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Production of $CuInSe_2$ thin films by a sequential processes of evaporations and selenization

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Thin films of copper indium diselenide ($CuInSe_2$) were prepared by selenization of $CuInSe_2$-Cu-In multilayered structure on glass substrate. The selenization procedure was carried out in a vapour of elemental selenium in a vacuum chamber. The obtained films were characterised by XRD and SEM measurements. The effects of substrate temperature on the structural, electrical and optical properties were studied. It was found that single phase $CuInSe_2$ thin films with significant adhesion to substrate can be produced by selenization of $CuInSe_2$-Cu-In multilayered structure at 450 °C, when the first non single phase $CuInSe_2$ layer was deposited at substrate temperature of 400 °C. The thin films were found to be direct band gap semiconductors with a band gap of 0.97 eV. © *1999 Kluwer Academic Publishers*

1. Introduction

The ternary chalkopyrites of type Cu-III-VI_2 appear to be the most promising materials in photovoltaic device applications. Among these materials $CuInSe_2$, due to its direct band gap (1.02 eV), high absorption coefficient (up to the order of 10^5 cm^{-1}), good thermal and electrical stability as well as better radiation tolerance than single crystalline Si or GaAs devices [1], can be used as effective absorber in solar cells. Devices based on $CuInSe_2$/CdS have already demonstrated conversion efficiencies of over 15% [2].

By now several techniques such as evaporation, sputtering, spray pyrolysis, electroplating, liquid phase epitaxtion, etc. [3–5] have been used for producing $CuInSe_2$ thin films. Among them coevaporation of elemental materials from three separated sources [6], MBE [7] and selenization of Cu-In layers in a flow of H_2Se [8–10] have succeeded in fabrication of single phase $CuInSe_2$. However these methods are rather complex or need poisonous gases H_2Se as well as having some adhesion problems in the last one.

In this study, we followed a new method for producing a single phase $CuInSe_2$ films with significantly good adhesion by (i) evaporating $CuInSe_2$ powder on glass substrate from a single source (ii) evaporating Cu and In on this sample (iii) selenization of this multilayer structure. To avoid the highly toxic H_2Se, selenization process is carried out by using elemental selenium evaporator in a vacuum chamber.

2. Experimental

In this study, $CuInSe_2$ thin films were prepared in two stages. In the first stage $CuInSe_2$ films ("type a") were deposited on to the glass substrate by thermal evaporation of polycrystalline powder of $CuInSe_2$ in a vacuum of $\sim 10^{-4}$ Pa. During the deposition of films, the source temperature was kept at about 1200 °C. The substrate temperature was varied in the range 200–600 °C. The polycrystalline $CuInSe_2$ ingots were prepared by melting the stoichiometric amounts of the components in an evacuated and sealed quartz tube at 1100 °C and keeping at this temperature for about 10 h, and then cooling to room temperature by shutting up the furnace.

In the second stage of preparation of $CuInSe_2$ thin films, "type a" films were covered with Cu and In layers by sequential evaporation. The obtained films are called "type b" films. The thickness of Cu and In layers were chosen so that the atomic ratio Cu : In was as 1 : 1. During the deposition of Cu and In layers, the substrates intentionally were not heated. Then the obtained multilayer structures were subjected to selenization procedure; the temperature of the structure was raised up to 150 °C (below the melting point of In), kept at this temperature for 1 h in order to make Cu and In layers interdiffused. Then the temperature was raised up to the selenization temperature; in our case the selenization temperature was varied in the range 300–600 °C. During the selenization, the temperature of the Se source was kept at 200 °C. The samples were kept at the selenization temperature for 10 min, and then the heaters of the Se source and substrate were shut off, and the samples were cooled to room temperature in a vacuum. The crystalline structure of the films were examined by X-ray diffraction measurements (XRD) by using a Rigaku D/Max-III C diffractometer with CuK_α radiation over the range

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$2\theta = 3$–$70°$. The surface morphology of the films was studied by using a JEOL JST-6400 scanning electron microscope.

