JOURNAL OF MATERIALS SCIENCE 27 (1992) 646–652

Some optical properties of Se–Ge–As amorphous chalcogenide glasses

M. M. EL-SAMANOUDY, M. FADEL
Physics Department, Faculty of Education, Ain Shams University, Cairo, Egypt

The effects of composition, film thickness, substrate temperature, and annealing of amorphous thin films of $Se_{75}Ge_{25-x}As_x$ ($5 \leqslant x \leqslant 20$) on their optical properties have been investigated. X-ray diffraction revealed the formation of amorphous films. The absorbance and transmission of vacuum-evaporated thin films were used to determine the band gap and refractive index. Optical absorption measurements showed that the fundamental absorption edge is a function of glass composition and the optical absorption is due to indirect transition. The energy gap increases linearly with increasing arsenic content. The optical band gap, E_{opt}, was found to be almost thickness independent. The shapes of the absorption edge of annealed samples displayed roughly the same characteristic as those of the unannealed films, but were shifted towards shorter wavelengths; as a result, E_{opt} increased and E_e, the width of the band tails, decreases. The increase in E_{opt} is believed to be associated with void removal and microstructural re-arrangement during annealing. The influence of substrate temperature on the optical parameters is discussed.

1. Introduction

Analysis of optical absorption spectra is one of the most productive tools for understanding and developing the band structure and energy gap of both crystalline and amorphous non-metallic materials. The absorption coefficients, $\alpha(\omega)$, of the optical absorption near the band edge in many amorphous semiconductors show an exponential dependence on photon energy, $\hbar\omega$, and obey Urbach's empirical relation [1]

$$\alpha(\omega) = \alpha_0 \exp \hbar\omega/E_e \qquad (1)$$

where α_0 is a constant, ω is the angular frequency of the incident photon, $\hbar$ is Planck's constant h divided by 2π, and E_e is the width of the band tails of the localized states in the band gap.

In the high absorption region (where absorption is associated with interband transitions), the form of $\alpha(\omega)$ with photon energy was given in quadratic form by Tauc *et al.* [2], and discussed in more general terms by Davis and Mott [3], whose equation was of the form

$$\alpha(\omega) = \beta(\alpha\hbar\omega - E_{opt})^M/\hbar\omega \qquad (2)$$

where β is a constant equal to $4\pi\sigma_0/nCE_e$, c is the speed of light, σ_0 is the extrapolated conductivity at $1/\pi = 0$, n is the refractive index, E_{opt} is the optical gap and M is a number that characterizes the transition process.

The absorption coefficient, $\alpha(\omega)$, can be calculated from the optical absorption spectra using the relation

$$\alpha(\omega) = 2.303\, A/d \qquad (3)$$

where d is the film thickness and A is defined by $A = \log(I_0/I_t)$. I_0 and I_t are the intensities of the incident and transmitted beams, respectively.

The degree of disorder and defects present in the amorphous structure changes due to heat treatment [4]. The decrease in the disorder and defects in the structural bonding is known to increase the optical band gap, E_{opt}. Thus a study of the variation of E_{opt} as a function of temperature and time of heat treatment may provide a deeper insight into the mechanism of disorder and defect formation in the amorphous chalcogenide.

Various optical properties of chalcogenide glasses have been reported [5–7]. The optical properties of amorphous semiconductors are known to be sensitive to the preparation conditions [8, 9] and the subsequent annealing treatment [10–12].

2. Experimental procedure

Amorphous materials used in the present work to produce thin films of $Se_{75}Ge_{25-x}As_x$ where $5 \leqslant x \leqslant 20$. Raw materials with purity 99.999% were weighed using an electric balance and sealed into evacuated silica tubes under a vacuum of 10^{-5} torr (1 torr = 133.322 Pa). In order to avoid the oxidation of arsenic, above processes were performed as quickly as possible. The tube was kept in furnace at 1000 °C for 15 h. Synthesis was accomplished in an oscillatory furnace designed to ensure homogeneity. The tubes were rapidly quenched in ice-cold water. After removing the ingot from the ampoule, it was used to fabricate thin film samples.

Thin evaporated films of $Se_{75}Ge_{25-x}As_x$ of different compositions were deposited by thermal evaporation techniques on to clean quartz substrates held at a pressure of the order of 1×10^{-5} torr. The thickness of the films was measured by an interferometric method.

Annealing was carried out for 2 h in vacuum of 1×10^{-5} torr, followed by cooling to room temperature.

Absorption measurements in the wavelength range 350–900 nm were carried out using a varian DMS 100 S spectrophotometer.

3. Results and discussion

3.1. Structural properties

3.1.1. X-ray diffraction patterns of $Se_{75}Ge_{25-x}As_x$ glasses in a powder form

Fig. 1a shows the X-ray diffraction (XRD) patterns of four different compositions of the chalcogenide glass system $Se_{75}Ge_{25-x}As_x$ where $5 \leqslant x \leqslant 20$. It is clear from these patterns that no sharp diffraction lines are present. This indicates that all the compositions investigated in powder form are in the amorphous state.

