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V.M. Rubish¹, M.M. Pop², O.A. Mykaylo², A.A. Kryuchyn¹,
V.M. Maryan¹, M.O. Durkot¹, T.I. Yasinko¹, S.O. Kostyukevich³,
K.V. Kostyukevich³

¹ Institute for Information Recording, NAS of Ukraine, 4, Zamkovi Skhody str., 88000 Uzhgorod, Ukraine

e-mail: center.uzh@gmail.com

² Uzhgorod National University, 3, Narodna sq., 88000, Uzhgorod, Ukraine

³ V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, 41, Prosp. Nauky, 03028 Kyiv, Ukraine

LASER-INDUCED CHANGES IN THE OPTICAL CHARACTERISTICS OF AMORPHOUS FILMS OF THE As-Sb-S SYSTEM

Abstract. The optical transmission spectra of amorphous $As_{40-x}Sb_xS_{60}$ films with small antimony content ($x=0, 0.8, 1.6, 4, 6$) prepared by the thermal evaporation of glasses of corresponding compositions have been measured over the whole 400-750 nm spectral range. It is established that the laser irradiation and annealing of films leads to an absorption edge shift into the long-wave spectral region. The values of pseudoforbidden gap width E_g and refractive index n of films have been determined. The parameters of a single-oscillator model (oscillator energy E_0 , dispersion energy E_d , and effective coordination number per cation N_c) for the studied films are estimated. The maximum changes in optical characteristics are found for $As_{36}Sb_4S_{60}$ films. Changes in the optical parameters of films are caused by structural transformations taking place in them under the irradiation and annealing.

Keywords: chalcogenide amorphous films, transmission spectra, photoinduced effects, optical properties, structural transformations.

Introduction

Due to the broad spectrum of photo-induced phenomena, chalcogenide glass-like semiconductors are widely applied as the media for information recording, fabrication of surface relief structures, optical sensors, waveguides, etc. [1-15].

As inorganic photoresists with high resolving power, amorphous films of As-S-Se system are most widely used in systems of optical recording of information and holography [2, 4-7, 11, 16-18]. In the thin layers of such materials, the structural transformations, which are accompanied by essential changes in optical parameters, occur under the action of a laser emission or a thermal heating. In this case, the level of structural transformations is determined by a chemical composition of amorphous films and the conditions of fabrication, heating, and irradiation. In this aspect, $As_{40-x}Sb_xS_{60}$ amorphous films

are not practically studied. Earlier, we revealed [19] that under the same conditions of exposure of as-prepared films of the given system, the film $As_{36}Sb_4S_{60}$ is characterized by the highest level of photoinduced changes in optical parameters (shift in the absorption edge, changes in the pseudoforbidden gap width E_g and the refractive index n). However, in that work, the films with $x=0, 4, 6, 8,$ and 10 were investigated. The films with $0 < x < 4$ were not considered, though the compositions of films with a high level of changes in optical characteristics are, possibly, present just in this interval of concentrations.

In the present work, we describe the results of studies of the influence of a laser irradiation on the transmission spectra and, respectively, the optical parameters of $As_{40-x}Sb_xS_{60}$ amorphous films with low content of antimony ($x=0.8, 1.6, 4,$ and 6).

Experimental

$As_{40-x}Sb_xS_{60}$ ($0 \leq x \leq 6$) glasses were prepared using the vacuum melting method (~ 0.01 Pa) of the corresponding mixture of As_2S_3 and Sb_2S_3 components. Arsenic and antimony sulfides were produced by means of the direct synthesis from high pure As, Sb, and S. During the synthesis, we applied the stepwise increase in temperature. The homogenization temperatures for melts of As_2S_3 and Sb_2S_3 were 780 and 870 K, respectively. The homogenization time of melts was 48 h. The melts were periodically mixed. Cooling of melts was performed in the regime of a switched-off furnace. Under the such conditions of cooling, As_2S_3 and Sb_2S_3 were obtained, respectively, in the form of a glass and a polycrystalline ingot. Similarly, $As_{40-x}Sb_xS_{60}$ glasses were produced. The homogenization temperature for $As_{40-x}Sb_xS_{60}$ melts was 780-830 K, and the homogenization time was 36 h. Cooling of melts was carried out in air.

$As_{40-x}Sb_xS_{60}$ thin films were produced on unheated glass substrates by means of chalcogenide glasses vacuum evaporation of the corresponding compositions from quasi-closed effusive cells on improved vacuum setup BYII-5 equipped with a thickness control system. The thickness of films was ~ 1 μm . Constancy of layer thickness in the working zone was ensured by the planetary rotation of substrates.

