ISSN 1330–0008
CODEN FIZAE4

STRUCTURE AND OPTICAL PROPERTIES OF THIN POLYCRYSTALLINE FILMS OF $CuGa_xIn_{1-x}Se_2$

B. A. MANSOUR[a], S. A. ABD EL-HADY[b], A. ABDEL-ALL[b], I. K. EL ZAWAWI[a] and H. SHABAN[a]

[a]*Solid State Physics Laboratory, National Research Centre Dokki, Cairo, Egypt*

[b]*Physics Department, Faculty of Science, Helwan University, Cairo, Egypt*

Received 4 December 2002; Accepted 7 April 2003
Online 19 April 2004

Structural and optical properties of $CuGa_xIn_{1-x}Se_2$ $(0 \le x \le 0.75)$ polycrystalline thin films deposited by vacuum evaporation were studied as a function of composition. The optical absorption spectra of $CuGa_xIn_{1-x}Se_2$ thin films ($x \neq 0$) show four energy gaps (E_{g_1}, E_{g_2}, E_{g_3} and E_{g_4}) which are attributed to the fundamental edge, band splitting by crystal-field and spin-orbit splitting, and to transitions originating from copper 3d levels, respectively. The primary transition energies exhibit bowing behaviour expressed by the relationship $E_{g_1}(x) = 1.011 + 0.448x + 0.186x^2$. The second and third transition energies are higher than the primary transition energies by 0.10–0.11 eV and 0.18–0.185 eV, respectively. The effect of thermal treatment on the values of energy gaps is discussed in terms of the structure of the films. The primary transition energies of annealed $CuGa_xIn_{1-x}Se_2$ can be fitted by the parabolic form $E_{g_1}(x) = 1.04 + 0.46x + 0.22x^2$.

PACS numbers: 78.66.Jg, 68.60.Dv, 71.20.Nr UDC 538.958, 538.975
Keywords: polycrystalline thin films, $CuGa_xIn_{1-x}Se_2$ $(0 \le x \le 0.75)$, optical absorption spectra, energy gaps, thermal treatment, fit to primary transition energies

1. Introduction

The semiconductor $CuGa_xIn_{1-x}Se_2$ is currently of interest as a thin-film window material in conjunction with $CuInSe_2$ used for photovoltaic solar cells. Studies of $CuGa_xIn_{1-x}Se_2$ thin films as an absorber material [1–5] are more attractive as this system allows tailoring of the band gap (1.04 to 1.68 eV for $CuInSe_2$ and $CuGaSe_2$, respectively) and other material properties. Results of previous optical studies of this alloy system vary widely with respect to the degree of optical bowing present in single crystals [6–8] and in polycrystalline thin films [9–11].

In the present work, we report an analysis of optical absorption near and above the fundamental absorption edge, and the results are discussed considering the crystal structure of the films.

2. Experimental details

$CuGa_xIn_{1-x}Se_2$ thin films were prepared by thermal evaporation in vacuum (10^{-4} Pa, i.e. about 10^{-6} Torr) of synthetic chalcopyrites grown in the laboratory. A polycrystalline ingot was synthesized by fusing spec. pure copper, gallium, indium and selenium (99.999%, Matthey Chemicals Ltd.) in stoichiometric ratio in a quartz ampoule under a pressure of about 10^{-3} Pa. 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 ingot polycrystalline powder of $CuGa_xIn_{1-x}Se_2$ was evaporated from a molybdenum boat. The distance between boat and substrates was 17 cm. The films were deposited on freshly cleaned glass substrates and carbon chips.

The vacuum during the deposition process was held at about 10^{-4} Pa. In addition, liquid air was supplied using a liquid nitrogen trap facility in the coating unit to improve the vacuum during the suction of the diffusion pump. The conditions of evaporation were controlled by three factors, the substrate temperature (300–603 K), the rate of evaporation (3–4 and 4–6 nm/s), and the film thickness (200–320 nm) The post deposition annealing processes for samples were done in vacuum of 10^{-3} Pa, at temperature 453 K for two hours. The thickness of the film was determined by a quartz thickness monitor and confirmed by multiple beam interferometry. The details of the preparation and evaporation of ingot and thin films are given in Refs. [12] and [13], respectively.

The composition of thin films was analyzed by XRD using a Philips type PW 1373 diffractometer and energy dispersive X-ray analysis (EDAX).

To eliminate substrate effects and interface reflections and, hence, to obtain the transmittance, T_f, and reflectance, R_f, of the films, the following relations were used [1]

$$\begin{aligned} T_f &= T_{\rm obs}\frac{1 - R_{\rm obs}R_s}{1 + R_s} \\ R_f &= R_{\rm obs} - \frac{T_f^2 R_s}{1 - R_{\rm obs}R_s}\,, \end{aligned} \tag{1}$$

where $R_s = (n_s - 1)^2/(n_s + 1)^2$, n_s is the refractive index of the glass (1.54), and $T_{\rm obs}$ and $R_{\rm obs}$ are, respectively, the observed transmittance and reflectance of the film deposited on a glass substrate.