3.1.2. X-ray diffraction patterns of $Se_{75}Ge_{15}As_{10}$ glasses in thin film form after heat treatment

In order to investigate the effect of increasing the annealing temperature on the structure of the $Se_{75}Ge_{15}As_{10}$ (thickness 381.0 nm), the prepared samples were annealed at three different elevated temperatures (323, 373 and 403 K) below T_g (418 K), in addition to room temperature, 293 K. The XRD patterns are represented in Fig. 1b. As shown, the sample in thin film form when annealed for 2 h under vacuum and 1 h at elevated temperature up to 403 K, retain the amorphous structure.

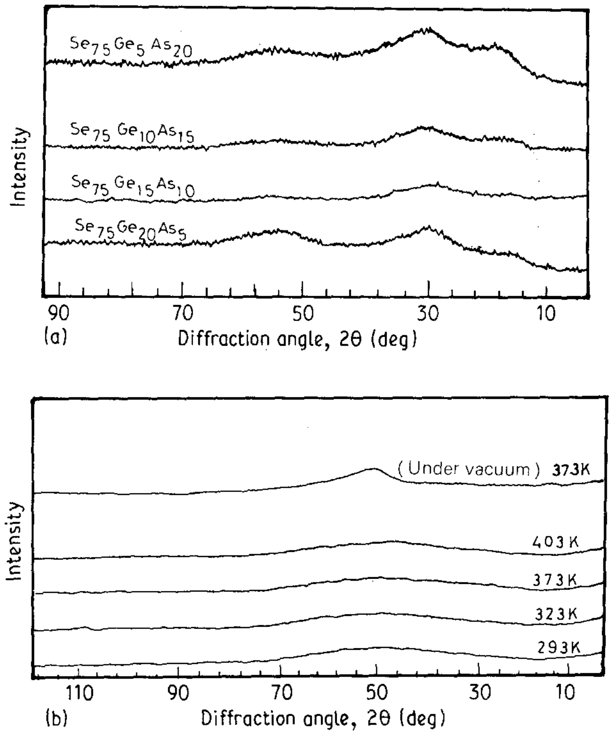

Figure 1 X-ray diffraction patterns of (a) glass samples containing different compositions (powder), (b) glass samples of $Se_{75}Ge_{15}As_{10}$ annealed at different temperatures (thin film).

3.2. Effect of composition on the optical band gap at room temperature

The variation of optical absorbance as a function of wavelength for samples having different composition is shown in Fig. 2a. It is clear that there is no sharp absorption edge and this is a characteristic of the glassy state. It is seen from this figure that the position of the fundamental absorption edge shifts to the higher wavelength region with increasing arsenic content.

The usual method for determining the value of E_{opt} involves plotting a graph of $(\alpha\hbar\omega)^M$ versus photon energy $\hbar\omega$. If an appropriate value of M is used to linearize the graph, the value of E_{opt} will be given by intercept on the $\hbar\omega$ axis.

The present results were found to obey Equation 2 with $M = 2$, as shown in Fig. 2b corresponding to data of Fig. 2a, indicating that indirect photon transitions are involved. E_{opt} and constant β calculated from the curves are listed in Table I.

Fig. 2c demonstrates that the exponential behaviour of the absorption edge, via Equation 1 is satisfied in our glassy films, values of the width, E_e, of the band-tails are also given in Table I. Zanini and Tauc [13] have suggested that it arises from electron transitions between localized states where the density of the localized states is exponentially dependent on energy. But Davis and Mott [3] reported that this explanation is not valid for all disordered materials, because the slope of the observed exponential behaviour remains unchanged for many crystalline and non-crystalline materials.

In conclusion, as the arsenic content increases in the glass structure, deeper band tails extended in the gap and led to an increase in the value of E_e and a decrease in the value of E_{opt}. The energy gaps increase linearly with increasing arsenic content (see Fig. 2d).

3.3. Effect of thickness on the optical band gap

Fig. 3a shows the absorption spectra near the fundamental edge for a series of $Se_{75}Ge_{15}As_{10}$ of various thicknesses. As seen from this figure, the absorption edge moves to a higher wavelength as the thicknesses of the glass films are increased.