The transmission spectra were studied in 450-750 nm range at room temperature using a diffraction monochromator MДP-23. The spectral resolution was no worse than 10^{-3} eV. Light exposure of films was carried out using defocused semiconductor laser ($\lambda = 530$ nm) with a power 100 mW.

Results and discussion

In Figs. 1 and 2 we show the transmission spectra of $As_{39.2}Sb_{0.8}S_{60}$ and $As_{36}Sb_4S_{60}$ amorphous films, which are typical for all studied materials. It is seen that, as antimony content in film composition increases, the absorption edge shifts some to the long-wave spectrum part, indicating a decrease in their pseudoforbidden gap width E_g . In this case, the edge slope is practically unchanged. This means that the type of structural matrix of

As-Sb-S system films is unchanged at the transition from As_2S_3 to Sb_2S_3 .

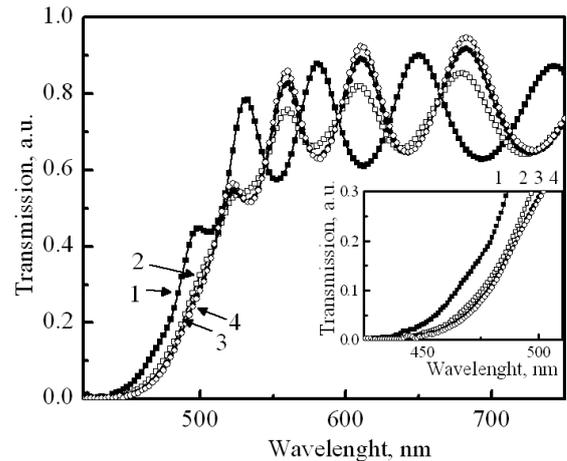


Fig. 1. Dependences of the transmission spectra inherent to $As_{39.2}Sb_{0.8}S_{60}$ films on the exposure time: 1 – 0; 2 – 1; 3 – 3; 4 – 5 min.

The structural studies of glasses and films of As_2S_3 - Sb_2S_3 system with Sb_2S_3 content up to 60 mol.% by methods of vibrational (Raman and Infrared) spectroscopy [6, 11, 20- 23] showed that they have the nanoheterogeneous structure. Their matrix is constructed mainly of trigonal AsS_3 and SbS_3 pyramids linked through a common twofold coordinated atoms of sulfur and contains also a considerable number of structural fragments with homopolar bonds As-As and S-S (e.g., As_4S_4 , S_n).

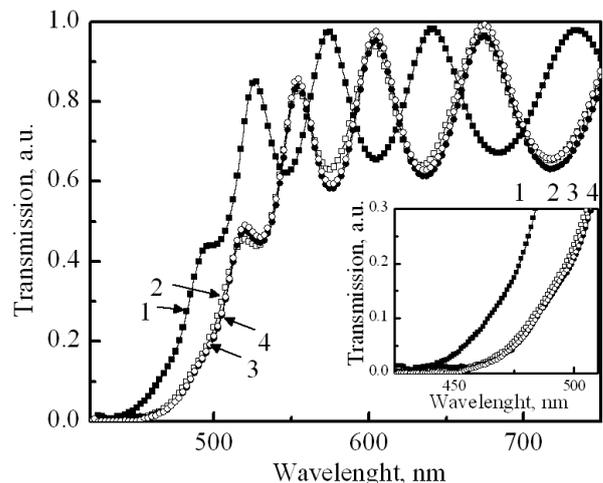


Fig. 2. Dependences of the transmission spectra inherent to $As_{36}Sb_4S_{60}$ films on the exposure time: 1 – 0; 2 – 1; 3 – 3; 4 – 5 min.

The concentration of such fragments (which depends on the chemical composition and technological conditions of preparation) in films is higher. No structural units with

homopolar bonds Sb-Sb were found in the studied materials.

