PACS 78.30.-j, 78.66.Jg
DOI: 10.24144/2415-8038.2017.42.14-26
V.M. Rubish\textsuperscript{1}, M.M. Pop\textsuperscript{2}, O.A. Mykaylo\textsuperscript{2}, A.A. Kryuchyn\textsuperscript{1}, V.M. Maryan\textsuperscript{1}, M.O. Durkot\textsuperscript{1}, T.I. Yasinko\textsuperscript{1}, S.O. Kostyukevich\textsuperscript{3}, K.V. Kostyukevich\textsuperscript{3}
\textsuperscript{1} Institute for Information Recording, NAS of Ukraine, 4, Zamkovi Skhody str., 88000 Uzhgorod, Ukraine
\textsuperscript{2} Uzhgorod National University, 3, Narodna sq., 88000, Uzhgorod, Ukraine
\textsuperscript{3} V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, 41, Prosp. Nauky, 03028 Kyiv, Ukraine

\textbf{LASER-INDUCED CHANGES IN THE OPTICAL CHARACTERISTICS OF AMORPHOUS FILMS OF THE As-Sb-S SYSTEM}

\textbf{Abstract.} The optical transmission spectra of amorphous As\textsubscript{40-x}Sb\textsubscript{x}S\textsubscript{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 $N_e$) for the studied films are estimated. The maximum changes in optical characteristics are found for As\textsubscript{30}Sb\textsubscript{2}S\textsubscript{60} films. Changes in the optical parameters of films are caused by structural transformations taking place in them under the irradiation and annealing.

\textbf{Keywords:} chalcogenide amorphous films, transmission spectra, photoinduced effects, optical properties, structural transformations.

\textbf{Introduction}

Due to the broad spectrum of photoinduced 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\textsubscript{40-x}Sb\textsubscript{x}S\textsubscript{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\textsubscript{30}Sb\textsubscript{2}S\textsubscript{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\textsubscript{40-x}Sb\textsubscript{x}S\textsubscript{60} amorphous films with low content of antimony (x=0.8, 1.6, 4, and 6).
Experimental
As₄₀₋₅Sb₃₅S₆₀ (0≤x≤6) glasses were prepared using the vacuum melting method (~0.01 Pa) of the corresponding mixture of As₂S₃ and Sb₂S₃ 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 As₂S₃ and Sb₂S₃ 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, As₂S₃ and Sb₂S₃ were obtained, respectively, in the form of a glass and a polycrystalline ingot. Similarly, As₄₀₋₅Sb₃₅S₆₀ glasses were produced. The homogenization temperature for As₄₀₋₅Sb₃₅S₆₀ melts was 780-830 K, and the homogenization time was 36 h. Cooling of melts was carried out in air.

As₄₀₋₅Sb₃₅S₆₀ 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 BYTI-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 МДР-23. The spectral resolution was no worse than 10⁻³ eV. Light exposure of films was carried out using defocused semiconductor laser (λ=530 nm) with a power 100 mW.

Results and discussion
In Figs. 1 and 2 we show the transmission spectra of As₃⁹Sb₀₃S₆₀ and As₃⁶Sb₃₃S₆₀ 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 As₂S₃ to Sb₂S₃.

![Fig. 1. Dependences of the transmission spectra inherent to As₃⁹Sb₀₃S₆₀ films on the exposure time: 1 – 0; 2 – 1; 3 – 3; 4 – 5 min.](image1)

The structural studies of glasses and films of As₂S₃–Sb₂S₃ system with Sb₂S₃ 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 AsS₃ and SbS₃ 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., As₄S₈, S₈).

![Fig. 2. Dependences of the transmission spectra inherent to As₃⁶Sb₃₃S₆₀ films on the exposure time: 1 – 0; 2 – 1; 3 – 3; 4 – 5 min.](image2)
homopolar bonds Sb-Sb were found in the studied materials.

![Graph](image_url)

**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 $\text{As}_{0.8}\text{Sb}_{3}\text{S}_{60}$ (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]