Normal incidence transmittance and reflectance spectra were recorded at room temperature in the range 300–2500 nm using a double-beam spectrophotometer, model JASCO V-570. Using the measured values R and T, the absorption coefficient

α was calculated from [14]

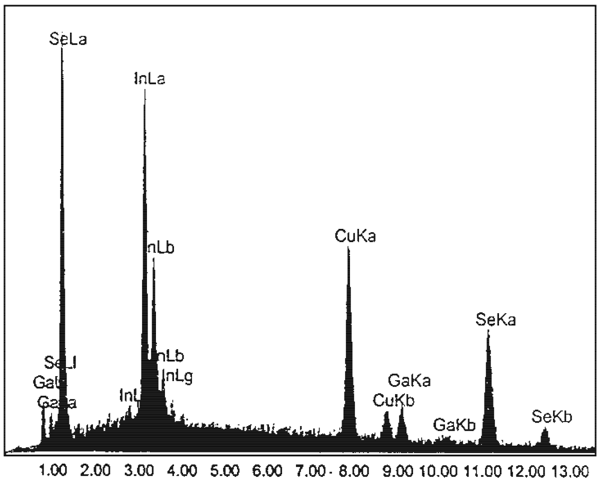
$$\alpha = \frac{1}{d} \ln \left[\frac{(1-R)^2}{2T} + \sqrt{\frac{(1-R)^4}{4T^2} + R^2} \right], \qquad \alpha = 4\pi k/\lambda \,, \tag{2}$$

where d is the thickness and the relation of α and the extinction coefficient k is given at right.

3. *Results and discussion*

3.1. *Determination of composition*

The composition of thin films was determined by energy-dispersive X-ray analysis (EDAX). The calculated contents of copper, gallium, indium and selenium wt.% were comparable with wt.% of the starting materials. Figure 1 shows the profile and the table of compositions of $CuGa_{0.25}In_{0.75}Se_2$ compound. The results of energy dispersive X-ray analysis (EDAX) for $CuGa_xIn_{1-x}Se_2$ compounds are shown in Table 1. It is found that the composition of thin films deposited at $T = 603$ K and deposition rate 4–6 nm/s has approximately the stoichiometric composition.



EDAX ZAF Quantification (Standardless); Element Normalized

Element	Wt %	At %	Z	A	F
InL	25.47	17.96	0.9632	0.8125	1.0000
CuK	19.57	24.93	1.0678	0.9576	1.0390
GaK	5.62	6.52	1.0356	0.9493	1.0559
SeK	49.34	50.59	0.9947	0.9729	1.0000
Total	100.00	100.00			

Fig. 1. EDAX of $CuGa_{0.25}In_{0.75}Se_2$ *compound: profile (top) and table (below).*

TABLE 1. Results of EDAX of $CuGa_xIn_{1-x}Se_2$ *compounds.*

Se (weight %)		In (weight %)		Ga (weight %)		Cu (weight %)		x
Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	
45.61	46.96	35.75	34.14	–	–	18.64	18.90	0
49.34	48.59	25.47	26.49	5.62	5.363	19.57	19.55	0.25
50.41	48.93	24.06	24.90	6.10	6.48	19.42	19.69	0.30
50.41	52.09	11.16	9.22	17.27	16.98	20.98	21.71	0.75

3.2. Structural study by X-ray diffraction

The structure of the films was analyzed by XRD using a Philips type PW 1373 diffractometer.

Figure 2 shows the XRD diagrams corresponding to a powder sample and thin films of different compositions ($x = 0$, 0.25, 0.30 and 0.75), evaporated at different substrate temperatures T_s. It is clear that the evaporated thin films of all compositions obtained by evaporation on substrate with temperature ranging from room temperature to $T_s < 473$ K consist mainly of the amorphous phase. The amorphous

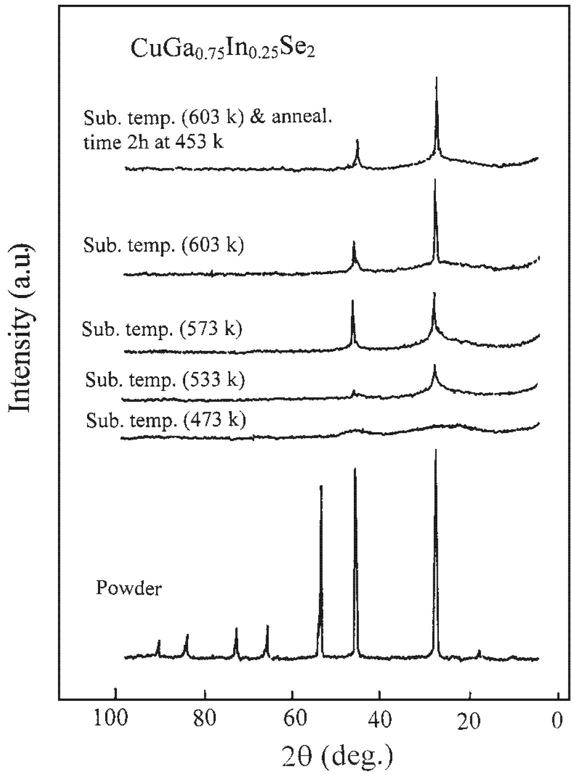


Fig. 2. A sample of XRD patterns of powder and of thin films: the $CuGa_{0.75}In_{0.25}Se_2$ *compound.*

phase diminishes with the raise of T_s. The optimal conditions to obtain the single tetragonal phase are substrate temperature $T_s = 603$ K, deposition rate of 4–6 nm/s, thickness of $d \geq 180$ nm and a glass substrate.

