Journal of Optoelectronics and Advanced Materials Vol. 4, No. 1, March 2002, p. 41 - 44

ELECTRON-INDUCED CHANGES IN ABSORPTION EDGE OF AMORPHOUS Ge-As-Se FILMS

N. D. Savchenko

Uzhgorod National University, Department of Engineering, 13 Kapitulna St., Uzhgorod 88000, Ukraine

The experimental results on the effect of thermal annealing and high-energy electron (6.5 MeV) irradiation on the absorption edge for thin films obtained by thermal evaporation of bulk $Ge_x(As_2Se_3)_{1-x}$ (x = 0.038 - 0.167), $(GeSe_2)_y(As_2Se_3)_{1-y}$ (y = 0.4 - 0.8) glasses have been given along with the results of computations of the optical band gap. To account for the possible bond configurations in the investigated films the ordered bond network model and the random bond network model have been used. The mechanism for thermal and electron-induced changes in the structure and optical properties of the amorphous films under investigation has been discussed.

(Received June 25, 2001; accepted March 4, 2002)

Keywords: Chalcogenides, Electron-induced changes, Thin films, Optical band gap

1. Introduction

Thin films based on ternary chalcogenide glasses of Ge-As-Se family have attracted considerable interest because of the changes in their structure and electronic properties observed under thermal treatment and illumination [1 - 4]. The structural changes should be expected also under the high-energy electron irradiation, resulting, e.g., from the displacement of atoms by the impact mechanism [5]. Thin Ge-As-Se films are usually prepared in non-equilibrium conditions and is one of this reasons for the origin of chemical structure disordering. In this work the experimental results on the effect of thermal treatment and high-energy electron (6.5 MeV) irradiation on the absorption edge for thin films obtained by thermal evaporation of bulk $Ge_x(As_2Se_3)_{1-x}$ (x = 0.038, 0.057, 0.090, 0.107, 0.138, 0.167), $(GeSe_2)_y(As_2Se_3)_{1-y}$ (y = 0.4, 0.5, 0.6, 0.8) glasses have been given. Theoretical computations of the optical band gaps for the glassy compositions under studies have been carried out by linear combination of atomic orbitals [6].

2. Experimental and computational procedure

Thin films 1 μm thick have been deposited from the starting glasses of $Ge_x(As_2Se_3)_{1-x}$ (x = 0.0380 - 0.167) and $(GeSe_2)_y(As_2Se_3)_{1-y}$ (y = 0.4 - 0.8) families by thermal evaporation in vacuum of 10^{-3} Pa. Bulk glasses have been prepared be melting high purity As, Se and Ge (5N) component mixtures in evacuated and sealed silica ampoules followed by melt quenching. Tailor-made effusion cells were used for the vapour sources. The film deposition rate was about (10.0 ± 0.1) nm/s. Thin films have been deposited onto unheated optical glass substrates. The irradiation of the films have been carried out on M-10 microtron with 6.5 MeV energy electrons at total electron flux of 1×10^{16} cm^{-2} and beam density of 10^{11} cm^{-2} s^{-1}. Film annealing has been performed in vacuum at a temperature of 25 degrees below melting point of the starting glass, during two hours. Optical

transmittance of the samples has been measured within an accuracy of ± 1 %. The absorption coefficient (α) has been calculated by Swanepoel method [7]. The optical band gap has been determined using a Tauc plot $(\alpha h\nu)^{1/2} = f(h\nu)$.

The calculation of the optical band gap has been carried out by the linear combination of atomic orbitals method [6] by summing over the contributions of different chemical bonds. To judge the possible bond arrangements in ternary compounds under investigation two models have been used: the network with bond ordering (the model of cross-linked chains) and the model of a network with bond disordering. The optical band gap has been derived from the equations:

$$E_o = 3.6 \times \{V_2 + V_3\}^{1/2} - 1/2[\, x_1(V_1^{As} + V_1^{Se}) + x_2(V_1^{Ge} + V_1^{Se}) + x_3(V_1^{Ge} + V_1^{As})] + \\ + x_4 V_1^{As} + x_5 V_1^{Ge} + x_6 V_1^{Se}\}, \quad (1)$$

$$V_2 = k/(\Sigma\, x_i d_i)^2, \quad (2)$$

$$V_3 = x_1^* (\varepsilon_h^{Se} - \varepsilon_h^{As})/2 + x_2^* (\varepsilon_p^{Se} - \varepsilon_h^{Ge})/2 + x_3^* (\varepsilon_p^{As} - \varepsilon_h^{Ge})/2, \quad (3)$$

where x_1 - x_6, x_i* are the molar fractions for the chemical bond, ε_p, ε_h, $V_1^{a,c}$ are atomic terms taken from the generalized periodic table [6], d_i are covalent bond distances, k = 0.16459 eV × nm^2. The following covalent bond distances have been used in the calculations: $d_{As\text{-}Se}$ = 0.241 nm, $d_{Ge\text{-}Se}$ = 0.236 nm [8], $d_{Ge\text{-}As}$ = 0.248 nm, $d_{As\text{-}As}$ = 0.249 nm, $d_{Se\text{-}Se}$ = 0.234 nm $d_{Ge\text{-}Ge}$ = 0.247 nm [9]. The computational error was not larger than 2 %.