Fig. 3b shows the variation of $(\alpha\hbar\omega)^{1/2}$ as a function of $\hbar\omega$; E_{opt}, β and E_e (estimated from Equations 1 and 2) are given in Table II. It may be noted that the optical band gap is independent of film thickness. The exponential dependence of $\alpha(\omega)$ on $\hbar\omega$ for the films indicates that they obey Urbach's rule. Also, as the values of E_e are very much larger than 0.05 eV and vary with composition, Tauc's model based on electronic transitions between localized states in the band-edge tails may well be valid in our materials; an unambiguous interpretation of the nature of the absorption edge requires that the effect of temperature must be considered. The values of β given in Tables I

TABLE I The optical properties of thin film glasses having different composition

Composition	Thickness (nm)	As-evaporated			After annealing		
		E_{opt} (eV)	β (10^5 cm^{-1} eV^{-1})	E_e (eV)	E_{opt} (eV)	β (10^5 cm^{-1} eV^{-1})	E_e (eV)
$Se_{75}Ge_{20}As_5$	605.4	1.975	6.542	0.160	2.07	7.160	0.14
$Se_{75}Ge_{15}As_{10}$	607.4	1.880	6.602	0.166	1.96	7.490	0.138
$Se_{75}Ge_{10}As_{15}$	510.0	1.810	6.575	0.217	1.89	9.070	0.152
$Se_{75}Ge_5As_{20}$	437.5	1.710	4.649	0.255	1.82	5.268	0.20

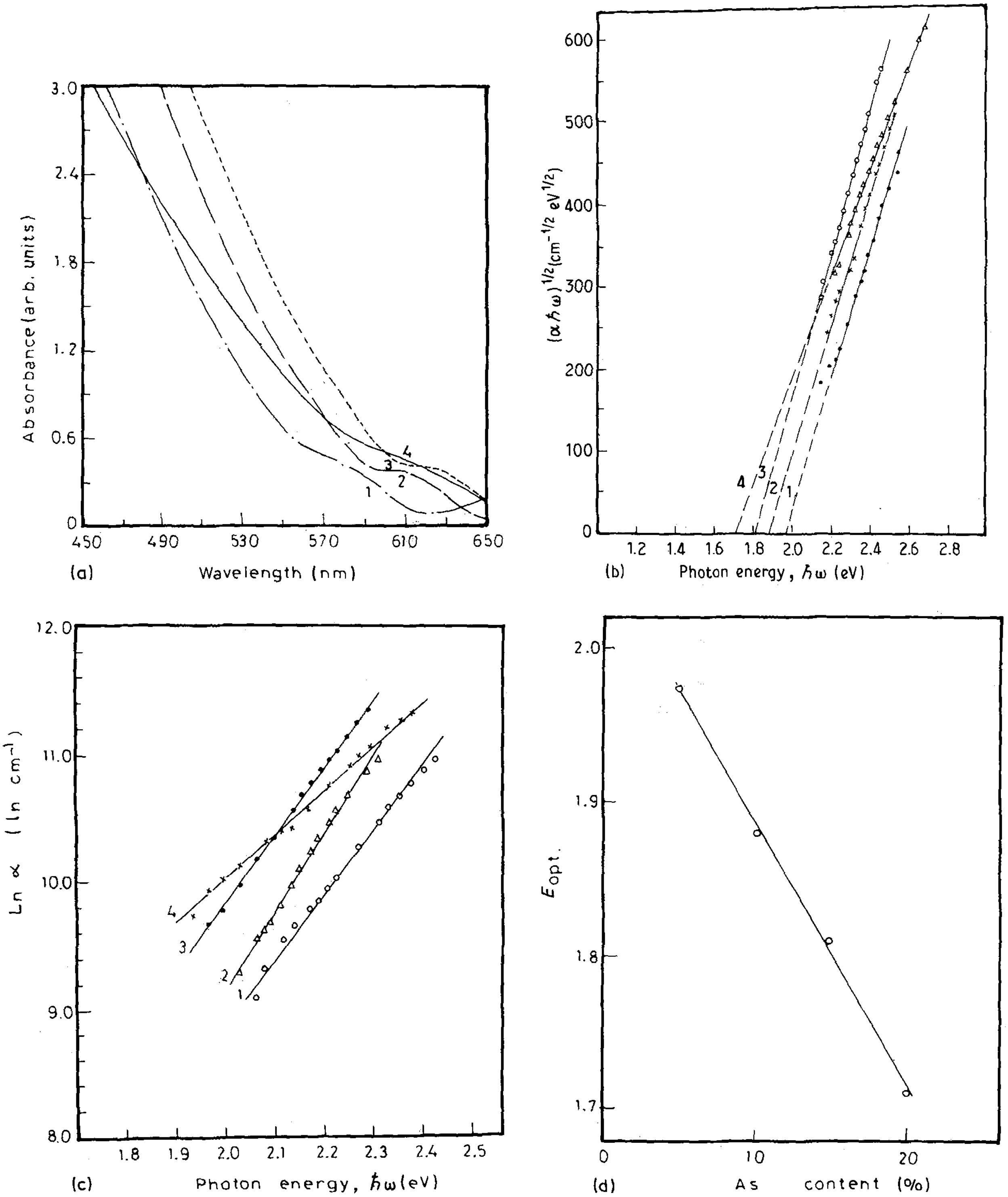

Figure 2 (a) Optical absorption spectra of $Se_{75}Ge_{25-x}As_x$ thin films (compositions as in Table I). (b) Optical absorption data of (a) replotted in accordance with absorption by indirect transitions. (c) Data of (a) plotted in accordance with the Urbach law (Table I). (d) Data derived from (b) showing E_{opt} as a function of arsenic content. 1, $Se_{75}Ge_{20}As_5$; 2, $Se_{75}Ge_{15}As_{10}$; 3, Se_{75}, $Ge_{10}As_{15}$; 4, $Se_{75}Ge_5As_{20}$.