$$\alpha(h\nu) = \frac{B(h\nu - E_g)^2}{h\nu},$$  \hspace{1cm} (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 $\alpha(h\nu) \geq 10^4$ cm$^{-1}$. The values of $E_g$ for $\text{As}_{40-x}\text{Sb}_x\text{S}_{60}$ films were determined via extrapolation of $[\alpha(h\nu) h\nu]^{-1/2} \approx f(h\nu)$ 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 $\text{As}-\text{Sb}-\text{S}$ 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 $\text{As}_{40}\text{S}_{60}$, $\text{As}_{36}\text{Sb}_{1.8}\text{S}_{60}$, and $\text{As}_{34}\text{Sb}_{3}\text{S}_{60}$ 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>
<thead>
<tr>
<th>$\tau$, min.</th>
<th>Parameter</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_g$, eV</td>
<td>$\text{As}<em>{39.2}\text{Sb}</em>{0.8}\text{S}_{60}$</td>
</tr>
<tr>
<td>0</td>
<td>2.354</td>
<td>2.349</td>
</tr>
<tr>
<td></td>
<td>2.275</td>
<td>2.284</td>
</tr>
<tr>
<td>1</td>
<td>2.308</td>
<td>2.309</td>
</tr>
<tr>
<td></td>
<td>2.323</td>
<td>2.316</td>
</tr>
<tr>
<td>3</td>
<td>2.292</td>
<td>2.305</td>
</tr>
<tr>
<td></td>
<td>2.332</td>
<td>2.320</td>
</tr>
<tr>
<td>5</td>
<td>2.287</td>
<td>2.297</td>
</tr>
<tr>
<td></td>
<td>2.340</td>
<td>2.326</td>
</tr>
</tbody>
</table>

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]

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

(2)

where

$$N = 2s \frac{T_{\text{max}} - T_{\text{min}}}{T_{\text{max}} + T_{\text{min}}} + s^2 + 1$$

(3)

The dispersion of refractive index of As$_{40-x}$Sb$_x$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]:

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

(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), $h\nu$ is the frequency, at which $n$ is measured. The film parameters $E_0$ and $E_d$ were determined from the linear dependences $\left[ n^2(h\nu) - 1 \right]^{-1} - f( h\nu )^2$ (Fig. 4, b) by the slope of $(E_0E_d)^{-1}$ 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 As$_{40}$Sb$_{60}$ down to 4.68 eV for As$_{34}$Sb$_4$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 As$_{40-x}$Sb$_x$S$_{60}$ films changes very slightly, as the composition is varied (Table 2). Minimum value of $E_d$ is found for As$_{34}$Sb$_4$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

![Fig. 4. Dispersion of the refractive index (a) and the dependence of ($n^2$ - 1)-1 on $h\nu^2$ (b) for As$_{40-x}$Sb$_x$S$_{60}$ films, at. %: 1 – 0; 2 – 4; 3 – 6.](image-url)
As$_{40}$S$_{60}$ film is equal to 20.61 eV [29]. Earlier [11], while studying the optical characteristics of As$_{40}$S$_{60}$-Se$_2$ films we determined the value $E_d$=20.52 eV for As$_{40}$S$_{60}$. Such insignificant difference in the values of $E_d$ for As$_{40}$S$_{60}$ 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 Sb$_{40}$S$_{60}$ film determined in [30] is equal to 21.3 eV.

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

$$E_d = \beta N_e z_a N_e.$$  

Here, $\beta$ is a constant equal to 0.37±0.04 eV for covalent materials; $N_e$ is the coordination number of the cation nearest neighbor 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$_{40-3}$Sb$_3$S$_{60}$ films with 0$\leq$x$\leq$6, we get the coordination number $N_e=2.67-2.80$ (Table 2). The value $N_e=2.8$ determined by us for As$_{40}$S$_{60}$ film differs from the coordination number value for the film with the same composition in [29] ($N_e\approx3.0$).

<table>
<thead>
<tr>
<th>Composition</th>
<th>$E_0$ (eV)</th>
<th>$E_d$ (eV)</th>
<th>$N_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As$<em>{40}$S$</em>{60}$</td>
<td>4.82</td>
<td>19.66</td>
<td>2.80</td>
</tr>
<tr>
<td>As$<em>{39.2}$Sb$</em>{0.8}$S$_{60}$</td>
<td>4.78</td>
<td>19.40</td>
<td>2.76</td>
</tr>
<tr>
<td>As$<em>{38}$Sb$</em>{1.2}$S$_{60}$</td>
<td>4.74</td>
<td>19.24</td>
<td>2.74</td>
</tr>
<tr>
<td>As$<em>{36}$Sb$</em>{3}$S$_{60}$</td>
<td>4.70</td>
<td>18.81</td>
<td>2.67</td>
</tr>
<tr>
<td>As$<em>{34}$Sb$</em>{5}$S$_{60}$</td>
<td>4.68</td>
<td>19.06</td>
<td>2.71</td>
</tr>
</tbody>
</table>

For as-prepared As$_{40-3}$Sb$_3$S$_{60}$ 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 As$_2$S$_3$-Sb$_3$S$_3$. This becomes clear, if we take into consideration that As$_2$S$_3$-Sb$_3$S$_3$ 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 As$_2$S$_3$ and Sb$_2$S$_3$ are close to 3. In addition, the production conditions for As$_{40-3}$Sb$_{3}$S$_{60}$ 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 studing materials are very close.

