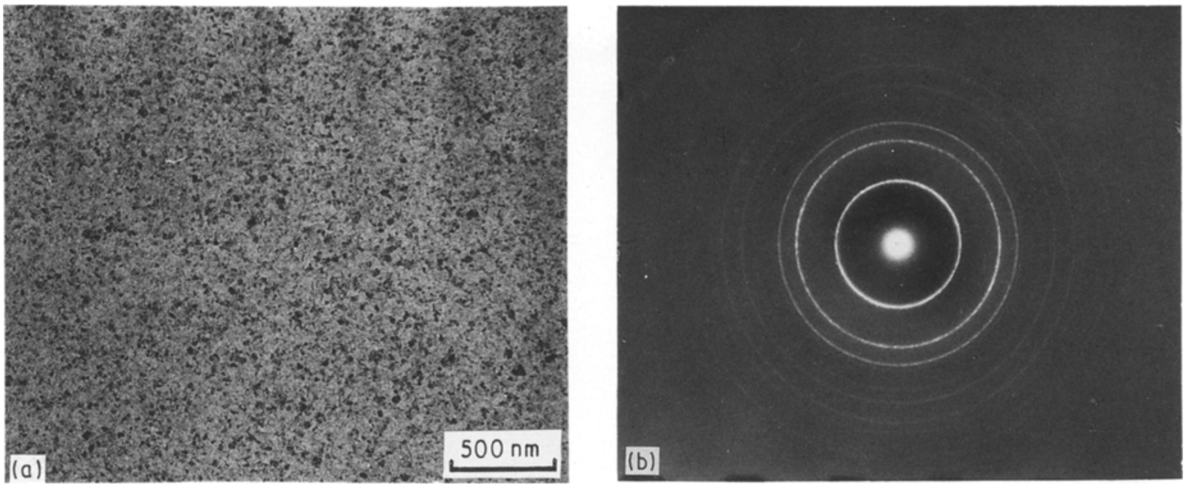

Figure 2 (a) A typical electron micrograph of $CuGa_{0.5}In_{0.5}Se_2$ thin film deposited at substrate temperature 473 K and (b) its corresponding transmission electron diffraction pattern (voltage 80 kV).

deposited at 723 K. The lines in the diffraction patterns tend to become continuous and broad as T_s increases, complimenting the observed decrease in grain size.

The spectral distribution of the transmittance and reflectance at normal incidence in the wavelength range 400 to 1200 nm are illustrated in Figs 3 and 4 for $CuGa_{0.5}In_{0.5}Se_2$ films of different thickness deposited at 303 K. At long wavelengths below the absorption edge, it was observed that $T_f + R_f = 1$ for most of the samples thus indicating transparency of the film and unscattered light. The optical constants of very thin absorbing films on non-absorbing substrates can be determined from the evaluated values of T_f and R_f, namely from Equations 1 and 2, and the thickness of the film, t, by using an iterative method based on Tomlin equations [23] which are given by the following:

$$\frac{1+R}{T} = \left(\frac{1}{4n_o n_s(n_f^2 + k_f^2)}\right)[(n_o^2 + n_f^2 + k_f^2) \{(n_f^2 + n_s^2 + k_f^2 + k_s^2)\cosh 2\alpha_1 + 2(n_f n_s + k_f k_s)\sinh 2\alpha_1\} + (n_o^2 - n_f^2 - k_f^2)\{(n_f^2 - n_s^2 + k_f^2 - k_s^2)\cos 2\gamma_1 + 2(n_f k_s - n_s k_f) \times \sin 2\gamma_1\}] \quad (3)$$

and

$$\frac{1-R}{T} = \frac{1}{2n_s(n_f^2 + k_f^2)}[n_f\{(n_f^2 + n_s^2 + k_f^2 + k_s^2) \sinh 2\alpha_1 + 2(n_f n_s + k_f k_s)\cosh 2\alpha_1\} + k_f\{(n_f^2 - n_s^2 + k_f^2 - k_s^2)\sin 2\gamma_1 - 2(n_f k_s - n_s k_f)\cos 2\gamma_1\}] \quad (4)$$

where $\alpha_1 = 2\pi k_f t/\lambda$, $\gamma_1 = 2\pi n_f t/\lambda$, n is the refractive index, k is the absorption index, and the subscripts o, f and s stand for air, film and substrate, respectively.