The conductivity was measured by a standard direct current four-probe technique. Silver paste was used for making ohmic contacts. The absorption coefficient α at room temperature was determined from the transmission spectrum (T) by using the following equation [11]:

$$\alpha = -\frac{1}{d}\ln\left[\frac{[(1-R)^4 + 4T^2R^2]^{1/2} - (1-R)^2}{2TR^2}\right]$$

Here d is the thickness and R is the reflectivity of the film. In the calculation, the value of $R = 0.257$ was used [12].

3. Results and discussion

3.1. XRD and SEM measurements

The XRD and SEM measurements showed that "type a" samples are very sensitive to the growth parameters such as the temperatures of the source and substrate. The films tended to be Cu deficient unless the source temperature was exceeded 1200 °C. The substrate temperature was found to have a significant influence on the structure and surface properties of the films. The XRD spectra of the "type a" films fabricated at substrate temperatures of 600 °C, 400 °C are shown in Fig. 1a and b respectively. Fig. 1c shows the XRD pattern of the selenized "type b" film. Here, to obtain "type b" films, "type a" films produced at a substrate temperature of 400 °C were used. The "type a" films fabricated at a substrate temperatures $T_s > 550$ °C contain not only $CuInSe_2$ phase but also Cu_2Se phase (Fig. 1a).