The lattice parameters (a and c) together with c/a ratio as a function of composition ratio x are shown in Fig. 3. It was found that both c and a appear to follow

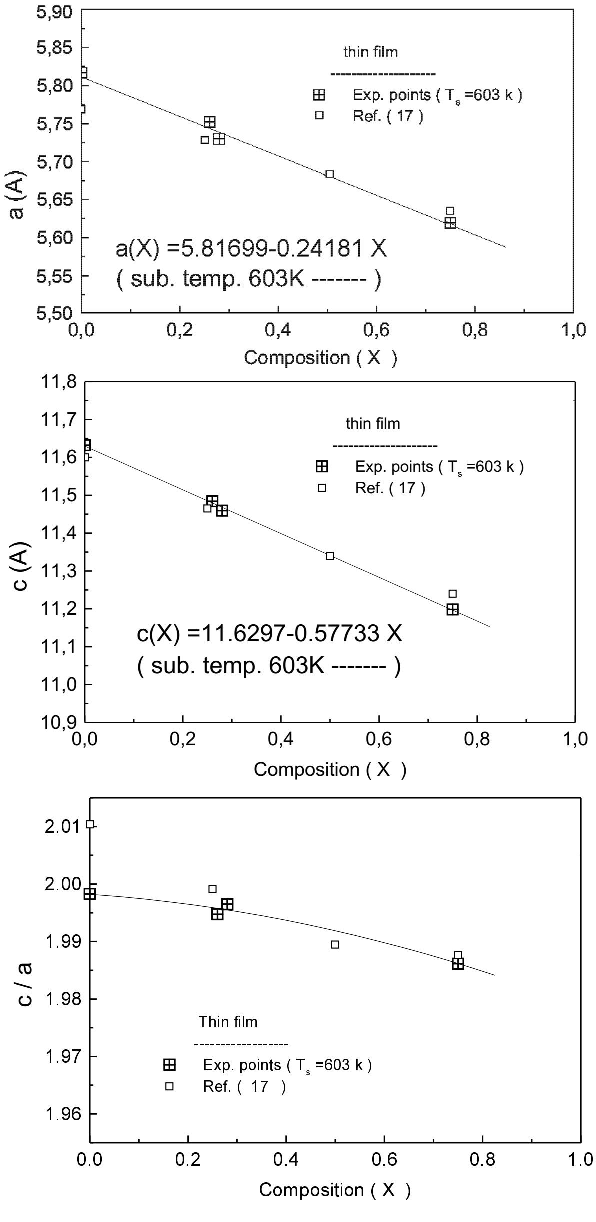


Fig. 3. Variation of lattice parameters with the composition x of $CuGa_xIn_{1-x}Se_2$ compounds: (top) lattice parameter a, (middle) lattice parameter c and (bottom) the ratio of the lattice parameters c/a. The solid lines represent the theoretical fits to the data.

to follow the usual linear Vegard behaviour over the whole composition range. The variation of a and c with x is given by

$$a(x) = 5.817 - 0.242x,$$
$$c(x) = 11.63 - 0.577x.$$

These fits are shown in Fig. 3 by solid lines. The c/a experimental values decrease with x, where c/a varies from 1.998 to 1.986 as x increases from 0.0 to 0.75.

The effect of thermal treatments was examined by annealing all investigated films at 453 K for 2 h under vacuum 10^{-3} Pa. The data show that the 2θ values of all films and intensity decreased with annealing. This may be attributed to the change in the lattice. This is in agreement with the results of Ref. [12] for $CuGaSe_2$ thin films and of Ref. [15] for $CuGaTe_2$ thin films which reported that the structure changes from tetragonal phase and approaches the cubic phase by annealing at 453 K for 2 h.

3.3. Optical properties

Representative curves of α vs. $h\nu$ for four samples with different compositions are shown in Fig. 4. The absorption edge shifts to higher photon energy with increasing Ga content x in the thin film. The absorption coefficients above the fundamental band edge for all thin films exceed 3×10^4 cm^{-1}, and hence are suitable for the fabrication of thin film photovoltaic devices. It is of interest to note that $CuInSe_2$ thin film exhibits very little subgap absorption and the transition is very sharp, indicating a small density of defect and/or impurity states in the energy gap. But $CuGa_xIn_{1-x}Se_2$ thin films ($x \neq 0$) have slight subgap absorption which is observed below the absorption edge with increasing x. Moreover, there are two different absorption regions.

In the first region, for $h\nu \approx E_g$, all compositions of $CuGa_xIn_{1-x}Se_2$ films have three direct transitions to conduction-band minima (the direct valence- to conduction-band transition E_{g_1}, and the corresponding valence-band splitting E_{g_2} and E_{g_3}). However, $CuInSe_2$ thin film, has two characteristic transition energies (E_{g_1} and E_{g_3}) because the two uppermost levels of the valence band in it are degenerated [16]. These direct energy gaps can be extracted from

$$\alpha = \frac{A}{h\nu}\sqrt{h\nu - E_g}. \tag{3}$$

Figure 5 shows the first transition corresponding to direct fundamental gap. The values obtained were between 1.01 and 1.45 (accurate to ± 0.02 eV) for $0 \leq x \leq 0.75$. These values of E_{g_1} correspond to the transition $\Gamma_{7\nu} - \Gamma_{6\nu}$ (valence-band maximum to conduction-band minimum). In a similar way, the second (E_{g_2}) and third (E_{g_3}) direct energy gaps can be determined as shown in Figs. 6a and 6b, respectively. The values of E_{g_2} (1.24–1.55, accuracy ± 0.02 eV) and E_{g_3} (1.21–1.73, accuracy ± 0.02

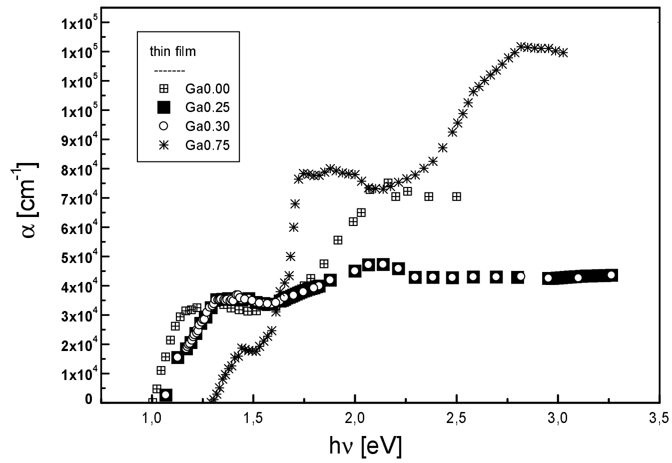


Fig. 4. The variation of absorption coefficient α with the photon energy $h\nu$ for different compositions.