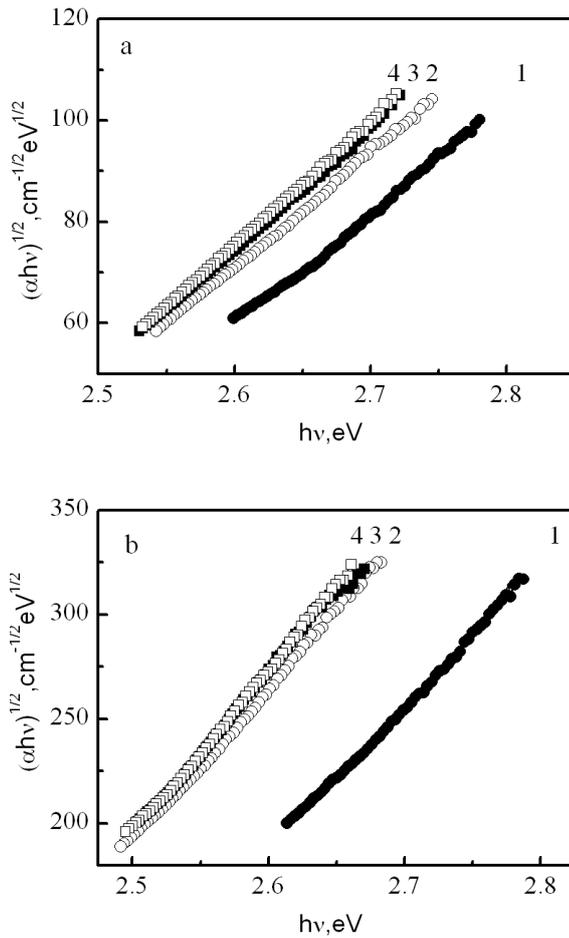


Fig. 3. Dependence of the absorption edge position on the photon energy for $\text{As}_{39.2}\text{Sb}_{0.8}\text{S}_{60}$ (a) and $\text{As}_{36}\text{Sb}_4\text{S}_{60}$ (b) films unexposed (1) and exposed (2 – 4) for 1 (2), 3 (3), and 5 (4) min.

The value of E_g can be determined from the Tauc relation [24]

$$\alpha(h\nu) = \frac{B(h\nu - E_g)^2}{h\nu}, \quad (1)$$

where $\alpha(h\nu)$ - the absorption coefficient, $h\nu$ - the photon energy, B is a constant, which depends on the film material and characterizes the slope of Tauc absorption edge. Relation (1) is correct in the high-energy region for $\alpha(h\nu) \geq 10^4 \text{ cm}^{-1}$. The values of E_g for $\text{As}_{40-x}\text{Sb}_x\text{S}_{60}$ films were determined via extrapolation of $[\alpha(h\nu) \cdot h\nu]^{1/2} \approx f(h\nu)$ dependences to $\alpha(h\nu) = 0$ (Fig. 3, curves 1). For films with $x=0, 0.8, 1.6, 4$, and 6 , the pseudoforbidden gap widths are 2.376, 2.354, 2.349, 2.334, and 2.324 eV, respectively. We note that the value of E_g determined by us (Table 1) for $\text{As}_{40}\text{S}_{60}$ film is in good agreement with that adduced in [24] (2.38 eV).

As the content of antimony in film compositions of As-Sb-S system increases, the pseudoforbidden gap width decreases (Table 1). It is worth to note that the values of E_g determined in our work for as-prepared films of $\text{As}_{40}\text{S}_{60}$, $\text{As}_{36}\text{Sb}_4\text{S}_{60}$, and $\text{As}_{34}\text{Sb}_6\text{S}_{60}$ are slightly different from those in [19] for the same compositions. This difference is related, apparently, to some distinctions in the deposition processes of films and their thicknesses.

Table 1. Dependences of E_g and n for $\text{As}_{40-x}\text{Sb}_x\text{S}_{60}$ films on the exposure time

τ , min.	Parameter	Composition			
		$\text{As}_{39.2}\text{Sb}_{0.8}\text{S}_{60}$	$\text{As}_{38.4}\text{Sb}_{1.6}\text{S}_{60}$	$\text{As}_{36}\text{Sb}_4\text{S}_{60}$	$\text{As}_{34}\text{Sb}_6\text{S}_{60}$
0	E_g , eV	2.354	2.349	2.334	2.324
	n	2.275	2.284	2.366	2.442
1	E_g , eV	2.308	2.309	2.264	2.276
	n	2.323	2.316	2.430	2.496
3	E_g , eV	2.292	2.305	2.262	2.270
	n	2.332	2.320	2.442	2.508
5	E_g , eV	2.287	2.297	2.260	2.267
	n	2.340	2.326	2.448	2.514

The influence of technological factors on the properties of chalcogenide materials is testified also by the studies of the pseudoforbidden gap width for glasses of $\text{As}_2\text{S}_3\text{-Sb}_2\text{S}_3$ system produced under different conditions. For example, for $\text{As}_{40-x}\text{Sb}_x\text{S}_{60}$ glasses with

$x=0, 8$, and 10 that were synthesized in the regimes used in this work, the values of E_g are 2.41, 2.255, and 2.215 eV, respectively [25]. For glasses with the same compositions that were produced by hardening of melts homogenized at 1173 K for 48 h in water, the values

of E_g are equal to 2.23, 2.13, and 2.105 eV were presented in [23].

