OPTICAL PROPERTIES OF As-Se-Te(S) CHALCOGENIDE GLASSES

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Abstract- The transmission spectra of the thin film with compositions $As_{40}Se_{60}$, $As_{40}Se_{30}Te_{30}$ and $As_{40}Se_{30}S_{30}$ were measured in the spectral range 190-1100 nm. Change of the optical and energy parameters has established by analysis of the optical transmission spectra depending on the chemical composition. The results are explained with changes in the degree of disorder and concentration local defects depending on the chemical composition.

Keywords: Thin Film, Chalcogenide Glasses, Optical and Energy Parameters, Chemical Composition.

I. INTRODUCTION

The chalcogenide vitreous semiconductors (CVS) are characterized by unique physical properties, has received special attention in connection with the broad forecast for using these materials in photolithography, holography, and microelectronics [1-3].

The purpose of this paper is to study the optical properties of chalcogenide glasses, with compositions $As_{40}Se_{60}$, $As_{40}Se_{30}Te_{30}$ and $As_{40}Se_{30}S_{30}$. The optical studies provide information on the relationship of the local structure and physical properties.

II. EXPERIMENTAL DETAILS

A. Sample Preparation and Optical Experiments

The glassy samples with compositions of $As_{40}Se_{60}$, $As_{40}Se_{30}Te_{30}$ and $As_{40}Se_{30}S_{30}$ were synthesized from 5N purity elements by the conventional melt-quenching method. The components of a proper composition were placed in a quartz ampoule which was evacuated to a residual pressure of 10^{-3} Pa. The syntheses were performed in a rotary furnace as the ampoules were heated up to 950 °C and kept at this temperature for 12 h, rotating the furnace for homogeneous melting. After finishing the synthesis, the ampoules were pulled out and were quenched in air.

The transmission spectra of the thin film in the spectral range 190-1100 nm were obtained using ultraviolet visible-near infrared spectrophotometer (SPEKOL-1500). The spectrophotometer was set with a slit width of 2 nm. All the measurements reported were taken at the room temperature.

B. Optical Investigations

The optical transmission spectra exhibit interference maxima and minima in the wavelength range 600÷1100 nm. The transmission spectra were measured at 2mk (2mk = 2×10^{-6} m) thick samples; d = 2mk is the thickness of thin films. The spectral dependencies, ($T(\lambda)$) have been reestablished in the transparency area to see more clearly the interference fringes (Figure 1(a)-1(c)).
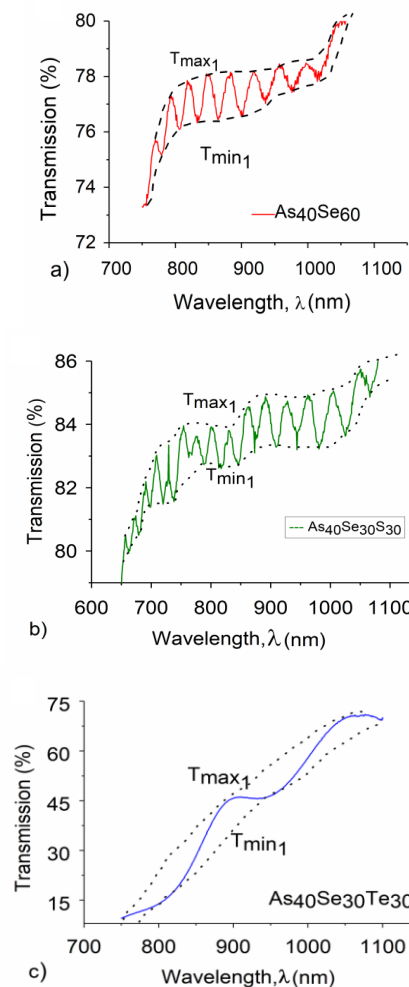

Figure 1. Detailed transmission spectra of the $As_{40}Se_{60}$ (a), $As_{40}Se_{30}S_{30}$ (b) and $As_{40}Se_{30}Te_{30}$ (c) samples

As seen from Figure 1 is observed an interference view in the relatively long wavelength region. According to the model Swanepoel's in the region of weak and medium absorption for transmission can be written as

$$T_a = \sqrt{T_{max} T_{min}} \tag{1}$$

where, T_a is the geometric mean of T_{max} and T_{min}, which are the experimental values indicated by the punctuation in spectral dependencies, $T(\lambda)$. The linear refractive index is calculated using the method proposed by the authors of [5]. The value of the refractive index in the short-wavelength region of the spectrum is calculated by an empirical formula [5-6]:

$$n = a + \frac{b}{\lambda^2} \tag{2}$$

where, λ is the wavelength in vacuum and a, b are constants whose values are determined from experimental data. The optical transmission spectra (a) and the refractive index, dispersion (b) of the materials studied are shown in Figure 2.
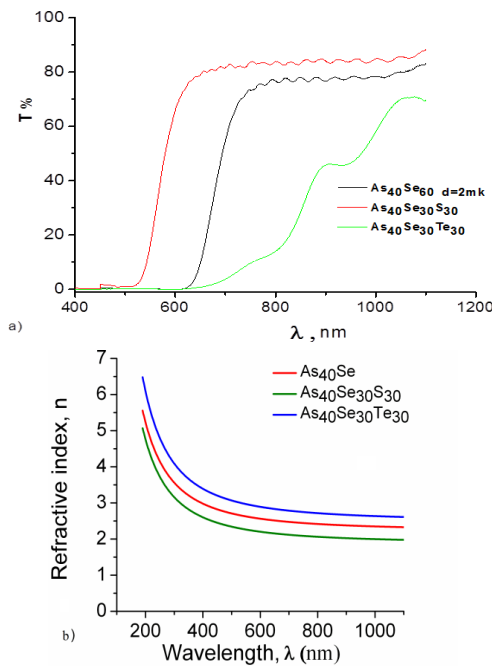

Figure 2. Optical transmission spectra (a) and the refractive index, dispersion (b) of the materials studied

The refractive index (n) is calculated on the base Swanpoel's method in the wavelength region [5]: 600-1100 nm. But, the value of the refractive index in the short-wavelength region of the spectrum is calculated by an empirical Equation (2). For this purpose, the formula 2 is written for two different wavelengths, as follows:

$$n_1 = a + b / \lambda_1^2, \ n_2 = a + b / \lambda_2^2$$

As a result, the values of refractive index (n_1, n_2) calculated by the Swanpoel's method are taken into account in the above formulas. Thus, the equation is solved system equation and empirical values of a and b constants are calculated for the following compositions:

$$n_{As40Se60} = 2.22998 + 0.1200198 / \lambda_2^2$$

$$n_{As40Se30Te30} = 2.49201 + 0.14398 / \lambda_2^2$$

$$n_{As40Se30S30} = 1.8832 + 0.11496 / \lambda_2^2$$

Figure 2 shows all of the compositions exhibit normal dispersion. According to [5-6], the error is ±1% in determining the refractive index outside the spectral region of transparency according to the proposed method. According to [7-8], within the framework of a single-oscillator model, the dispersion of optical parameters is described by the formula:

$$n^2 = 1 + \frac{E_0 E_d}{E_0^2 - E^2} \tag{3}$$

where, E is the photon energy; and E_0 and E_d are parameters of the single-oscillator model. The E_0 is the energy of the oscillator associated with the average binding energy between atoms entering the amorphous matrix. The E_d is the dispersion energy characterizing the strength of the interband.

The author of [9] showed that the relation between the energy oscillator and the optical band gap determined by the method Tauc [10] is performed by $E_0 \approx 2E_g$ relation. The dispersion parameters are determined from dependency curves by $(n^2-1)^{-1}$ from E^2 (Figure 3), but the optical band gap from energy dependences E (Figure 4) of $(\alpha \cdot h\nu)^{0.5}$, which results are presented in Table 1. As seen from Table 1 for all compositions $E_0 \approx 2E_g$ relations are performed.
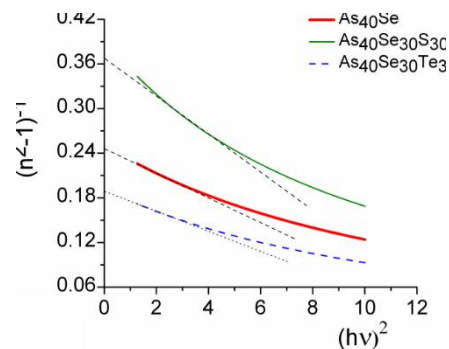

Figure 3. The plots as $(n^2-1)^{-1}$ vs E^2 (b) for the $As_{40}Se_{60}$, $As_{40}Se_{30}S_{30}$ and $As_{40}Se_{30}Te_{30}$ samples

Table 1. Optical band gap from energy dependences E of $(\alpha \cdot h\nu)^{0.5}$ for all of the compositions

Composition	E_g (eV)	E_g (eV) (calculated from relation $E_0 \sim 2E_g$)	E_0 (eV)	E_d (eV)
$As_{40}Se_{60}$	1.82	1.9	3.8	15.81
$As_{40}Se_{30}Te_{30}$	1.59	1.625	3.25	19.93
$As_{40}Se_{30}S_{30}$	1.98	1.93	3.86	10.27