TABLE II The effect of thickness on the fundamental absorption edge of $Se_{75}Ge_{15}As_{10}$

Thickness (nm)	As-evaporated			After annealing		
	E_{opt} (eV)	β (10^5 cm^{-1}eV^{-1})	E_e (eV)	E_{opt} (eV)	β (10^5 cm^{-1} eV^{-1})	E_e (eV)
167.1	1.85	5.63		1.98	8.403	0.157
381.0	1.85	5.74	0.23	1.97	5.800	0.179
607.4	1.86	6.57	0.168	1.96	7.490	0.138
661.0	1.86	5.92	0.139	1.96	8.210	0.139
783.3	1.85	7.97	0.143	1.96	9.285	0.145

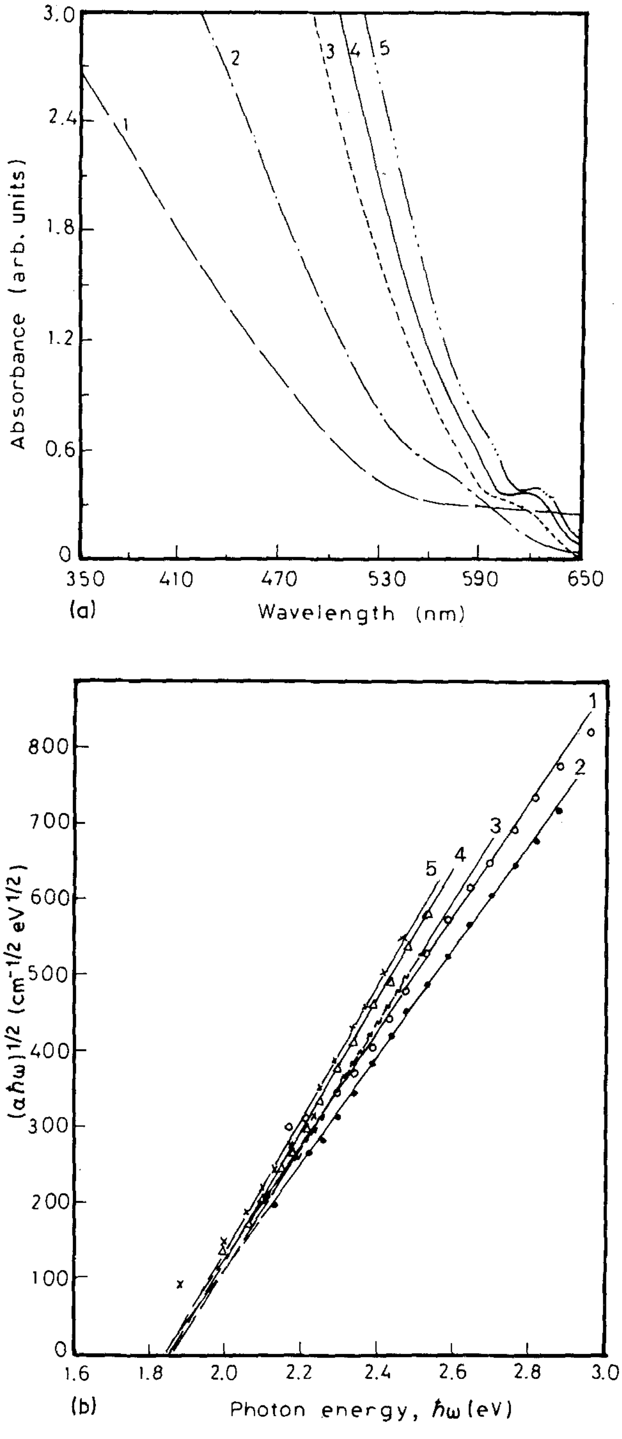

Figure 3 (a) Absorption spectra as a function of wavelength for $Se_{75}Ge_{15}As_{10}$ thin films at different thickness. (b) Data of (a) replotted in accordance with the theory of indirect transitions for $Se_{75}Ge_{15}As_{10}$. 1, 167.1 nm; 2, 381.0 nm; 3, 607.4 nm; 4, 661.0 nm; 5, 783.3 nm.

and II are in good agreement with the theoretical values [8, 14].