By substituting known values of t, n_o (1 for air), n_s (1.52 for glass), k_s (0 for glass, neglecting absorption in glass) and choosing several trial values of n_f and k_f, Equations 3 and 4 were used to calculate R and T. The iteration was done with the help of a computer program and the trial values of n_f and k_f were reduced until the difference $(R_f - R_{cal})$ and $(T_f - T_{cal})$ was within the experimental measuring error of ± 0.5%.

The spectral distributions of n_f and k_f for $CuGa_{0.5}In_{0.5}Se_2$ film of thickness 200 nm deposited at 303 K are shown in Figs 5 and 6, respectively. No variation either in n_f or in k_f with the film thickness could be observed within the limit of experimental error.

The absorption coefficient, $\alpha = 4\pi k_f/\lambda$, is shown in Fig. 7 as a function of photon energy. The absorption spectrum was always of the form shown in this figure regardless of the film thickness which was varied from 50 to 200 nm. It can be seen that the absorption curve

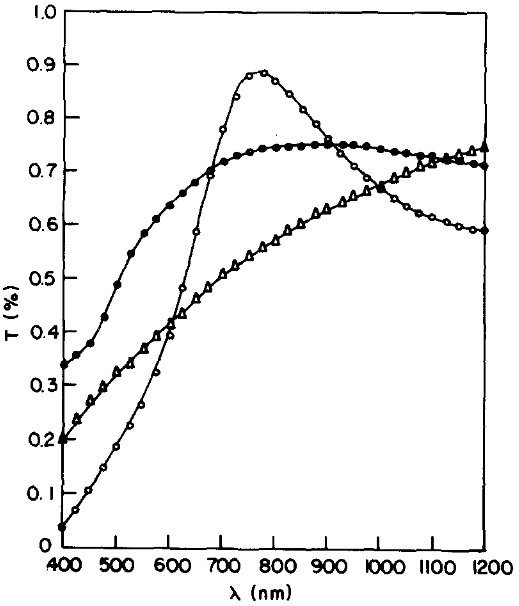

Figure 3 The spectral behaviour of the transmittance for $CuGa_{0.5}In_{0.5}Se_2$ films of different thickness, deposited on glass substrate at 303 K: (●) 50 nm, (△) 100 nm, (○) 200 nm.

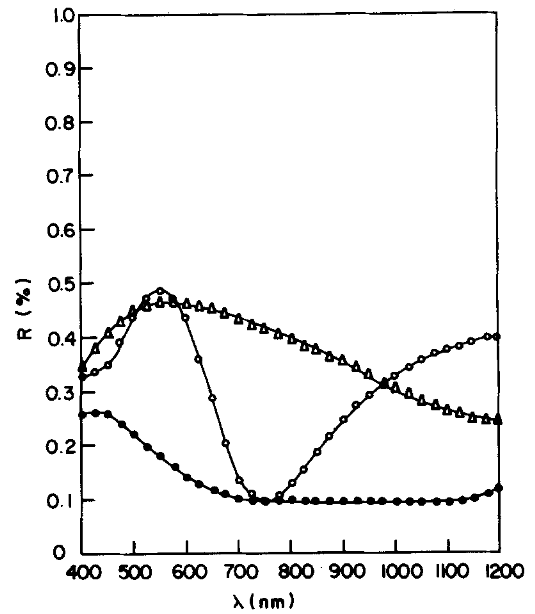

Figure 4 The spectral behaviour of the reflectance of $CuGa_{0.5}In_{0.5}Se_2$ films under the conditions and thickness shown in Fig. 3.

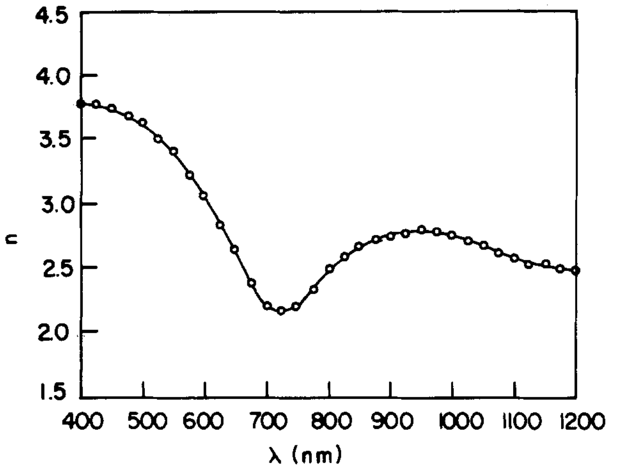

Figure 5 The spectral behaviour of the refractive index of $CuGa_{0.5}In_{0.5}Se_2$ film.