Table 2. Optical constants for all of the compositions

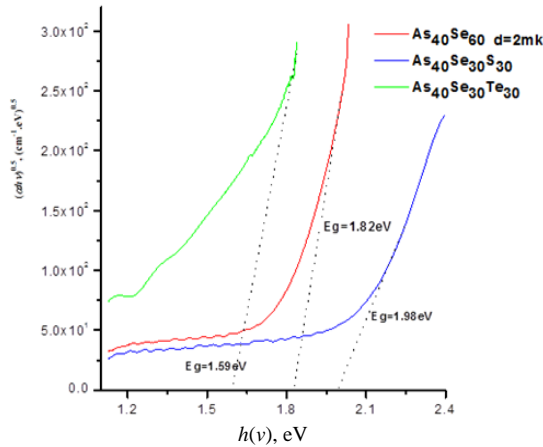| Composition	n_0	k	ε_∞	Average molar energy of bonds (kc/mol)
$As_{40}Se_{60}$	2.37	0.0096	5.61	223.6
$As_{40}Se_{30}Te_{30}$	2.51	0.042	6.3	215
$As_{40}Se_{30}S_{30}$	2.25	0.0054	5.06	238

Figure 4. Variation of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) for different $As_{40}Se_{60}$, $As_{40}Se_{30}S_{30}$ and $As_{40}Se_{30}Te_{30}$ samples

III. DISCUSSION

As seen from Table 1 and Table 2, the optical constants (n_0, k, E_0, E_d, E_g) investigated materials undergo a change depending upon the chemical composition. When half of selenium atoms are replaced by sulfur atoms the numerical values of the coefficients of refractive index (n_0) and extinction (k) for $As_{40}Se_{60}$ composition are decreased, but replaced by tellurium atoms numerical values of the coefficients are increased.

A numerical value of the oscillator energy (E_0), oscillator strength (E_d), the band gap (E_g), determined according Tauc methods [10] and the dispersion increases with selenium replaced by sulfur atoms, but decreases by replacing tellurium atoms. Change of the refractive index is apparently due to a change in the molar volume of matter. The participation of sulfur atoms leads to a decrease of the molar volume, but tellurium atoms leads to the growth. In the first case, the polarization ability of a substance is weakened and in the second case, it is amplified, which is reflected in the values of the refractive index.

As already mentioned, the substitution part of selenium atoms with sulfur contributes to the improvement of an amorphous matrix and tellurium to their partial destruction, i.e. increase in the degree of disorder, whereby in the first case, the substance becomes more transparent (k-decrease) than $As_{40}Se_{60}$ and in the second of their transparency deteriorates (k-increases).

It can also be seen from Table 2 that the widths of the band gap determined by the Tauc method and by dispersion are almost the same. The changes in the numerical values of said parameter may occur as a result of changes in the average molar energy of different bonds present in the material and as a result of changes in the degree of disorder of the amorphous matrices. Using the energy of different bonds [11], the average molar energy of bonds is calculated and their numerical values are shown in Table 2, whence it is clear that the participation of sulfur atoms increases and tellurium leads to a decrease of this parameter. The data relating to the absorption of light at shorter wavelengths correspond to interband electronic transitions and is expressed with law Tauc [14].

$$\alpha \cdot h\nu = A(h\nu - E_g)^2 \qquad (4)$$

where, $h\nu$ is the energy of the incident photon and A is constant depending on the probability of electronic transitions. The graph of the dependence $(\alpha h\nu)^{1/2}$ on $h\nu$ is presented in Figure 4. The optical band gap (E_g) is determined by extrapolation of the linear part of the graph to the zero value of the absorption coefficient and the results are presented in Table 1. As seen from the table, the values of E_g for the $As_{40}Se_{60}$, $As_{40}Se_{30}S_{30}$ and $As_{40}Se_{30}Te_{30}$ chalcogenide glasses compositions are 1.82, 1.98 and 1.59 eV, respectively.

Such a change in the values of E_g depending on the chemical composition can be explained with the assistance of considerations proposed by the authors of [15], taking into account the values of bond energy, cohesive energy and atomic density in the studied compositions. According to Kastner et al. the binding atoms in the condensed environment up valence band are formed from lone-pair (LP) electron states, and the conduction area from anti bonding (σ^*) states. The changes of the band gap (E_g) depending on the chemical composition can be explained by the change occurring in the energy states.

According to Kastner et al., the growth in bonding energies and cohesive energy causes a wide splitting between the bonding (σ) and anti-bonding (σ^*) orbitals and as a result increase the values of E_g. The energy of heteropolar bonds is determined according to the formula proposed by the Pauling [16].

$$U(A-B) = [U(A-A) \cdot U(B-B)]^{1/2} + 30(\chi_A - \chi_B)^2 \qquad (5)$$

where, $U(A–A)$ and $U(B–B)$ are energy homopolar bonds and χ_A and χ_B is electronegativity of atoms A and B. The cohesive energy is calculated using the chemical bond approach method taking the magnitude of the bonding energy of the additive according to the formula:

$$CE = \sum_i C_i E_i \qquad (6)$$

where, E_i is bond energy of individual bonds, and C_i is their number.