The refractive index of films was determined from the relation [26]

$$n = \left[N + (N^2 - s^2)^{1/2} \right]^{1/2}, \quad (2)$$

where

$$N = 2s \frac{T_{max} - T_{min}}{T_{max} \cdot T_{min}} + \frac{s^2 + 1}{2}. \quad (3)$$

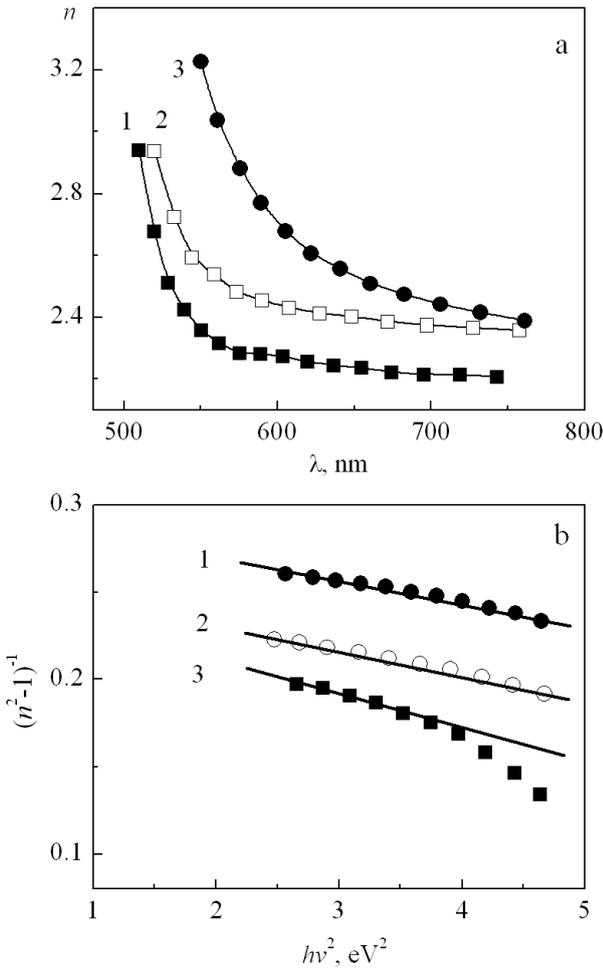


Fig. 4. Dispersion of the refractive index (a) and the dependence of $(n^2 - 1)^{-1}$ on $h\nu^2$ (b) for $\text{As}_{40-x}\text{Sb}_x\text{S}_{60}$ films, x , at. %: 1 – 0; 2 – 4; 3 – 6.

In these formulas, s is the refractive index of a substrate; T_{max} and T_{min} are the interference maxima and minima of the transmission spectra in the wavelengths region, where there is no dispersion of the refractive index.

The values of n for $\text{As}_{40-x}\text{Sb}_x\text{S}_{60}$ films determined at $\lambda=700$ nm are given in Table 1. It is seen that the refractive index increases with growing of antimony content in film compositions.

The dispersion of refractive index of $\text{As}_{40-x}\text{Sb}_x\text{S}_{60}$ films is shown in Fig. 4, a. In transparency region ($\lambda > 600$ nm), we see the normal spectral behavior of n , which indicates the absence of absorption bands in this spectral region. The absorption effect is accompanied by a sharp increase in the refractive index. As the Sb content in film compositions increases, the dependences $n(\lambda)$ like the spectral dependences of absorption effect shift to the long-wave spectral region.

In the transparent region the dispersion of n is well described within the single-oscillator model [27, 28]:

$$n^2(h\nu) = 1 + \frac{E_0 E_d}{E_0^2 - (h\nu)^2}, \quad (4)$$

where E_0 and E_d are the parameters of the one-oscillator model (E_0 is the energy of an effective oscillator related to the average energy gap; E_d is the dispersion energy, which characterizes the intensity of interband transitions), ν is the frequency, at which n is measured. The film parameters E_0 and E_d were determined from the linear dependences $[n^2(h\nu) - 1]^{-1} \sim f(h\nu)^2$ (Fig. 4, b) by the slope of $(E_0 E_d)^{-1}$ and the intersection of E_0/E_d with the ordinate axis.

The calculations showed that, as the antimony content in film compositions increases, the oscillator energy E_0 decreases from 4.82 eV for $\text{As}_{40}\text{S}_{60}$ down to 4.68 eV for $\text{As}_{34}\text{Sb}_6\text{S}_{60}$ (Table 2). The dependence of E_0 on x (within the measurement errors) is close to a linear one. The similar concentration dependence is obtained also for the pseudoforbidden gap width E_g determined from the spectral dependence of film absorption edges. Such symbatic changes of E_0 and E_g with the composition becomes clear, if we consider the fact that the relation $E_0 \approx 2E_g$ is valid for the non-crystalline chalcogenide materials [28].