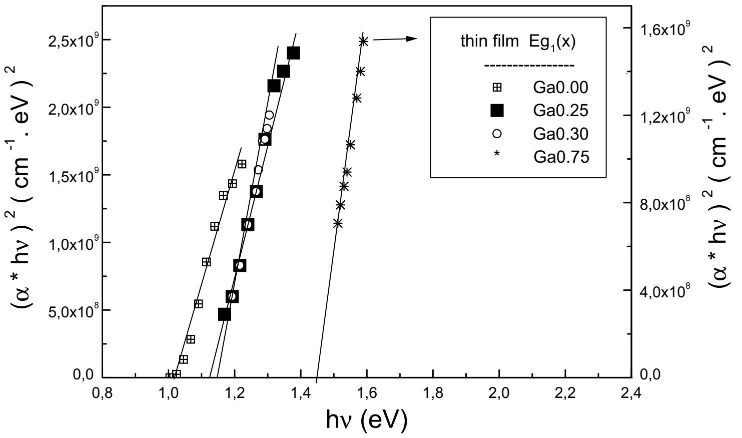


Fig. 5. $(\alpha h\nu)^2$ vs. $h\nu$ for different compositions; $E_{g_1}(x)$.

eV) correspond to the transition $\Gamma_{6\nu} - \Gamma_{6c}$ (crystal-field-split level to conduction-band minimum) and $\Gamma_{7\nu} - \Gamma_{6\nu}$ (spin-orbit-split level to conduction-band minimum). Similar results were obtained by other researcher for $CuGa_xIn_{1-x}Se_2$ thin films produced by vacuum evaporation [9,10,17] and by RF sputtering [16]. Moreover, in other I-III-VI_2 ternary semiconductors, $AgGaSe_2$, $CuAlS_2$ and $CuGaTe_2$, three transition energies corresponding to the valence-band splitting have been reported by other researchers [15,18].

At higher energy, $h\nu > 2$ eV, additional absorption results in a further increase of the slope of $(\alpha h\nu)^2$ vs. $h\nu$ which shows a straight line region with $1.71 \leq E_{g_4} \leq 2.2$ (accuracy ± 0.02 eV) as x increases from 0 to 0.75, as shown

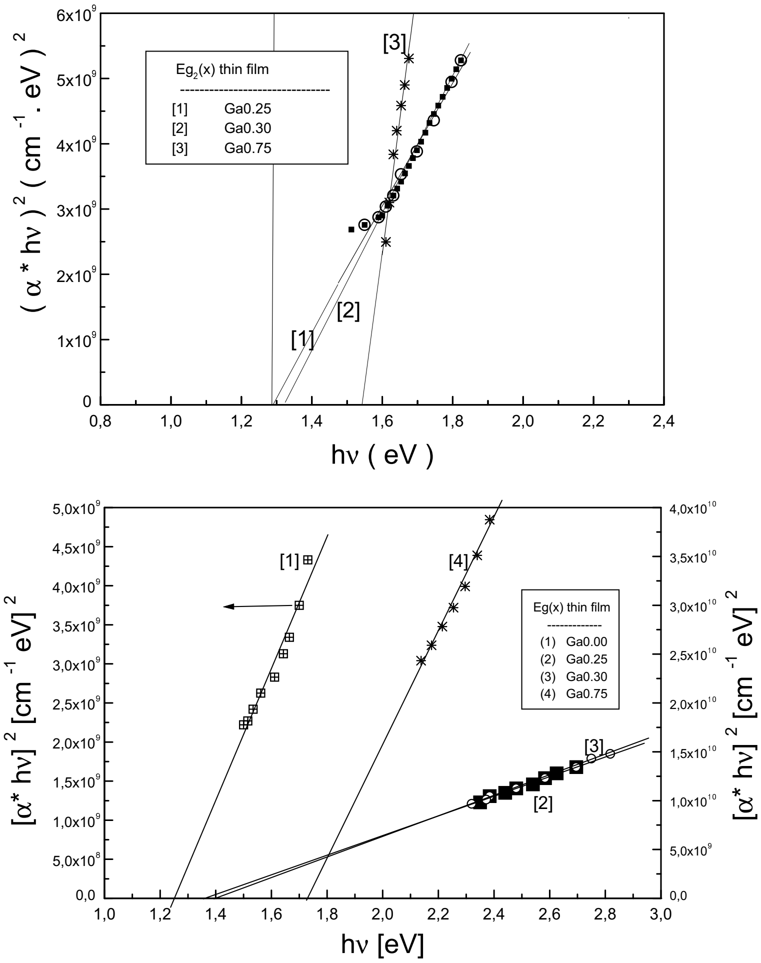


Fig. 6. $(\alpha h\nu)^2$ vs. $h\nu$ for different compositions; (a) $E_{g_2}(x)$ and (b) $E_{g_3}(x)$.