It was determined that, the $As_{40}Se_{60}$ composition have As-As ($Z = 0.67$), As-Se ($Z = 2.36$) and Se-Se ($Z = 0.45$) bonds which correspond to the energy of 32.1, 41.2 and 44 kcal/mol. When replacing half selenium atoms with tellurium atoms ($As_{40}Se_{30}Te_{30}$ composition) decreases substantially the coordination number of bonds As-As ($Z = 0.36$), As-Se ($Z = 1.35$) and Se-Se ($Z = 0.1$) instead of them appear As-Te ($Z = 1.30$); Se-Te ($Z = 0.15$) and Te-Te ($Z = 0.1$) bonds which have energy 32.7, 43.16 and 33 kcal/mol.

When replacing half selenium atoms with sulfur atoms ($As_{40}Se_{30}S_{30}$ composition) decreases twice the coordination number of bonds As-Se ($Z = 1.18$) and Se-Se ($Z = 0.2$) instead of them appear bonds As-S ($Z = 1.09$); Se-S ($Z = 0.3$) and S-S ($Z = 0.25$) which have bond energy 45.18, 47.7 and 50.9 kcal/mol. As seen from these comparisons some of the bonds in $As_{40}Se_{60}$ are replaced by stronger bonds, and some case by weak bonds. The value of cohesive energy in $As_{40}Se_{60}$ is equal 40.2 kcal/mol. This value is less than in the composition

of $As_{40}Se_{30}S_{30}$ (43.15 kcal/mol), more than in the composition of $As_{40}Se_{30}Te_{30}$ (36.95 kcal/mol). Such a change in bond energies and cohesive energy leads to the observed changes in the width of the band gap.

It should be noted that a stronger change in the widths of the band gap in comparison with the composition of $As_{40}Se_{60}$ is observed in the composition of $As_{40}Se_{30}Te_{30}$. This different change of band gap apparently due to the fact that the atomic density obtains the highest values in the composition $As_{40}Se_{30}S_{30}$. According to [15], the conduction band edge position depends on the atomic density its growth is accompanied by a decrease in the energy of the conduction band edge that should influence the value of the band gap. Thus, the simultaneous increase in bond energy, cohesive energy and atomic density causes a relatively small change in the width of the band gap of $As_{40}Se_{30}S_{30}$ in comparison with the binary composition.

The representation of features of the structural defects in condensed matter was first put forward by Anderson [17] and developed by Mott and Street [18]. The further development of these concepts belongs to Kastner, Adler, and Fritsche [19]. According to [18] the breaking of the chemical bond leads to the formation of defects having positive, negative charges (D^+, D^-) and neutral types (D^0). Due to the negative correlation energy defects energetically is favorable to be charged states D^+ and D^-, i.e. neutral defects (D_0) transform into charged defects by the exothermic reactions.

$$2D^0 \rightarrow D^+ + D^- \qquad (7)$$

The authors of [20] developed representations of charge defects on the example of amorphous selenium and have taken symbols C_3^+ and C_1^-, where C denotes the chalcogen symbol and indexes 3 and 1 show the coordination number. The presence of LP electrons in the chalcogen atom and their participation in the formations of the binding and anti-bonding orbitals leads to the formation of three-coordinated (C_3^+) and one-coordinated centers (C_1^-).

As already mentioned existing chemical bonds in $As_{40}Se_{60}$, $As_{40}Se_{30}Te_{30}$ and $As_{40}Se_{30}S_{30}$ compositions differ in strength. Moreover, weaker bonds (As-Te, Se-Te and Te-Te) are present in the $As_{40}Se_{30}Te_{30}$ composition. Therefore, these bonds are more easily broken and the concentration of structural charged defects of this composition is higher than in other compositions. This leads to an increase in the degree of disorder and fluctuations in the electrostatic potential, which is accompanied by a shift of the optical absorption edge in the low-energy side.

Firstly, the chemical bonds with tellurium due to a lower binding energy of the atoms is easier to break off [12], which leads to an increase in concentration of charged local defects such as D^+ and D^- [13]. Secondly, tellurium atoms tend to hybridize 5d, 6s and 6p electron orbits in chemical bonds, which lead to the appearance of composite defects [4]. The energy positions of these defects correspond to the band gap to the edges of the allowed zones and cause narrowing it, i.e. decrease in E_0, E_g.

IV. CONCLUSION

As a result, analysis of the optical transmission spectra has been established changes occurring in the optical and energy parameters depending on the chemical composition. The results are explained with changes in the degree of disorder and concentration local defects depending on the chemical composition. The simultaneous increase in bond energy and cohesive energy causes a relatively small change in the width of the band gap of $As_{40}Se_{30}S_{30}$ in comparison with the binary composition.

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