In the studied concentration range, the composition dependence of E_d is close to a linear one. In this case, the dispersion energy of as-prepared $\text{As}_{40-x}\text{Sb}_x\text{S}_{60}$ films changes very slightly, as the composition is varied (Table 2). Minimum value of E_d is found for $\text{As}_{36}\text{Sb}_4\text{S}_{60}$ film. We note that the measured dispersion energy of arsenic sulfide amorphous film is in good agreement with the values of E_d in [7, 28, 29]. For example, the value of E_d for

As₄₀S₆₀ film is equal to 20.61 eV [29]. Earlier [11], while studying the optical characteristics of As₄₀S_{60-x}Se_x films we determined the value $E_d=20.52$ eV for As₄₀S₆₀. Such insignificant difference in the values of E_d for As₄₀S₆₀ films

obtained by different authors is caused by technological factors and, as a consequence, by differences in their structures. The value of E_d for Sb₄₀S₆₀ film determined in [30] is equal to 21.3 eV.

Table 2. Parameters of the single-oscillator model for As_{40-x}Sb_xS₆₀ films

Composition	E_0 (eV)	E_d (eV)	N_c
As ₄₀ S ₆₀	4.82	19.66	2.80
As _{39.2} Sb _{0.8} S ₆₀	4.78	19.40	2.76
As _{38.4} Sb _{1.6} S ₆₀	4.74	19.24	2.74
As ₃₆ Sb ₄ S ₆₀	4.70	18.81	2.67
As ₃₄ Sb ₆ S ₆₀	4.68	19.06	2.71

According to [27, 28], the parameter E_d obeys the simple empiric relationship

$$E_d = \beta N_c z_a N_e. \quad (5)$$

Here, β is a constant equal to 0.37 ± 0.04 eV for covalent materials; N_c is the coordination number of the cation nearest neighbour to the anion; z_a is the formal valency of anion; and N_e is the effective number of valence electrons per anion.

Taking $z_a=2$ for sulfur in As_{40-x}Sb_xS₆₀ films with $0 \leq x \leq 6$, we get the coordination number $N_c=2.67-2.80$ (Table 2). The value $N_c=2.8$ determined by us for As₄₀S₆₀ film differs from the coordination number value for the film with the same composition in [29] ($N_c \approx 3.0$).

For as-prepared As_{40-x}Sb_xS₆₀ films ($0 \leq x \leq 6$), no change in dispersion energy E_d is practically observed. Moreover, like for E_0 , we found an insignificant deviation from the additivity on the concentration cut As₂S₃-Sb₂S₃. This becomes clear, if we take into consideration that As₂S₃-Sb₂S₃ system is pseudobinary (a continuous series of solid solutions is formed in it). Arsenic and antimony belong to the same group of the Periodic Table, and the values of formal chemical valency for them in stoichiometric compounds As₂S₃ and Sb₂S₃ are close to 3. In addition, the production conditions

for As_{40-x}Sb_xS₆₀ films with a low content of antimony, like those for glasses with the corresponding compositions, are practically identical. Therefore, the average values of

coordination numbers of cations in studied materials are very close.

As mentioned above, the structure of As_{40-x}Sb_xS₆₀ glasses and films is mainly determined by AsS_{3/2} and SbS_{3/2} trigonal pyramids. However, it includes also a significant amount of structural fragments with homopolar bonds As-As and S-S. For example, in glassy As₂S₃, the equilibrium concentration of homopolar bonds, which is “frozen” in hardening process of melt at the temperature 463 K, is $2.7 \cdot 10^{26} \text{ m}^{-3}$ [31]. The value of N_c (2.8) obtained by us for As₄₀S₆₀ film is essentially lower than for the glass with corresponding composition (3.2 [27] and 3.74 [32]). Such difference in values of N_c is caused by distinctions in the structure of film and massive glasses. The structural network of films contain a significantly larger number of fragments with homopolar bonds As-As and S-S. The concentration of such bonds in arsenic chalcogenides films, according to [2, 7, 11, 32, 33], is 30-32 %. Just this reason is a cause for lower values of the coordination numbers of films.

At laser illumination of films, the absorption spectra shift to the long-wave region (Figs. 1 and 2, curves 2-4). It occurs photodarkening of films. At the same conditions of exposure, this shift in As_{40-x}Sb_xS₆₀ films is significantly larger than in As₄₀S₆₀ film. For example, the absorption edge shifts (ΔE) of films with $x=0.8, 1.6, 4,$ and 6 on the transmission level 0.2 at irradiation for 1 min are 0.047, 0.057, 0.098, and 0.76 eV, respectively. For As₄₀S₆₀ film ΔE is 0.018 eV.