3.4. Effect of annealing and substrate temperature on the optical parameters

The effect of annealing *in vacuo* ~ 10^{-5} torr for 2 h at 373 K on the optical properties of $Se_{75}Ge_{25-x}As_x$ of different compositions (Fig. 4a) and $Se_{75}Ge_{15}As_{10}$ (Fig. 4b), was investigated. The shapes of the absorption edges for annealed films display approximately the same properties, but they shift to shorter wavelengths and so the value of E_{opt} in general increases (Fig. 4c). The calculated values of E_{opt} and E_e from Fig. 4d are listed in Tables I and II. During the annealing process, the films will have time for some atomic rearrangement to take place. Some defects will be removed which, reducing the density of dangling bonds, re-distribute atomic distances and band angles and E_{opt} will then increase.

Fig. 5a shows the absorbance spectra of $Se_{75}Ge_{20}As_5$ at different substrate deposition temperatures in the range 323–403 K. Fig. 5b shows the plot of $(\alpha\hbar\omega)^{1/2}$ versus $\hbar\omega$. The values of E_{opt} and the band tailing, E_e, are listed in Table III. The substrate temperature does not affect E_{opt} appreciably in the temperature range 323–373 K; however, as the temperature increases to 403 K, E_{opt} decreases.

Variation of the optical gap in chalcogenide after various heat treatments has been reported by several workers [15–17].

3.5. The effect of composition and thickness on the refractive index of $Se_{75}Ge_{25-x}As_x$ thin film glasses

The refractive index of a solid is an important physical property which gives valuable information on the electronic polarizability and local field inside the material. It has also been used for determining the density of colour in thin films [18].

The optical properties were studied by measuring the transmission spectra between the wavelengths 400 and 900 nm. The refractive index was determined using a procedure devised by Manifacier *et al.* [20]. This is based on drawing envelope curves through minima (T_{min}) and (T_{max}) in the transmission spectrum. The variation in transmission is principally due to an