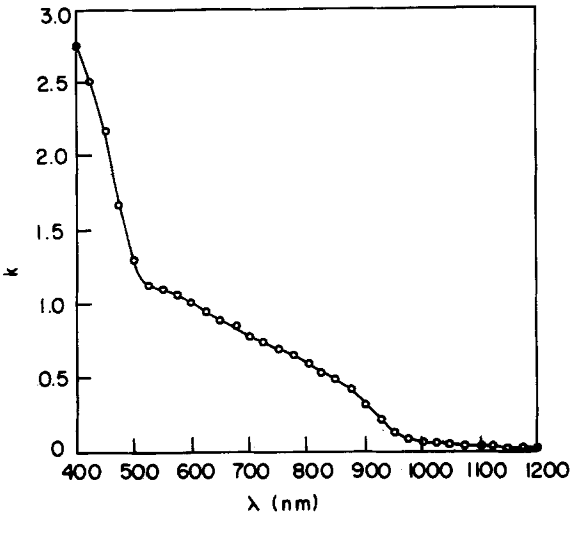

Figure 6 The spectral behaviour of the absorption index of $CuGa_{0.5}In_{0.5}Se_2$ film.

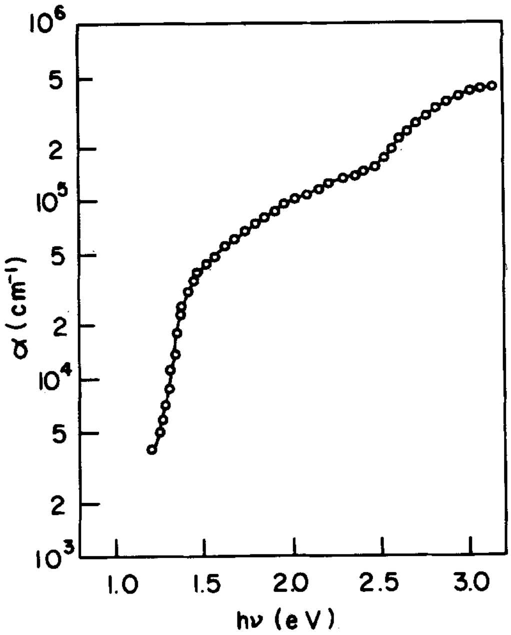

Figure 7 The absorption coefficient, α, as a function of the photon energy, $h\nu$, of $CuGa_{0.5}In_{0.5}Se_2$ film.

exhibits some pronounced structures from which it follows that the total absorption spectrum must be due to several optical transitions with different interband transition energies. The α values are small and practically constant for the lower energies. Beyond 1.20 eV, α increases by two orders of magnitude and reaches about $5 \times 10^5\ cm^{-1}$ in 3.0 eV range.

An analysis of the absorption coefficient shows that for $h\nu < 1.55$ eV the absorption spectrum can be described by a relation of the form [24]

$$\alpha_1 = \frac{A_1}{h\nu}(h\nu - E_{g_1})^{1/2} \qquad (5)$$

which indicates an allowed direct transition with an energy gap $E_{g_1} = 1.30 \pm 0.01$ eV corresponding to transition between parabolic bands. A plot of $(\alpha_1 h\nu)^2$ against $h\nu$ is shown in Fig. 8. This energy gap is in good agreement with the value of 1.29 eV of $CuGa_{0.5}In_{0.5}Se_2$ thin films, prepared by flash evaporation, by Nur Salad *et al.* [5] and corresponds to the transition $\Gamma^4_{7v} - \Gamma^1_{6c}$ (Structure A). The value of energy gap was also found to be in good agreement with the band gap data on $CuGa_{0.5}In_{0.5}Se_2$ single crystals [18, 25, 26]. However, if we calculate α_1 with A_1 and E_{g_1} determined from Fig. 8 for energies above 1.55 eV we find that α_1 becomes considerably smaller than the absorption coefficient α measured experimentally which can be explained only by the existence of additional absorption process. The additional absorption is characterized by an absorption coefficient, α_2, that is, $(\alpha - \alpha_1)$, the difference between the experimental absorption coefficient, α, and the extrapolated one, α_1, calculated using values of A_1 and E_{g_1} determined from the first absorption edge. An analysis of α_2 shows that α_2 can again be described by a direct allowed transition as given by Equation 5 with $E_{g_2} = 1.55 \pm 0.01$ eV. Figure 9 shows a plot of $(\alpha_2 h\nu)^2$ against $h\nu$ for $h\nu > 1.50$ eV. This transition may be