This testifies to a higher light sensitivity of Sb-containing films compared to $As_{40}S_{60}$.

The values of E_g for irradiated $As_{40-x}Sb_xS_{60}$ films calculated from dependences $[\alpha(h\nu) \cdot h\nu]^{1/2} \sim f(h\nu)$ (Fig. 3, cur-ves 2-4) are given in Table 1. It is seen that E_g decreases at laser irradiation. In this case, the largest and the smallest changes in the pseudoforbidden gap width are found, respectively, for $As_{36}Sb_4S_{60}$ and $As_{40}S_{60}$ films (at the irradiation for 1 min, ΔE_g for $As_{40}S_{60}$ equal 0.025 eV).

The refractive index of films increases at the irradiation. For example, the value n at $\lambda=700$ nm is 2.43 ($\Delta n=0.064$) at the irradiation of $As_{36}Sb_4S_{60}$ film for 1 min. For the other studied films of As_2S_3 - Sb_2S_3 system under the same conditions of exposure, the value Δn is less (for $As_{39.2}Sb_{0.8}S_{60}$ and $As_{34}Sb_6S_{60}$ films, the values Δn are 0.048 and 0.054, respectively).

We note that the largest absorption edge shift and changes in E_g and n are observed at small irradiation times. The level of photoinduced changes of given film parameters essentially decrease, as the light-striking increases.

Changes in optical characteristics of $As_{40-x}Sb_xS_{60}$ amorphous films (the shift of the absorption edge in long-wave spectral region, decreasing of E_g , increasing of n) are caused by structural transformations, which occur at laser irradiation. Similar changes are caused in chalcogenide glassy semiconductors at high-energy irradiation [32-36], with the only difference being that due to a high penetrating ability the optical properties are better expressed in massive glassy samples. There is a certain difference in the photo- and radiation-induced changes, however, the mechanisms of action of light and high-energy ionizing radiations on chalcogenide glassy semiconductors are similar [11, 32, 33].

The matrix of $As_{40-x}Sb_xS_{60}$ amorphous films, like the matrix of glasses of the corresponding compositions, is mainly constructed of pyramidal units $As(Sb)S_3$ connected with one another by S atoms. We revealed no molecular fragments with homopolar bonds Sb-Sb in it. But the structural groups with

homopolar bonds As-As and S-S are present in a large amount. The higher level of photoinduced changes in optical parameters (ΔE , ΔE_g , Δn) of $As_{40-x}Sb_xS_{60}$ films of the studied compositions, as compared to $As_{40}S_{60}$, can testify to the higher level of disordering of the structural network due to the higher content of molecular fragments with homopolar As-As bonds in it.

The irradiation of films leads to the breaking and switching of bonds As-As and S-S in structural fragments of As_4S_4 and S_n type, which are present in a larger amount in the matrix of as-prepared films, with the formation of structural units with heteropolar bonds As-S (AsS_3) [7, 11, 19, 37]. The destruction of some chemical bonds and the appearance of another ones is accompanied by the generation of a particular type of structural defects with over- and subcoordinated atoms of arsenic (As_2^- and As_4^+) and sulfur (S_3^+ and S_1^-) [6, 11, 19, 32, 37]. At the breaking of homopolar bonds As-As and S-S, the pairs of coordination defects (As_2^- , S_3^+) and (As_4^+ , S_1^-) are formed. Then the charged defect states are transformed (relax) into the structure of pyramidal AsS_3 units. The possibility for the metastable pairs of coordination defects (As_2^+ , S_1^-) to participate in these processes cannot be excluded [36]. The defectless photopolymerization of molecular fragments of As_4S_4 and S_n type into the structural network $AsS_{3/2}$ is possible as well [2, 11, 37]. However, such transformations are possible only at a high concentration of initial molecules. Indeed, they can run, if, at the simultaneous breaking of two homopolar bonds As-As and S-S, all four atoms are in the position that is suitable for the formation of two heteropolar bonds As-S, whereas the generation of a pair of charged defects (As_2^- , S_3^+) or (As_4^+ , S_1^-) requires that the given condition be satisfied only for two atoms. In this connection, the probability of such polymerization process for a film under its irradiation is significantly higher. It is obvious that the defectless polymerization process of the film dominates in the case of thermoexcitation [6, 7, 32], since the probability for the atoms of the structural skeleton to migrate increases.

With the aim to ascertain the influence of temperature on photoinduced changes in optical characteristics, we studied the

transmission spectra of films $As_{36}Sb_4S_{60}$ and $As_{34}Sb_6S_{60}$ annealed at 423 K for 1 h. The choice of films with just these compositions is determined by the fact that they are characterized by the highest level of photoinduced changes in optical parameters.