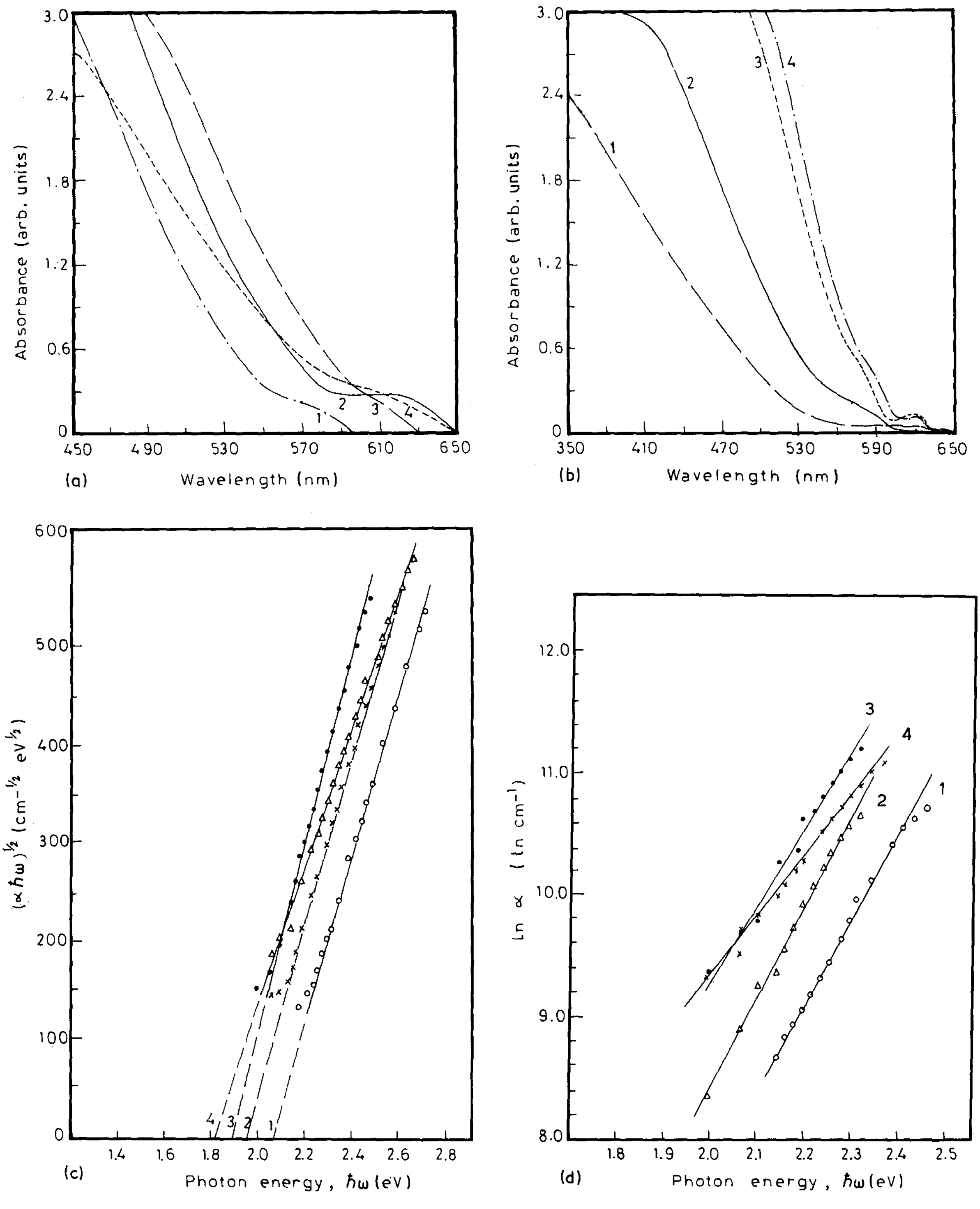

Figure 4 (a) Optical absorption spectra of annealed $Se_{75}Ge_{25-x}As_x$ thin films (compositions in Table I). 1, $Se_{75}Ge_{20}As_5$; 2, $Se_{75}Ge_{15}As_{10}$; 3, $Se_{75}Ge_{10}As_{15}$; 4, $Se_{75}Ge_5As_{20}$. (b) Absorption spectra as a function of wavelength of annealed $Se_{75}Ge_{15}As_{10}$ thin films at different thicknesses. 1, 167.1 nm; 2, 381.0 nm; 3, 661.0 nm; 4, 783.3 nm. Data of (a) replotted in accordance with the theory of indirect transitions for annealed $Se_{75}Ge_{25-x}As_x$. (d) Data of (a) replotted in accordance with the Urbach law for annealed $Se_{75}Ge_{25-x}As_x$.

TABLE III The effect of substrate temperature on the optical properties of $Se_{75}Ge_{15}As_{10}$

Thickness (nm)	Substrate temp (K)	E_{opt} (eV)	β (10^5 cm^{-1} eV^{-1})	E_e (eV)
165.3	323	1.94	7.972	0.198
164.1	373	1.94	7.062	0.174
169.3	403	1.78	2.845	0.172

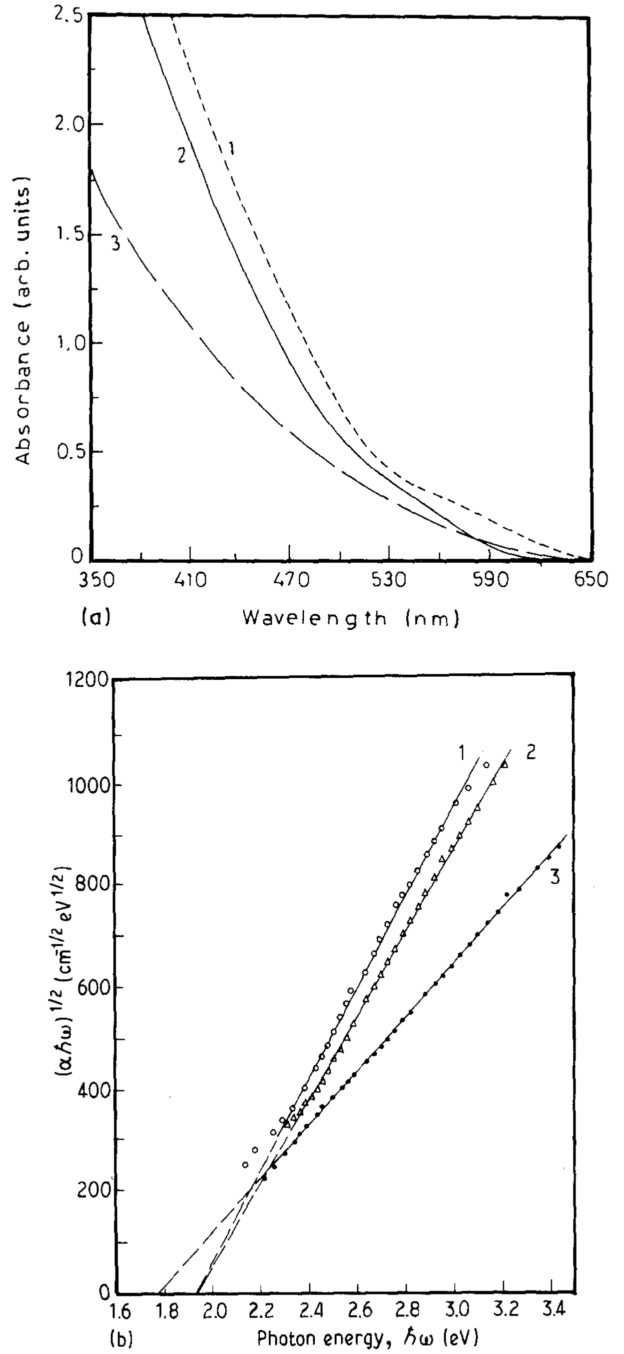

Figure 5 (a) Absorbance as a function of wavelength for $Se_{75}Ge_{20}As_5$ thin film deposited at (1) 323 K, (2) 373 K, (3) 403 K. (b) Data of (a) plotted in accordance with the theory of indirect transitions.