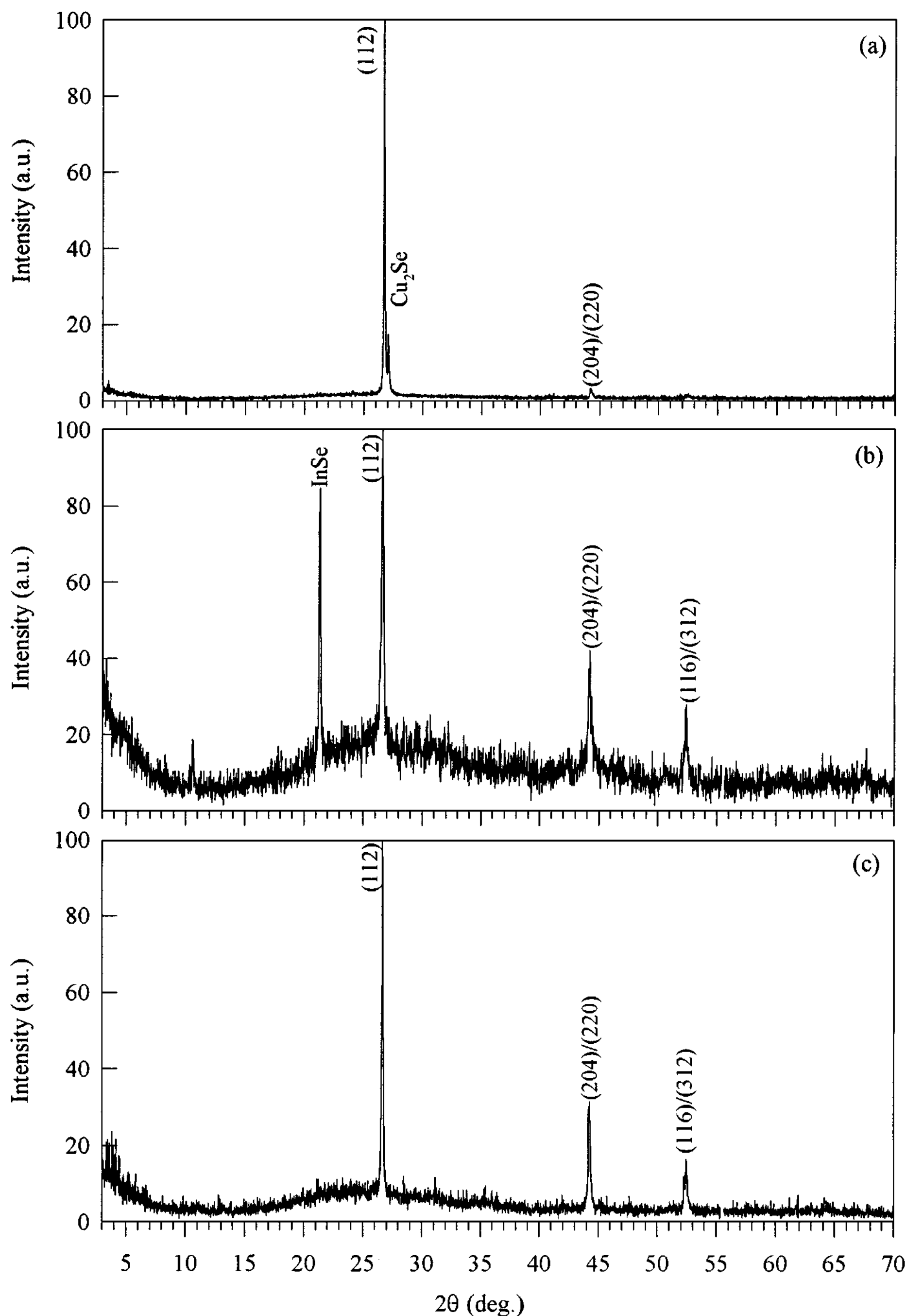

Figure 1 X-ray diffraction spectra of "type a" $CuInSe_2$ films formed at: (a) $T_s = 600$ °C, (b) $T_s = 400$ °C and (c) "type b" film selenized at 450 °C.

In addition to this, the films have poor adhesion and surface morphology. However the films fabricated at $T_s < 500\,^{\circ}\mathrm{C}$ contain, besides $CuInSe_2$ phase, also additional InSe phase (Fig. 1b). So the films fabricated at $T_s > 550\,^{\circ}\mathrm{C}$ and $T_s < 500\,^{\circ}\mathrm{C}$ temperatures exhibit to be Cu and In rich respectively. This behaviour may be explained by the back-evaporation of In from the film which had a higher substrate temperature. Fig. 2a and b