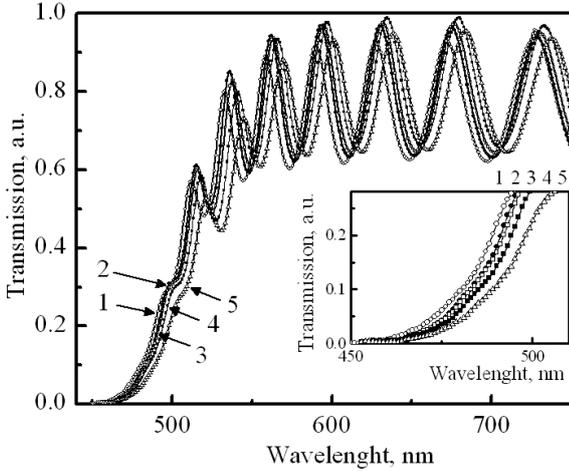


Fig. 5. Dependences of the transmission spectra of the as-prepared $As_{36}Sb_4S_{60}$ (1) and annealed at 423 K (2-5) films on the exposure time:

2 – 0; 3 – 1; 4 – 3; 5 – 10 min.

In Fig. 5 (curve 2), we show the transmission spectrum of $As_{36}Sb_4S_{60}$ annealed film. It is seen that compared to the spectrum of as-prepared film (Fig. 5, curve 1), it is shifted to the region of larger wavelengths. In this case, the absorption edge shift ΔE is 0.036 eV. For $As_{34}Sb_6S_{60}$ film this parameter is less (0.029 eV). This means that the pseudoforbidden gap width decreases at annealing. For annealed films $As_{36}Sb_4S_{60}$ and $As_{34}Sb_6S_{60}$, the values E_g are 2.296 and 2.290 eV, respectively. The refractive index of films increases at annealing. For the annealed films of given compositions, the values n determined at $\lambda=700$ nm are 2.412 and 2.480.

Like in the case of laser irradiation, the changes in optical characteristics of films at annealing are caused by the structural transformations. At the thermoexcitation, the breaking and switching of homopolar bonds As–As and S–S and the formation of structural units AsS_3 happen in structural fragments AsS_4 and S_n , which participate in the construction of the matrices of films. As was mentioned above, the thermopolymerization of molecular fragments AsS_4 and S_n into a structural network of $AsS_{3/2}$ type occurs by the defectless (dominant)

mechanism and with the formation of structural defects As_2^- , As_4^+ , S_3^+ , and S_1^- [11, 32, 33, 37].

In Fig. 5 (curves 3-5) the transmission spectra of $As_{36}Sb_4S_{60}$ film irradiated after annealing is given. Like in the previous case, the spectra are shifted to the long-wave spectral region at laser irradiation. It is seen that the absorption edge shift and, respectively, the change in E_g under laser radiation are significantly less in the annealed film than in the as-prepared one (Fig. 2, a). A change in the refractive index is less as well. For example, a change in E_g for as-prepared $As_{36}Sb_4S_{60}$ film after the irradiation for 1 min is 0.07 eV. For the annealed film, this value is equal to 0.032 eV. Changes in the refractive index of the annealed films under the irradiation are also less (0.064 and 0.028, respectively). In $As_{36}Sb_4S_{60}$, annealed films the levels of photoinduced changes of E_g and n are also lower ($\Delta E_g = 0.028$ eV, $\Delta n = 0.025$).

The lower level of photoinduced changes in optical characteristics of annealed films testifies to a lower level of photostructural transformations in them. This is caused by that the matrices of films after the annealing contain a much less number of structural fragments with homopolar bonds As–As and S–S, which can be polymerized under the laser irradiation.

This conclusion is confirmed by the results of studies of the refractive index dispersion and calculations of parameters E_0 , E_d , and N_c for films $As_{36}Sb_4S_{60}$ and $As_{34}Sb_6S_{60}$, which were irradiated for 1 min [$E_0(I)$, $E_d(I)$, and $N_c(I)$], annealed films [$E_0(II)$, $E_d(II)$, and $N_c(II)$], and films irradiated (1 min) after the annealing [$E_0(III)$, $E_d(III)$, and $N_c(III)$]. For $As_{36}Sb_4S_{60}$, film we get the following values of these parameters: $E_0(I)=4.56$ eV, $E_0(II)=4.64$ eV, $E_0(III)=4.60$ eV; $E_d(I)=20.2$ eV, $E_d(II)=19.87$ eV, $E_d(III)=20.57$ eV; $N_c(I)=2.88$ eV, $N_c(II)=2.83$ eV, $N_c(III)=2.93$ eV. For $As_{34}Sb_6S_{60}$, film the values of these parameters and the character of their changes are similar. As is seen from Table 2 and calculations, the irradiation and annealing of films lead to a slight decrease (increase) in E_0 (E_d). In this case, the coordination numbers N_c increase.