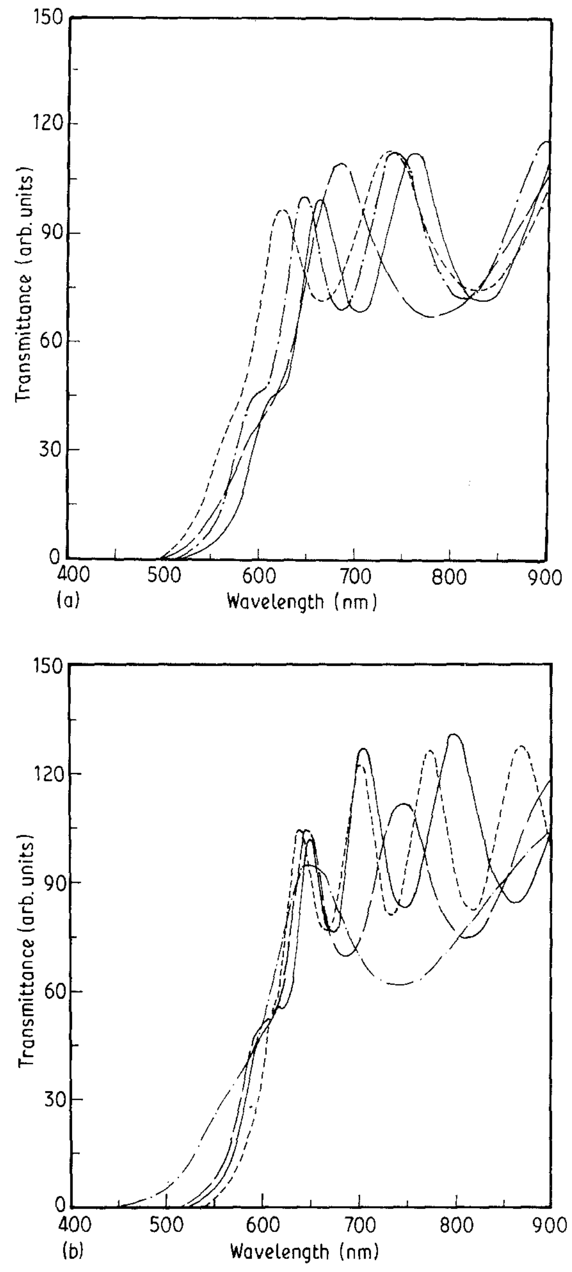

Figure 6 (a) The transmission spectrum for $Se_{75}Ge_{25-x}As_x$ thin films (compositions as in Table IVa). (— — —) $Se_{75}Ge_5As_{20}$, (——) $Se_{75}Ge_{10}As_{15}$, (- - -) $Se_{75}Ge_{15}As_{10}$, (—·—) $Se_{75}Ge_{20}As_5$. (b) The transmission spectrum for $Se_{75}Ge_{15}As_{10}$ at different thicknesses. (—·—) 381.0 nm, (——), 455.8 nm, (— — —) 607.4 nm, (- - -) 783.3 nm.

interference phenomenon. They obtained

$$n = [N + (N^2 - n_1^2)^{1/2}]^{1/2} \qquad (4)$$

with

$$N = 1 + \left(\frac{n_1^2}{2}\right) + 2n_1[(T_{\max} - T_{\min})]/T_{\max}T_{\min}$$

where n_1 is the refractive index of the glass substrates.

Fig. 6a and b gives transmission spectra for $S_{75}Ge_{25-x}As_x$ thin films at the different compositions listed in Table IVa and for $Se_{75}Ge_{15}As_{10}$ at different thicknesses (Table IVb). The calculated values of the refractive index, n, at various wavelengths are also listed in this table. It is seen that the refractive index of the thin films tends to increase slightly with increasing arsenic content, and to decrease to approach constant values at long wavelengths. The constancy of n at long wavelengths may be characteristic of a system with little free-carrier absorption. The refractive index of annealing samples at different compositions are listed in Table IV. It had no marked effect on annealing at 373 K under a vacuum of 10^{-5} torr.

4. Conclusion

In $Se_{75}Ge_{25-x}As_x$ thin films a systematic change in the value of E_e and E_{opt} with composition suggests that the degree of disorder in these systems is increased.