in Fig. 7. This transition may be attributed to a transition originating from copper 3d levels. The values of $E_{g_4} \approx (1.71 - 2.2$ eV) are in good agreement with the theoretical studies on various Cu-II-VI_2 compounds by Jaffe and Zunger [19,20]. They reported that there exists a group of bands with a strong d-character at about 2 eV below the top of the valence band. The presence of Cu 3d levels was also observed previously in various electroreflectance measurements in the energy range 3–4 eV. Reddy and Reddy Jayarama [21], Horig et al. [22] and Ebd El- Hady et al. [12] reported that CuGaSe2 thin films have optical transition originating from Cu 3d levels at 2.25, 2.7 and (2.01–2.25 eV), respectively. For $CuGaTe_2$ thin films, the optical transition from Cu 3d levels at 2.67 and 2.2 eV was reported in Refs. [15] and [23], respectively. Our observation of Cu-3d level at $h\nu > 2.0$ eV is

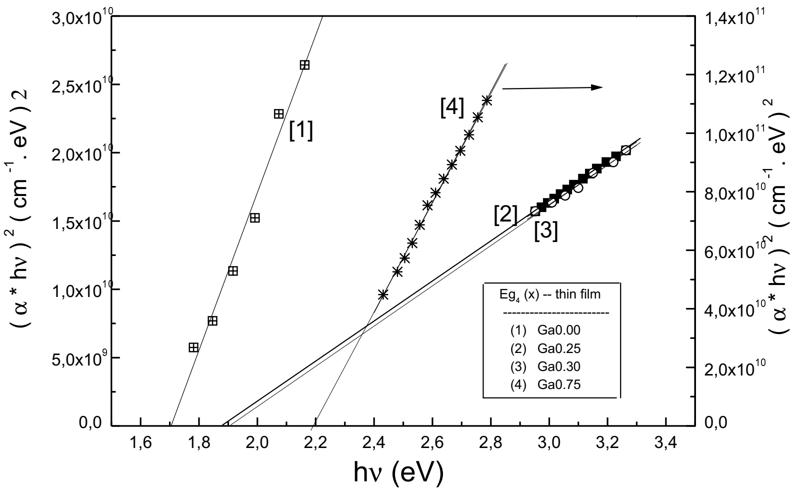


Fig. 7. $(\alpha h\nu)^2$ *vs.* $h\nu$ *for different compositions;* $E_{g_4}(x)$.

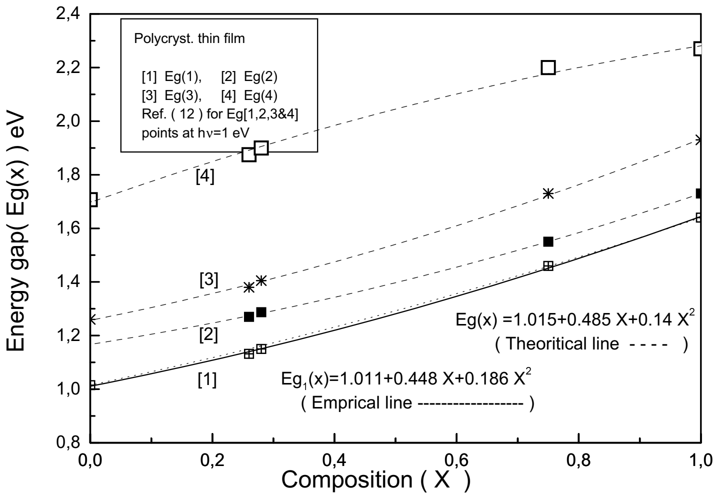


Fig. 8. Variation of the energy gap as a function of composition of $CuGa_xIn_{1-x}Se_2$ *compounds.*

consistent with the above studies.

Figure 8 shows the transition energies E_{g_1}, E_{g_2}, E_{g_3} and E_{g_4} for $CuGa_xIn_{1-x}Se_2$ thin films as a function of Ga content x. All values of optical energy gaps for $x = 1$ are taken from our previous work [12], with the samples prepared under the same conditions. It is observed that $CuGa_xIn_{1-x}Se_2$ thin films exhibit four transition energies, which increase as the Ga content increases, indicative of solid solution. These results are in good agreement with the data reported by other researchers [16,17].

The variation of primary transition energy $E_{g_1}(x)$ with x can be fitted by a parabolic form $E_{g_1}(x) = a + bx + cx^2$. The experimental data yield $a = 1.01$ eV, $b = 0.488$ eV and $c = 0.186$ eV, i.e., $E_{g_1}(x) = 1.011 + 0.488x + 0.186x^2$. This curve is shown in Fig. 8 by the solid line. The bowing parameter $c = 0.186$ eV is close to the published values for bowing behaviour in polycrystalline thin films 0.14 [9], 0.108 [10] and 0.13 [16] eV but very small compared to the value reported by Albin et al. [17] ($c = 0.249$ eV for near-stoichiometric thin film and $c = -0.046$ for Cu-poor film).

This parabolic behaviour and the c-value is also consistent with the results predicted by using a proposed theoretical model of Shaukat [24] which relates the bowing parameter observed in E_g versus composition curves of I-III-VI_2 alloys, with disorder effect in the alloy lattice. According to this model, the bowing parameter c in the mixed system of chalcopyrite is believed to be due to the difference in Philips electronegativities of the cations and/or anions constituting the mixed pseudobinary systems, Shaukat [24] has predicted that the bowing parameter c is 0.14 eV. Hence, he suggested the following relationship

$$E_{g_1}(y) \quad = \quad E_{g_1}(0)(1-y) + E_{g_1}(1)y + cy(y-1) \tag{4}$$

where y is the Ga content and $E_{g_1}(0)$ and $E_{g_1}(1)$ are the transition energies of the samples with $y = 0$ and 1.0, respectively, i.e, the compounds of $CuGaSe_2$ and $CuInSe_2$ respectively.