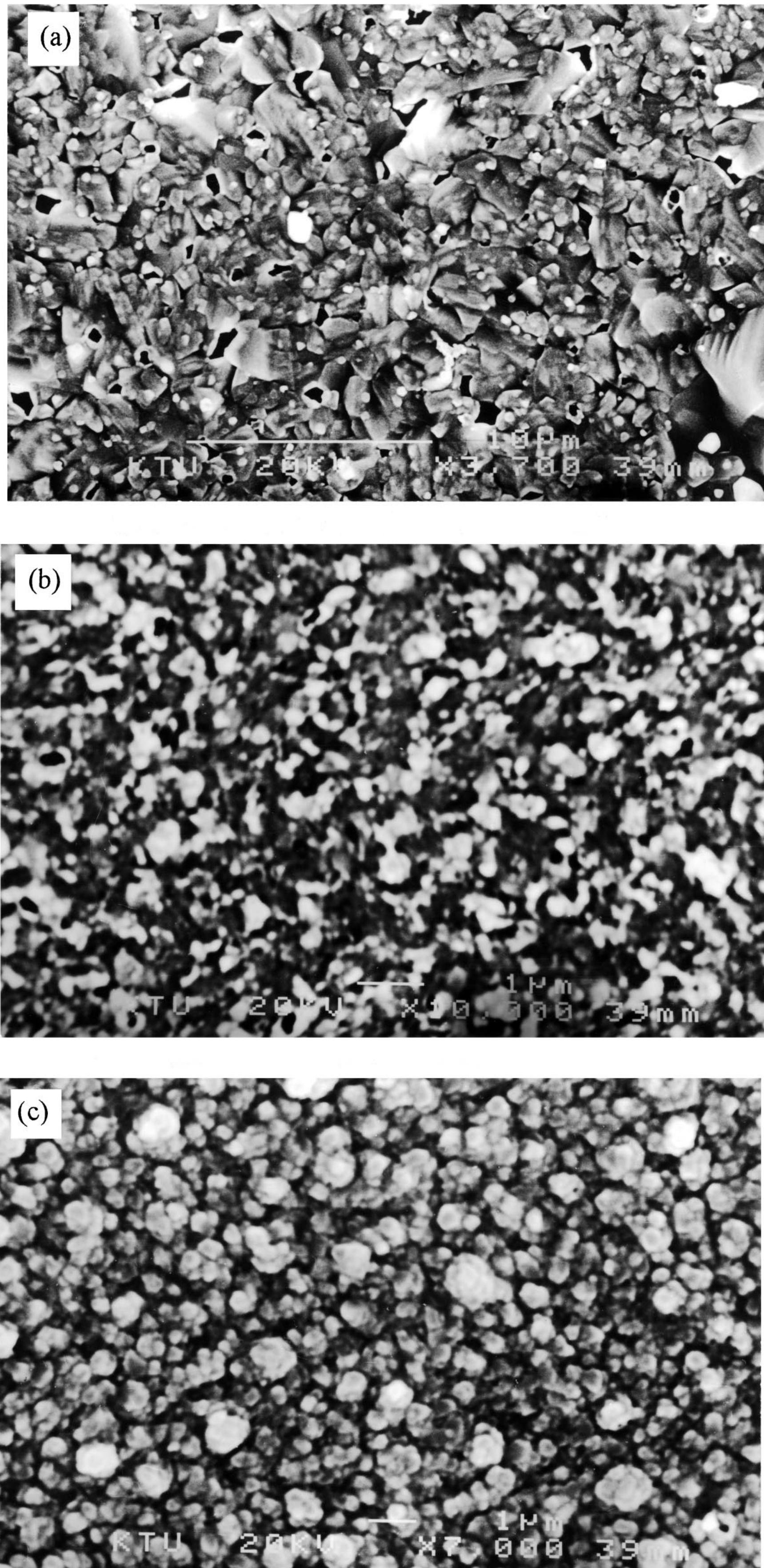

Figure 2 SEM micrographs of "type a" $CuInSe_2$ films fabricated at: (a) $T_s = 600\,^{\circ}\mathrm{C}$, (b) $T_s = 400\,^{\circ}\mathrm{C}$ and (c) "type b" film selenized at $450\,^{\circ}\mathrm{C}$.

shows the SEM micrographes of “type a” films fabricated at $T_s = 600$ and 400 °C respectively. Fig. 2c is a micrograph of the selenized “type b” film at 450 °C which will be discussed below. Some voids and a flaky structure were observed on the surface of “type a” film fabricated at 600 °C. However the film fabricated at $T_s = 400$ °C had more uniform surface. Thus, it is seen that producing $CuInSe_2$ films with the stoichiometric composition and good surface morphology is very difficult by evaporating from one source as concluded from the XRD and SEM measurements. Since the “type a” films fabricated at $T_s < 500$ °C appeared to have had better surface properties, we tried to transform these films into single phase $CuInSe_2$ films. For this purpose, Cu and In layers were thermally deposited in vacuum on the surface of “type a” films. Then, these multilayered structures were subjected to selenization procedure in Se atmosphere. It should be noted that the films directly exposed to selenization at high temperature appeared to have poor structural properties (the presence of secondary phase, InSe) and adhesion. These may be explained by the liquid-solid phase separation during the selenization process [13]. In order to improve the structural properties of these films, the following temperature profile was employed; the films were slowly heated to 150 °C in a vacuum, when the temperature reached this value the temperature of Se source was increased to 200 °C at a rate 20 °C/min. After keeping the samples at a temperature of 150 °C for 1 h, their temperature was raised to the selenization temperature (300–600 °C) at which the samples were kept for 10 min and then the source and substrate heaters were shut down.

It should be mentioned that the films selenized at temperatures below 350 °C still contained some additional phase of InSe. But all of the films subjected to selenization at above 400 °C contained only peaks corresponding to $CuInSe_2$ irrespective of the fabrication temperature of “type a” films. The characteristic XRD and SEM micrographs of the “type b” film selenized at 450 °C are shown in Fig. 1c and 2c respectively. Fig. 2c shows the grain structure with grain sizes approaching 1.3 μm. The film contained only $CuInSe_2$ phase contrary to the result reported in [8] and the growth occured predominantly in the [112] direction (Fig. 1c). The agreement between the d spacings of this film and the values from [8] is shown in Table I. One can see that the “type b” film selenized at 450 °C contains peaks corresponding only to $CuInSe_2$. The peaks (204) and (220) and also (116) and (312) are not separated in the XRD spectrum (Fig. 1c) which probably caused by the good crystalline quality with a reasonable low defect density [14].