The optical absorption spectra indicated that the optical gap decreases as the arsenic content in the

TABLE IV(a) The effect of composition on the values of the refractive index

Wavelength (nm)	As-evaporated				After annealing			
	Refractive index (n)				Refractive Index (n)			
	$Se_{75}Ge_{20}As_5$	$Se_{75}Ge_{15}As_{10}$	$Se_{75}Ge_{10}As_{15}$	$Se_{75}Ge_5As_{20}$	$Se_{75}Ge_{20}As_5$	$Se_{75}Ge_{15}As_{10}$	$Se_{75}Ge_{10}As_{15}$	$Se_{75}Ge_5As_{20}$
600	1.970	1.972	1.974	1.978	1.970	1.970	1.971	1.972
650	1.968	1.972	1.974	1.978	1.972	1.973	1.965	1.974
700	1.970	1.972	1.972	1.975	1.971	1.972	1.973	1.975
750	1.971	1.971	1.971	1.973	1.971	1.971	1.972	1.974
800	1.970	1.971	1.971	1.973	1.970	1.971	1.972	1.973
850	1.971	1.972	1.972	1.973	1.972	1.973	1.972	1.973

TABLE IV(b) The effect of thickness on the refractive index of $Se_{75}Ge_{15}As_{10}$ glasses

Wavelength (nm)	As evaporated thickness (nm)				After annealing thickness (nm)		
	381.0	455.8	607.4	783.3	381.0	455.8	783.3
600	1.977	1.973	1.974	1.971	1.975	1.972	1.973
650	1.973	1.972	1.974	1.970	1.974	1.970	1.972
700	1.973	1.971	1.972	1.971	1.974	1.971	1.972
750	1.974	1.972	1.972	1.970	1.974	1.970	1.972
800	1.974	1.972	1.971	1.971	1.974	1.970	1.970
850	1.974	1.972	1.971	1.971	1.974	1.970	1.970

glasses increases, and these glasses show an absorption which fits into an indirect interband transition, as discussed by Mott and Davis.

The optical data may also be fitted to an exponential Urbach formula.

It is reasonable to assume that the observed changes in the optical properties on annealing and high-temperature deposition are a result of microstructural re-arrangement initiated either during deposition or during annealing.

Acknowledgements

The authors thank Professor A. A. El-Shazly and Professor M. A. Afifi, for many useful and stimulating discussions and encouragement throughout this study.

References

1. F. URBACH, *Phys. Rev.* **92** (1953) 1324.
2. J. TAUC, R. GRIGOROVICI and A. VANCU, *Phys. Status Solidi* **15** (1966) 627.
3. E. A. DAVIS and N. F. MOTT, *Phil. Mag.* **22** (1970) 903.
4. S. HASEGAWA, S. YAZAKI and T. SHIMIZU, *Solid State Commun.* **26** (1978) 407.
5. MASAKUNI SUZUKI, HIROYOSHI OHDAIRA, TOSHIYUKI MATSUMI, MINORU KUMEDA and TATSUO SHIMIZU, *Jpn. J. Appl. Phys.* **16** (1977) 221.
6. T. KANAMORI, Y. TERUNUMA, S. TAKAHASHI and T. MIYASHITA *J. Non-Cryst. Solids* **69** (1985) 23.
7. A. M. FLANK, D. BAZIN, H. DEXPERT, P. LAGARDE, C. HERVO and J. Y. BARRAUD, *ibid.* **91** (1987) 306.
8. N. F. MOTT and E. A. DAVIS, "Electronic Process in Non-Crystalline Materials" (Clarendon Press, Oxford, 1971).
9. E. A. DAVIS, in "Electronic and structural properties of amorphous semiconductors", edited by P. G. Lecombe and J. Mart (Academic Press, London, New York, 1973) p. 425.
10. M. H. BRODSKY, *J. Vac. Sci. Technol.* **8** (1971) 125.
11. M. L. THEYE, *Mater. Res. Bull.* **6** (1971) 103.
12. G. D. CODY, T. TIEDGE, B. ABELES, B. BROOKS and Y. GOLDSTEIN, *Phys. Rev. Lett.* **47** (1981) 1480.
13. M. ZANINI and J. TAUC, *J. Non-Cryst. Solids* **23** (1977) 349.
14. J. TAUC, "Amorphous and Liquid Semiconductors" (Plenum Press, London, 1974) p. 159.
15. T. LGOOND and Y. TOYOSHIMA, *J. Non-Cryst. Solids* **11** (1973) 304.
16. J. J. BERKS, S. W. IXG and W. J. HILLEGES, *J. Appl. Phys.* **92** (1974) 908.
17. U. K. REDDY, *Phys. Status Solidi (a)* **89** (1985) 255.
18. S. K. DEB, *Phil. Mag.* **27** (1973) 801.
19. M. WOHLECKE, V. MARRELO and A. ONTON, *J. Appl. Phys.* **48** (1977) 1748.
20. J. C. MANIFACIER, J. GASIOT and J. P. FILLARD, *J. Phys. E* **9** (1976) 1002.

Received 20 September 1990
and accepted 25 March 1991