Molar fraction for chemical bonds have been calculated from the experimental density values ρ and concentration of the structural units following the procedure close to the one reported in [10]. The difference was in the use of the average molar mass value $\overline{M}$ instead of the conventional molar mass of the glass for determination of the molar volume $\bar{v} = \overline{M} / \rho$.

3. Results and discussion

Molar fraction for different chemical bonds, x_i, and optical band gap values, E_{g1}^o and E_{g2}^o, for two models (Model 1 - the model of cross-linked chains, Model 2 - network with bond disordering) along with the density (ρ) for the glasses of $Ge_x(As_2Se_3)_{1-x}$ and $(GeSe_2)_y(As_2Se_3)_{1-y}$ families are given in the Table 1. One observes that theoretical optical band gap increases with the increase in Ge content. The optical band gap values calculated following Model 1 are larger than that for the Model 2.

Table 1. Theoretical distribution of chemical bonds and calculated optical band gaps values for glasses of $Ge_x(As_2Se_3)_{1-x}$ and $(GeSe_2)_y(As_2Se_3)_{1-y}$ families.

x	y	ρ	Molar fraction for chemical bonds, x_i								E_{g1}^o,	E_{g2}^o,
			Model 1					Model 2				
		g/cm^3	As-Se	Ge-Se	As-Se	Ge-Se	Ge-As	As-As	Ge–Ge	Se-Se	eV	eV
0	-	4.58	1.00	-	0.50	-	-	0.15	-	0.25	1.70	1.66
0.05	-	4.55	0.83	0.17	0.42	0.08	0.07	0.18	0.03	0.22	1.80	1.68
0.10	-	4.49	0.63	0.37	0.31	0.19	0.12	0.13	0.06	0.19	1.93	1.75
0.15	-	4.48	0.42	0.58	0.25	0.25	0.18	0.08	0.08	0.16	2.09	1.85
-	0.4	4.47	0.58	0.42	0.30	0.20	0.12	0.10	0.04	0.24	1.96	1.74
-	0.5	4.44	0.48	0.52	0.26	0.24	0.13	0.08	0.06	0.23	2.02	1.77
-	0.6	4.43	0.38	0.62	0.22	0.28	0.13	0.06	0.09	0.22	2.09	1.85
	0.8	4.38	0.19	0.81	0.15	0.35	0.12	0.02	0.16	0.20	2.20	1.96

Correlation between experimental and theoretical (shown by solid lines) concentration dependences of optical band gap for $Ge_x(As_2Se_3)_{1-x}$ and $(GeSe_2)_y(As_2Se_3)_{1-y}$ thin films has been presented in Fig. 1 and 2. After electron irradiation of $Ge_x(As_2Se_3)_{1-x}$ films the optical band gap decreases as compared to that for the as-deposited) ones (rhombs and circles in Fig. 1). The highest change (about 0.07 eV) has been observed for the composition with x = 0.038. With an increase in Ge content the changes in optical band gap after irradiation tend to decrease, being of about 0.01 eV for x = 0.167 that is within experimental error, i. e. thin films deposited from the glasses with higher Ge content show higher radiation stability. In contrast to $Ge_x(As_2Se_3)_{1-x}$ films, an increase in optical band gap value of about 0.04 - 0.05 eV in result of electron irradiation has been seen for as-deposited thin films of the $(GeSe_2)_y(As_2Se_3)_{1-y}$ family (Fig. 2). The opposite sign of the changes in E_g^ovalue for as-deposited thin films of two composition lines under electron irradiation proves that the structural changes as a result of high-energy electron irradiation are different for these groups of compounds.

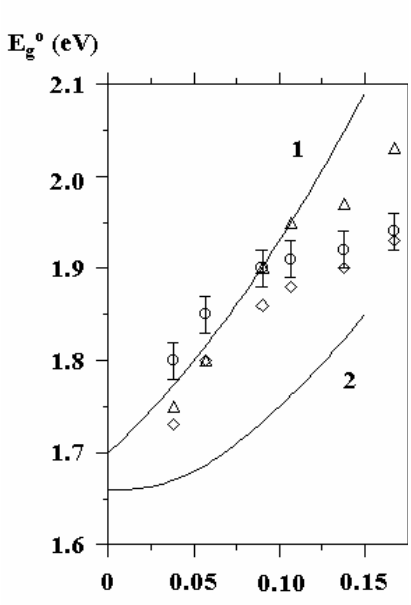

Fig. 1. Dependences on concentration of the optical band gap for $Ge_x(As_2Se_3)_{1-x}$ thin films: as-deposited (circles), after electron irradiation (rhombs) and thermal annealing (triangles). Curves 1 and 2 show theoretical values for Model 1 and Model 2, respectively (see Table 1).