With the substitutions in Eq. (5) $y = 1 - x$, $c = 0.14$ eV predicted by Shaukat [24], and the experimental values $E_{g_1}(0) = 1.01$ eV for $CuInSe_2$ and $E_{g_1}(1) = 1.64$ eV for $CuGaSe_2$ from Ref. [12], the relationship between E_{g_1} and x (the Ga content in present case) is given by

$$E_{g_1}(x) = 1.01 + 0.448x + 0.14x^2\,. \tag{5}$$

This expression is consistent with our experimental data (Fig. 8 dashed curve).

On the other hand, the second and third transition energies are located at 0.10–0.11 eV (except for $CuInSe_2$) and 0.18–0.185 eV, respectively, and are above the primary transition energies. The former corresponds to the transition from a crystal-field-splitting level to the conduction-band minimum and the latter comes from a spin-orbit-splitting level to the conduction-band minimum [25]. From the values of E_{g_1}, E_{g_2} and E_{g_3}, the energies of the two Γ_7 levels relative to the Γ_6 level [26], E_1 and E_2, are found to be (0.10–0.11 eV), (0.18–0.185 eV) respectively, for $CuGa_xIn_{1-x}Se_2$ thin films ($x{\neq}0$).

The spin-orbit parameter Δ_{SO} and crystal-field parameter Δ_{CF} follow the relation [26]

$$E_{1,2} = -\frac{1}{2}(\Delta_{SO} + \Delta_{CF}) \pm \sqrt{[\Delta_{SO} + \Delta_{CF}]^2 - \frac{8}{3}\Delta_{SO}\Delta_{CF}}. \tag{6}$$

For $CuGa_xIn_{1-x}Se_2$, the values of Δ_{CF} and Δ_{SO} are obtained in the range (0.13 – 0.15 eV) and (0.205 – 0.21 eV), respectively. Yamaguchi et al. [16] reported the values Δ_{CF} and Δ_{SO} in the range of (0.06 – 0.08 eV) and (0.22 – 0.27 eV), respectively.

Effects of thermal treatment on optical properties of thin films having different composition, deposited at $T_s = 603$ K and annealed at 453 K for 2 hours, were studied. Absorption coefficient α and E_{g_1}, E_{g_2} vs. $h\nu$ are shown in Figs. 9 and 10, respectively. It is clear that there is a slight change in all values of energy gaps and an absence of the intermediate energy levels E_{g_2}.

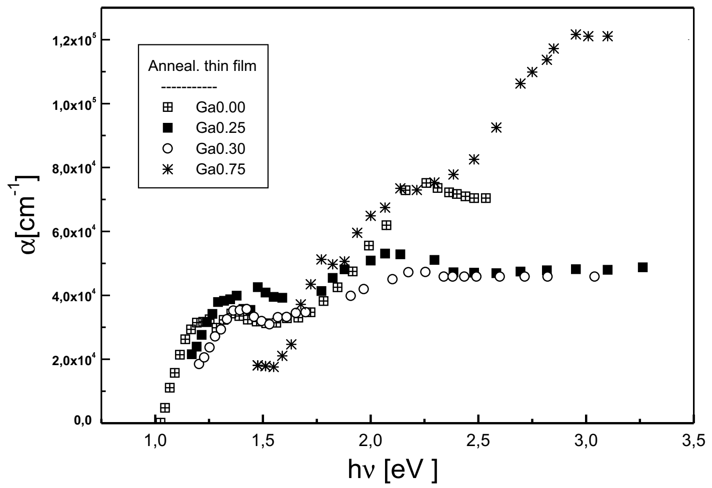


Fig. 9. The variation of absorption coefficient α with the photon energy $h\nu$ for different compositions of annealed thin films.

A similar behaviour has been reported for $CuGaSe_2$ [12] and $CuGaTe_2$ [15] annealed at 423 K for 2 hours. Abd El-Hady et al. studied by X-ray diffraction the variations in the (112) peak position due to changes in the annealing time and temperature. They also reported that after annealing at 423 K for 2 hours, all values of energy gaps changed and the intermediate energy levels E_{g_2} for $CuGaSe_2$ and $CuGaTe_2$ were absent. They attributed it to the effect of thermal treatment which caused a change in the structure from the tetragonal phase to near cubic phase or from the ordered phase to the disordered phase. For $CuGaSe_2$, Albin et al. [27] observed that copper-poor material, which contained a predominance of the cubic sphalerite phase, exhibited the spin-orbit effect alone at 1.992 eV, and that there was a change in band gap from 1.662 eV for the tetragonal phase to 1.718 eV for the sphalerite phase. Moreover, Bodnar et al. [28] reported that annealing in air of the deposited films improves their crystal structure and increases the band gap from 0.92 eV to 1.07 eV for $CuGa_{0.1}In_{0.9}Se_2$. Vacuum annealing at 573 K for 1 hour of the $CuGa_{0.25}In_{0.75}Se_2$ films results in a very small change in the composition [29]. However, data from other workers [30] have shown a loss of selenium from the surface when vacuum annealing was applied. These results are in good agreement with our results of thermal treatment and are confirmed by electrical measurements [13] which exhibit a highly compensated state.