TABLE I X-ray diffraction data of $CuInSe_2$

Literature			Observed		
d (Å)	I (%)	(hkl)	d (Å)	I (%)	(hkl)
3.344	100	(112)	3.339	100	(112)
2.049	44	(204)	2.044	17.8	204/220
2.045	22	(220)	—	—	—
1.750	9	(116)	—	—	—
1.745	24	(312)	1.744	10.1	116/312

3.2. Electrical and optical properties

All the selenized “type b” films were found to be in p-type conductivity and the resistivity behaviour of these samples showed strong dependence on fabrication temperature of “type a” films on which “type b” films were formed. In Fig. 3 are given the variation of resistivity of “type b” films selenized at 450 °C vs. the substrate temperatures of the corresponding “type a”

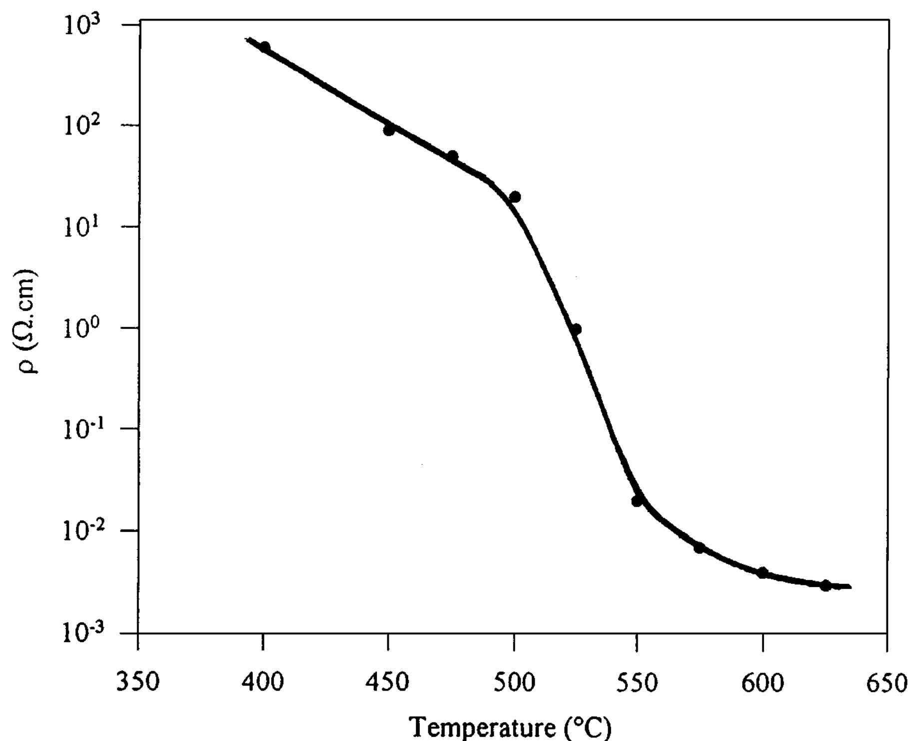

Figure 3 Variation of resistivity of “type b” $CuInSe_2$ films as a function of the substrate temperatures of the corresponding “type a” films.