The increase of N_c at the irradiation and annealing of films is caused by the

polymerization of molecular groups with homopolar bonds As-As and S-S and by the ordering of their structural network.

Conclusions

On the basis of studies of the transmission spectra of $As_{40-x}Sb_xS_{60}$ amorphous films we have established that the laser irradiation and the annealing induce the absorption edge shift to the long-wave region. In this case, the pseudoforbidden gap width of the films decreases, whereas the refractive index increases.

It is shown that, under the same conditions of irradiation and annealing, the largest changes in optical parameters occur in the films with $x=4$. The level of photoinduced changes in optical parameters of the annealed films is lower than for the as-prepared ones. Changes in the optical characteristics of films are caused by the photo- and thermostructural transformations, which are accompanied by decreasing in the number of structural fragments with homopolar bonds As-As and S-S in their matrix.

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В.М. Рубіш¹, М.М. Поп², О.А. Михайло², С.А. Костюкевич³,
А.А. Крючин¹, М.А. Дуркот¹, Т.І. Ясірко¹

¹Інститут проблем реєстрації інформації НАН України, 88000, Ужгород, вул.Замкові сходи, 4

²Ужгородський національний університет, 88000, Ужгород, вул. Волошина, 54

³Інститут фізики напівпровідників ім. В.Лашкарьова НАН України, 03028, Київ, просп. Науки, 41

ЛАЗЕРНО-ІНДУКОВАНІ ЗМІНИ ОПТИЧНИХ ХАРАКТЕРИСТИК АМОРФНИХ ПЛІВОК СИСТЕМИ $As-Sb-S$

В спектральній області 400-750 нм досліджені спектри пропускання аморфних плівок $As_{40-x}Sb_xS_{60}$ з малим вмістом Sb ($x=0, 0.8, 1.6, 4, 6$), одержаних методом термічного випаровування стекол відповідних складів на скляні підкладки. Встановлено, що лазерне опромінення та відпал плівок призводять до зсуву краю поглинання в довгохвильову ділянку спектру. Визначені ширина псевдозабороненої зони E_g та показник заломлення n плівок. Розраховані параметри одноосциляторної моделі (енергія осцилятора E_0 , дисперсійна енергія E_d та ефективне координаційне число N_c). Максимальні зміни оптичних характеристик виявлені для плівки $As_{36}Sb_4S_{60}$. Зміни оптичних параметрів плівок відбуваються в них при опроміненні та відпалі.

Ключові слова: халькогенідні аморфні плівки, спектри пропускання, фотоіндуковані ефекти, оптичні властивості, структурні перетворення.

В.М. Рубиш¹, М.М. Поп², О.А. Михайло², С.А. Костюкевич³,
А.А. Крючин¹, М.А. Дуркот¹, Т.И. Ясинко¹

¹Інститут проблем реєстрації інформації НАН України, 88000, Ужгород, ул. Замковий схід, 4

²Ужгородський національний університет, 88000, Ужгород, ул. Волошина, 54

³Інститут фізики напівпровідників ім. В.Лашкарьова НАН України, 03028, Київ, просп. Науки, 41

ЛАЗЕРНО-ИНДУЦИРОВАННЫЕ ИЗМЕНЕНИЯ ОПТИЧЕСКИХ ХАРАКТЕРИСТИК АМОРФНЫХ ПЛЕНОК СИСТЕМЫ As-Sb-S

В спектральной области 400-750 нм исследованы спектры пропускания аморфных пленок $As_{40-x}Sb_xS_{60}$ с небольшим содержанием сурмы ($x=0, 0.8, 1.6, 4.6$) полученных термическим испарением стекол соответствующих составов. Установлено, что лазерное облучение и отжиг пленок приводит к сдвигу края поглощения в длинноволновую область спектра. Определены значения ширины псевдозапрещенной зоны E_d и показателя преломления n пленок. Рассчитаны параметры одноосцилляторной модели (энергия осциллятора E_0 , дисперсионная энергия E_d и эффективное координационное число). Максимальные изменения оптических характеристик наблюдались в пленках $As_{36}Sb_4S_{60}$. Изменения оптических параметров пленок обусловлены структурными превращениями, происходящими в них при облучении и отжиге.

Ключевые слова: халькогенидные аморфные пленки, спектры пропускания, фотоиндуцированные эффекты, оптические свойства, структурные превращения.

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