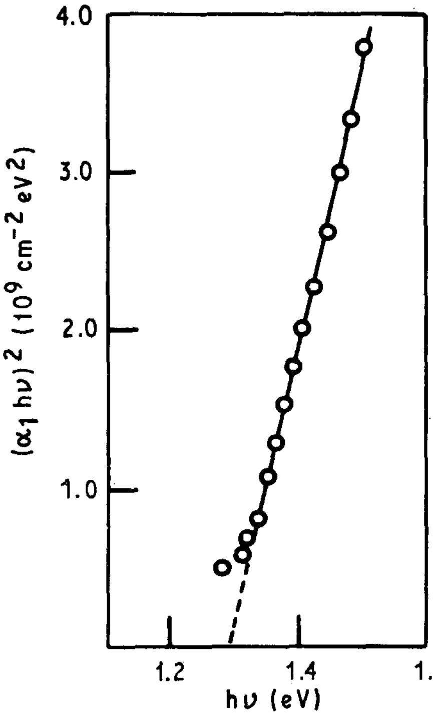

Figure 8 Plot of $(\alpha_1 h\nu)^2$ against $h\nu$ showing $E_{g_1} = 1.30\,eV$.

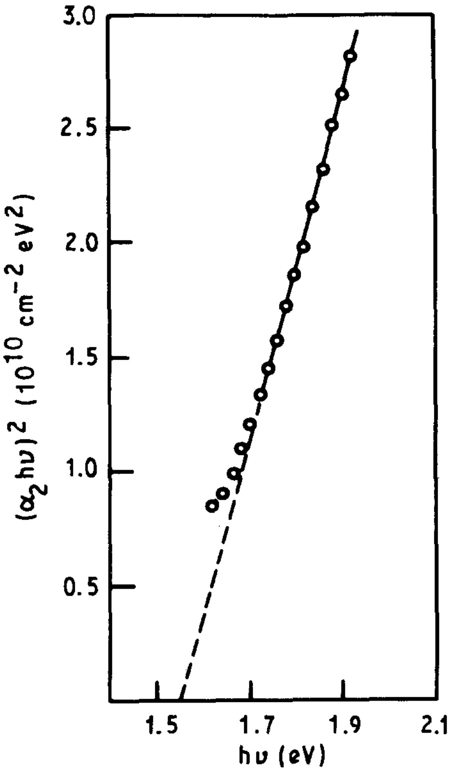

Figure 9 Plot of $(\alpha_2 h\nu)^2$ against $h\nu$ showing $E_{g_2} = 1.55\,eV$.

due to a B structure ($\Gamma^5_{6v} - \Gamma^1_{6c}$) which corresponds to the transition between crystal-field split level and conduction band minimum as observed in most of the I-III-VI_2 compounds [1, 10]. To our knowledge no such transition has been reported in the literature so far for $CuGa_{0.5}In_{0.5}Se_2$ thin films.

When $\alpha_1 + \alpha_2$ is evaluated using E_{g_2} and A_2 obtained from Fig. 9 at $h\nu > 1.9\,eV$, the experimental curve of α against $h\nu$ (Fig. 7) can be fairly well reproduced up to $h\nu \approx 2.5\,eV$. Thus, no indications of an influence of the structure C corresponding to the transition $\Gamma^5_{7v} - \Gamma^1_{6c}$ on α was found in our measurements. This may be due to the fact that the spin-orbit splitting of the two lower valence bands might be smaller than the line-width of the spectral lines, or the intensity of this transition could be much weaker than the other two transitions. A similar result was also observed in $CuGaSe_2$ films [16] and in $CuInSe_2$ films [27].