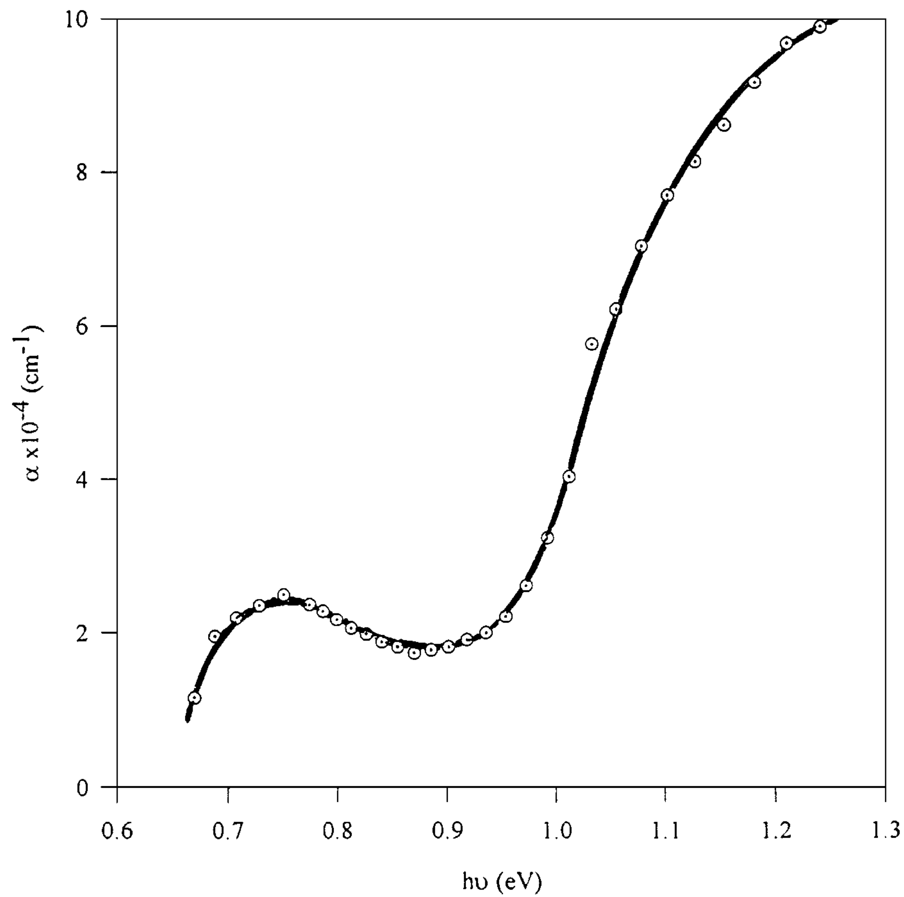

Figure 4 Optical absorption spectrum of "type b" $CuInSe_2$ film selenized at 450 °C.