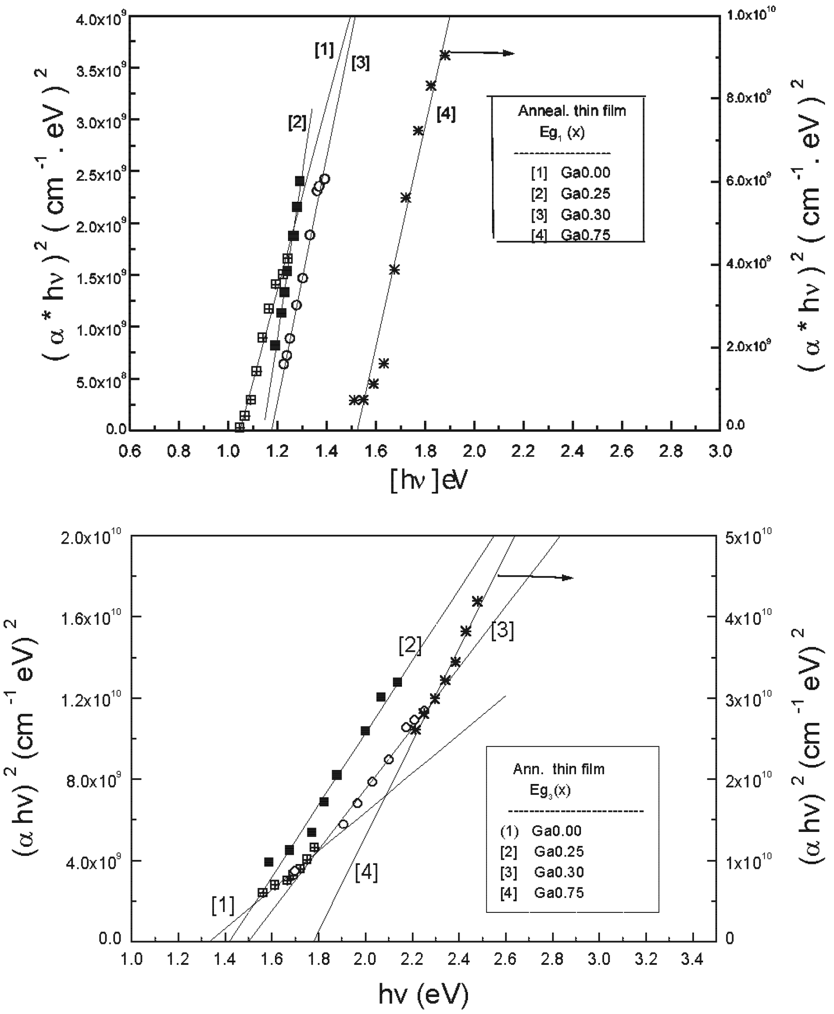


Fig. 10. $(\alpha h\nu)^2$ vs. $h\nu$ for different compositions of annealed thin films; (a) $E_{g_1}(x)$ and (b) $E_{g_3}(x)$.

The primary transition energies of annealed $CuGa_xIn_{1-x}Se_2$ films exhibit also a bowing behaviour as shown in Fig. 11, which can be fitted by a parabolic form,

$$E_{g_1}(x) \quad = \quad 1.04 + 0.46x + 0.22x^2. \tag{7}$$

By substituting the experimental values $E_{g_1}(0) = 1.04$ eV, $E_{g_1}(1) = 1.695$ eV (Ref. [12] in an our previous work) and the bowing parameter c predicted by Shaukat [24], the relationship between E_{g_1} and x is given by

$$E_{g_1}(x) \quad = \quad 1.03 + 0.54x + 0.14x^2. \tag{8}$$

This expression is also consistent with our experimental data for thermally treated films, as shown in Fig. 11 by the dashed line.

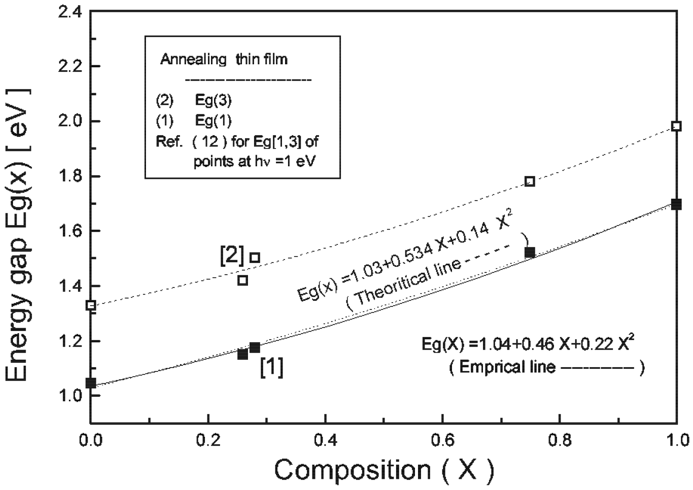


Fig. 11. Variation of the energy gap as a function of composition of annealed thin films of $\mathrm{CuGa}_x\mathrm{In}_{1-x}\mathrm{Se}_2$ *compounds.*

Our results partially throw new light on the description of the previously reported data and show a lack of understanding of the fundamental properties of $\mathrm{CuGa}_x\mathrm{In}_{1-x}\mathrm{Se}_2$ compounds.

References

[1] H. S. Ullal, J. L. Stone, K. Zweibel, T. Surek and R. L. Mitchell, *Proc. 6th Int. PV Science and Engineering Conf.*, New Delhi (1992) Oxford and IBH Publishing, New Delhi (1992) 81.

[2] J. R. Tuttle, M. Ruth, D. Albin, A. Mason, and R. Moufi, *Proc. 20th IEEE PV Specialists Conf.*, Las Vegas, 1988, IEEE (1988) 1525.

[3] W. E. Devaney, W. S. Chen, J. M. Stewart and R. A. Michelson, IEEE Trans. Electron Devices **37** (1990) 428.

[4] W. E. Devaney, J. M. Stewart and W. S. Chen, *Proc. 21st IEEE PV Specialists Conf.*, Kissimmee, 1990, IEEE (1990) 535.