For thin films of the first group, structural disordering could be suggested (Ge-Ge, As-As and Se-Se homopolar bonds could be formed under electron irradiation). It follows from the fact that the optical band gap values for the compositions with $x \geq 0.09$ have been found to approach the theoretical values derived in the Model 2. The highest number of homopolar bonds is characteristic to the composition with high content of germanium (x = 0.167) and defines their high radiation stability. The average coordination number for this composition is about 2.67. For chalcogenide glasses with the average coordination number close to this value, the possibility of $2D \rightarrow 3D$ transition had been suggested [11]. At this average coordination number value the compactness for Ge-As-Se glasses have been reported to be the lowest [4] and the fundamental absorption edge shift to be the highest [11] within the glass family. The opposing illumination and high-energy irradiation effect on the absorption edge (for the films) suggests different mechanisms for photo- and electron-induced changes in thin films. It is evident, that the electron irradiation of thin films of the second group leads to a structural ordering, since experimental E_g^o values are close to those, fitted in the Model 1. It has been found that the approach of E_g^o values to the E_{g1}^o values (curves 1). This suggests that structural ordering takes place under annealing. The most significant changes in the optical band gap (about 0.08 - 0.12 eV) resulted from thermal annealing have been revealed for $(GeSe_2)_y(As_2Se_3)_{1-y}$ thin films. Thus, more chemically disordered structure is formed in the process of deposition of $(GeSe_2)_y(As_2Se_3)_{1-y}$ thin films as opposed to $Ge_x(As_2Se_3)_{1-x}$ films.

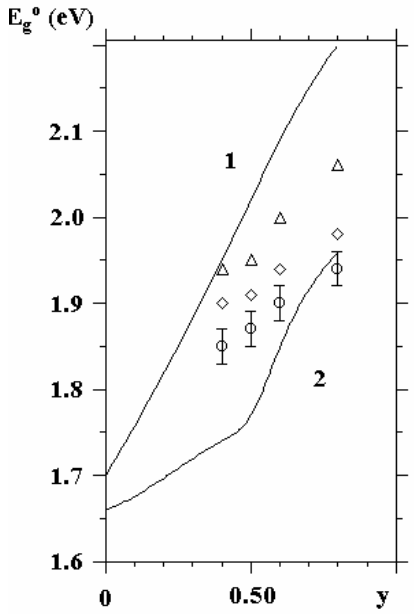

Fig. 2. Dependence on concentration of optical band gap for $(GeSe_2)_y(As_2Se_3)_{1-y}$ thin films: as-deposited (o), after electron irradiation (◊) and thermal annealing (Δ). Curves 1 and 2 show theoretical values for Model 1 and Model 2.

4. Conclusions

Theoretical and experimental data on the optical band gap for ternary chalcogenide materials of Ge-As-Se family have been compared.

For thin films deposited from $Ge_x(As_2Se_3)_{1-x}$ (x = 0.038 - 0.167) and $(GeSe_2)_y(As_2Se_3)_{1-y}$ (y = 0.4 - 0.8) glasses the high-energy electron irradiation (6.5 MeV) and thermal annealing effects on the optical band gap have been found to be of different nature. The highest stability to high-energy electron irradiation for the compositions under investigation has been observed for $Ge_x(As_2Se_3)_{1-x}$ films with x = 0.167.

Theoretical approach used in computation of the concentration dependence of the optical band gap gives results in agreement with the experimental ones.

References

[1] A. Madan, M. P. Shaw, The Physics and Application of Amorphous Semiconductors, Academic Press, Inc., Boston (1988).
[2] S. V. Svechnikov, V. V. Khiminets, N. I. Dovgoshey, Non-crystalline Multinary Non-crystalline Chalcogenides and Their Application in Optoelectronics, Naukova Dumka, Kiev (1992).
[3] A. M. Andriesh, Rus. J. Phys. & Techn. Semicond. **32**, No. 8, 970 (1998).
[4] E. R. Skordeva, D. D. Arsova, J. Non-Cryst. Sol. **192&193**, 665 (1995).
[5] A. O. Matkovsky, S. B. Uzbitsky, O. I. Shpotyuk, Sov. J. Solid State Physics **5**, 1790 (1990).
[6] W. A. Harrison, Electronic Structure and the Properties of Solids. The Physics of the Chemical Bond, W. H. Freeman & Company, San Francisco (1980).
[7] R. Swanepoel, J. Phys. **E16**, 1214 (1983).
[8] O. Uemura, Y. Nagata, T. Usuki, Y. Kameda, J. Non-Cryst. Sol. **192&193**, 74 (1995).
[9] Physical and Chemical Properties of Semiconductor Materials. Handbook, Science, Moscow (1979).
[10] Z. U. Borisova, The Chemistry of the Vitreous Semiconductors, Leningrad (1972).
[11] K. Tanaka, Phys. Rev. **B39** 1270 (1989).