At $h\nu > 2.5\,eV$, $(\alpha_1 + \alpha_2)$ was again found to deviate from the experimentally measured values of α indicating the presence of a further absorption process. An analysis of α_3(where $\alpha_3 = \alpha - \alpha_1 - \alpha_2$) in the region beyond 2.5 eV again revealed an absorption phenomenon of the type described by Equation 5 with $E_{g_3} = 2.46 \pm 0.01\,eV$ as shown in Fig. 10. This higher energy transition was attributed to the transition from the copper 3d-level to the conduction band as applicable to the I-III-VI_2 compounds.

A set of samples of $CuGa_{0.5}In_{0.5}Se_2$ films of the same thickness (280 nm) was prepared at a rate of $10\,nm\,min^{-1}$ on glass substrate at different substrate temperatures ranging from room temperature (303 K) to 723 K. Fig. 11 illustrates the spectral behaviour of absorption coefficient for such films computed from the measured transmittance and reflectance values. It can be seen that all the curves are similar in nature except for the fact that the absorption coefficient is a little higher for higher substrate temperature films. This could be explained by the decrease in the average grain size with increase in substrate temperature (Figs 1 and 2). Thus the curves in Fig. 11 are consistent with the observed grain size. No significant variation is seen in transition energies with the substrate temperature. Hence one may conclude that the optical properties are independent of the substrate temperature for $CuGa_{0.5}In_{0.5}Se_2$ films prepared by vacuum deposition technique. All the films show p-type conductivity at room temperature and work on transport properties is in progress.

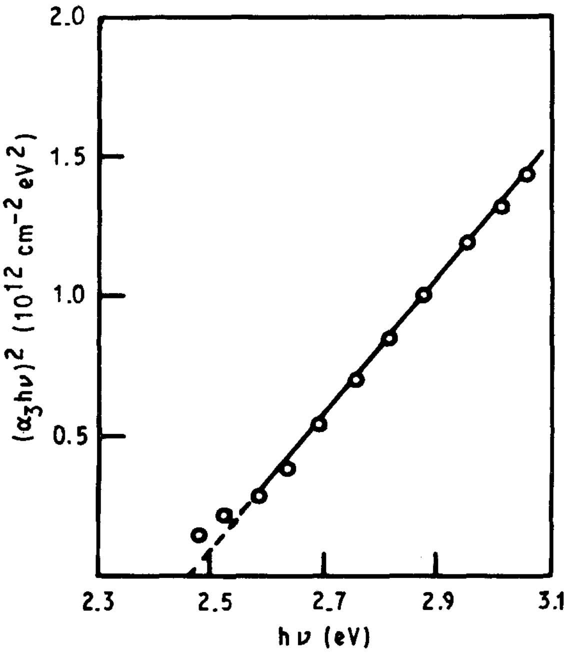

Figure 10 Plot of $(\alpha_3 h\nu)^2$ against $h\nu$ showing $E_{g_3} = 2.46\,eV$.

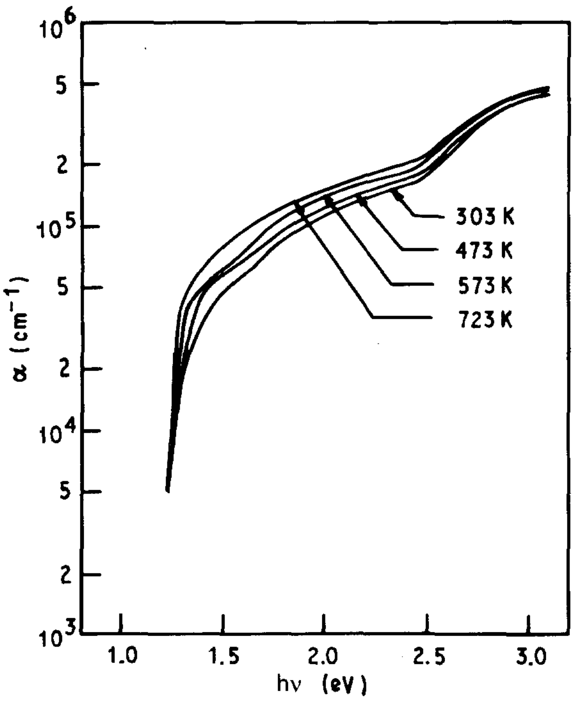

Figure 11 The spectral behaviour of absorption coefficient of $CuGa_{0.5}In_{0.5}Se_2$ films of the same thickness (280 nm) deposited on glass substrate at different substrate temperatures.

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