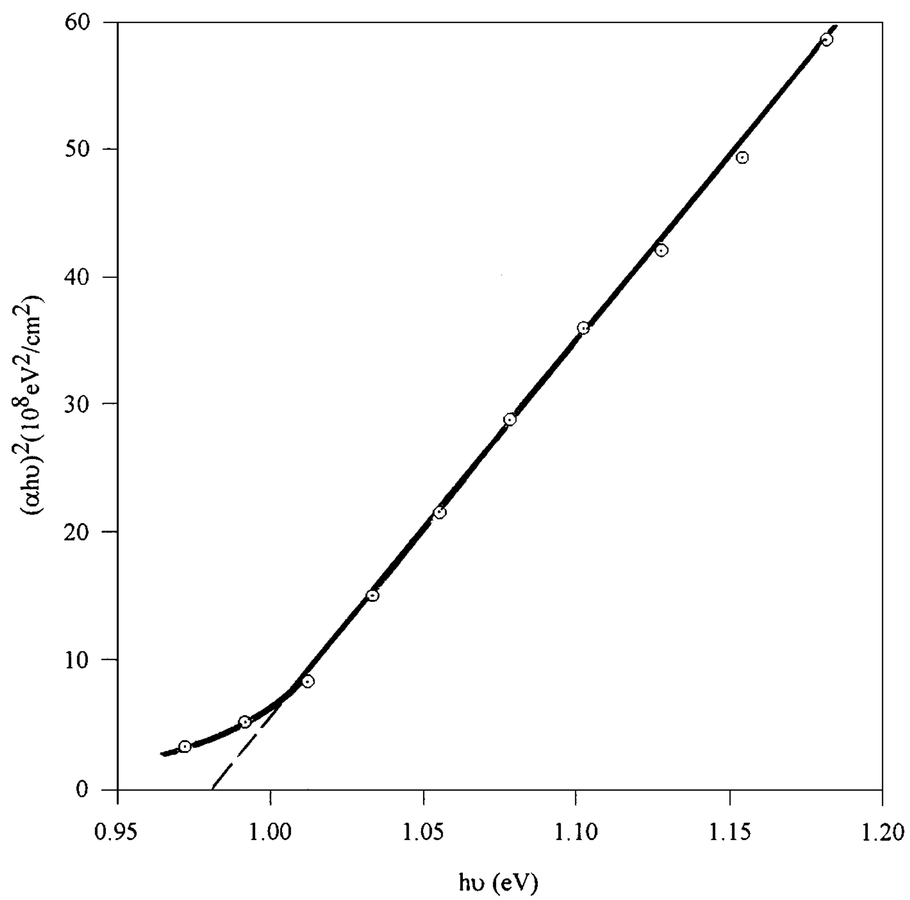

Figure 5 $(\alpha h\nu)^2$ vs. $h\nu$ plot of "type b" $CuInSe_2$ film selenized at 450 °C.

films. At the range $T_s < 500\,^\circ$C the resistivity changes weakly and then drops drastically at $T_s > 500\,^\circ$C. We had already shown that "type a" films contain additional InSe phase at $T_s < 500\,^\circ$C and Cu_2Se at $T_s > 550\,^\circ$C. This must lead to the excess of In and Cu in the selenized "type b" films respectively. Since a small departure of Cu/In ratio from the stoichiometry can lead to a change in resistivity by several orders of magnitude [15], the resistivity change observed in Fig. 3 may be caused by the antisite defects such as In_{Cu} (In in the site of Cu) and Cu_{In} (Cu in the site of In) [16]. In the case of $CuInSe_2$, In_{Cu} defects must behave as donors whereas Cu_{In} as acceptors. So in the range $T_s < 500\,^\circ$C the high resistance may be caused by the compensation of p-type conductivity due to the In_{Cu} donors. But the low resistance at $T_s > 550\,^\circ$C may be due to the intensification of p-type conductivity by the Cu_{In} acceptors.

The transmittance spectra of the films were measured in the wavelength range 0.8–2.0 μm. The variation of absorption coefficients of the film selenized at $450\,^\circ$C is shown in Fig. 4. The steep rise of absorption coefficients in the range $h\nu > 0.95$ eV corresponds to band-to-band transitions. In addition to this there is also a broad band at $h\nu = 0.75$ eV. A similar absorption band has also been observed in $CuGaSe_2$ and interpreated as a transition from a lower lying valance band (VB2) to an upper one (VB1) [18]. Similarly, the absorption band observed in our study can be attributed to such a transition. Fig. 5 gives $(\alpha h\nu)^2$ vs. $h\nu$ of the film the absorption spectrum of which was shown in Fig. 4. As can be seen in the near absorption edge region, the energy dependence of α is given by $(\alpha h\nu)^2 = A(E_g - h\nu)$ which is a characteristic behaviour for direct transitions [17], where A is a constant and E_g direct band gap width. The band gap width 0.97 eV determined from these measurements is the same as that of $CuInSe_2$ single crystal (0.97 eV). The $CuInSe_2$ single crystal and thin film have been found to be direct band gap semiconductors with band gap widths 0.97 and 1.02 eV respectively. The observed difference in the band gap widths has been related with the nonuniformities in composition of $CuInSe_2$ thin films [17]. In this study, since the band gap width (0.97 eV) of the selenized film at $450\,^\circ$C is the same as that of single crystal $CuInSe_2$ we conclude that there is not much difference in the structure and stochiometries between the film and single crystal.

4. Conclusions

In this study, we demonstrated that single phase $CuInSe_2$ films having good adhesion and structural properties could be formed with a relatively cheap method which includes the selenization process of $CuInSe_2$-Cu-In multilayer structure. Wide temperature ranges of substrates (200–600 °C) during the formation of initial $CuInSe_2$ layers and the following selenization process of $CuInSe_2$-Cu-In multilayer structures (300–600 °C) were employed. The structural and optical measurements showed that the best structural and optical properties were obtained when the initial $CuInSe_2$ films were produced at a substrate temperature of 400 °C followed by the selenization at 450 °C. $CuInSe_2$ films deposited by this procedure exhibited to be a direct band gap semiconductor ($E_g = 0.97$ eV) free from additional phases.

5. Acknowledgement

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