[5] N. G. Dhere, Thin Solid Films **193–194** (1990) 757.

[6] B. Abid, J. R. Gong, H. G. Goslowsky and K. J. Bachmann, *Proc. 19th IEEE PV Specialists Conf.*, New Orleans, 1987, IEEE (1987) 1305.

[7] T. F. Ciszek, R. Bacewicz, J. R. Durrant, S. K. Deb, and D. Dunlavy, *Proc. 19th IEEE PV Specialists Conf.*, New Orleans, 1987, IEEE (1987) 1448.

[8] J. Durrant, *Optical and Photoconductive Characteristics of* $\mathrm{CuIn}_y\mathrm{Ga}_{1-y}\mathrm{Se}_2$ *and* $\mathrm{Cu}_x\mathrm{Ag}_{1-x}\mathrm{InSe}_2$, SERI Technical Report RR-212-3064 (1987).

[9] W. S. Chen, J. M. Stewart, B. J. Stanbery, W. E. Devaney and R. A. Michelson, *Proc. 19th PV Specialists Conf.*, New Orleans, 1987, IEEE (1987) 1445.

[10] B. Dimmler, H. Dittrich, R. Menner and H. W. Schock, *Proc. 19th IEEE PV Specialists Conf.*, New Orleans, 1987, IEEE (1987) 1454.

[11] B. R Pamplin, T. Kiyosawa and K. Masumato, Prog. Cryst. Growth and Character **1** (1979) 331.

[12] S. A. Abd El-Hady, B. A. Mansour and M. A. El- Hagary, Thin Solid Films **248** (1994) 224.

[13] H. Shaban, Ph. D. Thesis, Helwan University (2001).

[14] R. E. Denton, R. D. Cambell and S. G. Tomlin, J. Phys. D **5** (1972) 852.

[15] S. A. Abd El-Hady, B. A. Mansour and S. H. Moustafa, phys. stat. sol. (a) **149** (1995) 601.

[16] T. Yamaguchi, J. Matsufusu and A. Yoshida, Jpn. J. Appl. Phys. **31** (1992) L 703.

[17] D. S. Albin, J. R. Tuttle, G. D. Mooney, J. J. Carapella, A. Duda, A. Mason, and R. Noufi, *Proc. 21st IEEE PV Specialists Conf.*, Kssimlmee, 1990, IEEE (1990) 562.

[18] J. L. Shay, B. Tell, H. M. Kasper and L. M. Schiavone, Phys. Rev. B **5** (1972) 5003.

[19] J. E. Jaffe and A. Zunger, Phys. Rev B **28** (1983) 5822.

[20] J. E. Jaffe and A. Zunger, Phys. Rev. B **29** (1983) 1882.

[21] K. T. Reddy and P. Reddy Jayarama, J. Mater. Sci. Lett. **8** (1989) 110.

[22] W. Horig, H. Neumann, B. Schumann and G. Kuhn, phys. stat. sol. (b) **85** (1978) 57.

[23] H. Neumann, W. Horig, E. Reccius, H. Sabotta, B. Schumann and G. Kuhn, Thin Solid Films **61** (1979) 13.

[24] A. Shaukat, J. Phys. Chem. Solids **51** (1990) 1413.

[25] L. Shay. and J. H. Wemick, *Ternary Chalcopyrite Semiconductors*, Pergamon, Oxford (1975).

[26] L. Artus, Y. Bertrand and C. Ance, J. Phys. C **19** (1986) 5937.

[27] D. Albin, J. Tuttle, J. Goral, A. Mason and R. Noufi, *Proc. 20th IEEE PV Specialists Conf.*, Las Vegas, 1988, IEEE (1988) 1495.

[28] I. V. Bodnar, V. P. Gremenok, E. P. Zaretskaja and I .V. Victorov, Thin Solid Films **207** (1992) 54.

[29] K. Zweibel, H. S. Ullal and B. V. Roedern, *Proc. Of 25th IEEE PV Specialists Conf.*, Washington, 1996, p. 745.

[30] J. J. Loferski, *Symp. non-Stoichiometry in Semiconductors Int. Conf. Advanced Materials-ICAM91*, Strassburg, 1991, p. 257.

GRAĐA I OPTIČKA SVOJSTVA TANKIH POLIKRISTALINIČNIH SLOJEVA $CuGa_xIn_{1-x}Se_2$

Proučavali smo strukturna i optička svojstva tankih polikristaliničnih slojeva $CuGa_xIn_{1-x}Se_2$, isparenih u vakuumu, u ovisnosti o sastavu ($0 \leq x \leq 0.75$). Optički apsorpcijski spektri tankih slojeva $CuGa_xIn_{1-x}Se_2$, ($x \neq 0$), pokazuju četiri energijska procijepa (E_{g_1}, E_{g_2}, E_{g_3} i E_{g_4}) koji se pridjeljuju osnovnom rubu, cijepanju vrpci kristalnim poljem i cijepanju spin-staza, odnosno prijelazima iz 3d stanja bakra. Prvotni prijelazi pokazuju kvadratnu ovisnost koju izražavamo relacijom $E_{g_1}(x) = 1.011 + 0.448x + 0.186x^2$. Druga i treća prijelazna energija su $(0.10 - 0.11$ eV) odnosno $(0.18 - 0.185$ eV) više od primarne prijelazne energije. Pomoću građe slojeva objašnjavamo učinak toplinske obrade na vrijednosti energijskih procijepa. Prvotne prijelazne energije opuštenog $CuGa_xIn_{1-x}Se_2$ mogu se predstaviti kvadratnim izrazom $E_{g_1}(x) = 1.04 + 0.46x + 0.22x^2$.