As mentioned above, the structure of As$_{40-3}$Sb$_3$S$_{60}$ 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 As$_2$S$_3$, the equilibrium concentration of homopolar bonds, which is “frozen” in hardening process of melt at the temperature 463 K, is $2.7 \cdot 10^{26}$ m$^{-3}$ [31]. The value of $N_e$ (2.8) obtained by us for As$_{40}$S$_{60}$ film is essentially lower than for the glass with corresponding composition (3.2 [27] and 3.74 [32]). Such difference in values of $N_e$ 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$_{40-3}$Sb$_3$S$_{60}$ films is significantly larger than in As$_{40}$S$_{60}$ film. For example, the absorption edge shifts ($\Delta E$) 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 As$_{40}$S$_{60}$ film $\Delta E$ 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$_{40}$-Sb$_{30}$S$_{60}$ films calculated from dependences $[\alpha(hv)\cdot hv]^{1/2} \sim f(hv)$ (Fig. 3, curves 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$_{30}$Sb$_{40}$S$_{60}$ and As$_{40}$Sb$_{60}$ films (at the irradiation for 1 min, $\Delta E_g$ for As$_{40}$Sb$_{60}$ 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$_{30}$Sb$_{60}$ film for 1 min. For the other studied films of As$_2$S$_3$-Sb$_2$S$_3$ system under the same conditions of exposure, the value $\Delta n$ is less (for As$_{39}$Sb$_{40}$S$_{60}$ and As$_{34}$Sb$_{60}$S$_{60}$ films, the values $\Delta n$ 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$_{40}$-Sb$_{30}$S$_{60}$ 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$_{40}$-Sb$_{30}$S$_{60}$ 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 ($\Delta E$, $\Delta E_g$, $\Delta n$) of As$_{40}$-Sb$_{30}$S$_{60}$ 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$_4$S$_4$ 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 overand 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$_4$S$_4$ 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$_3$S$_{60}$ and As$_{34}$Sb$_3$S$_{60}$ 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.

![Graph](image)

Fig. 5. Dependences of the transmission spectra of the as-prepared As$_{36}$Sb$_3$S$_{60}$ (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$_3$S$_{60}$ 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 $\Delta E$ is 0.036 eV. For As$_{34}$Sb$_3$S$_{60}$ film this parameter is less (0.029 eV). This means that the pseudoforbidden gap width decreases at annealing. For annealed films As$_{36}$Sb$_3$S$_{60}$ and As$_{34}$Sb$_3$S$_{60}$, 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$_{32}$ 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$_3$S$_{60}$ 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$_3$S$_{60}$ 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$_3$S$_{60}$, 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$_3$S$_{60}$ and As$_{34}$Sb$_3$S$_{60}$, 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$_3$S$_{60}$, film we get the following values of these parameters: $E_0(I)=4.56$ eV, $E_d(II)=4.64$ 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$_3$S$_{60}$, 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 trans mission spectra of $\text{As}_{40}-\text{Sb}_{56}$ 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.

**REFERENCES**


13. Rubish, V.M., Gera, E.V., Durcot, M.O. et.al. (2013), “Photo- and thermally-
induced changes in the optical properties of Ge-S-Se amorphous films”, Semiconductor Physics, Quantum Electronics & Optoelectronics, V.16, No.4, pp. 349-353.


32. Shplotyk, O.I., Shwarts, K.K., Kornelyuk, V.N. et.al. (1991),
В.М. Рубіш1, М.М. Поп2, О.А. Микайло2, С.А. Костюкевич3, А.А. Крючин1, М.А. Дуркот1, Т.І. Ясінко1
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 досліджено спектри пропускання аморфних плівок As₉₀₋ₓSbxSₓox 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. Зміни оптичних характеристик виявлені для плівки As₉₀₋ₓSbxSₓox зміни оптичних параметрів плівок відбуваються в них при опроміненні та відпалі.

**Ключові слова:** халькогенідні аморфні плівки, спектри пропускання, фотоіндукувані ефекти, оптичні властивості, структурні перетворення.
ЛАЗЕРНО-ИНДУЦИРОВАННЫЕ ИЗМЕНЕНИЯ ОПТИЧЕСКИХ ХАРАКТЕРИСТИК АМОРФНЫХ ПЛЕНОК СИСТЕМЫ As-Sb-S

В спектральной области 400-750 нм исследованы спектры пропускания аморфных пленок As$_{40}$Sb$_x$S$_{60}$ с небольшим содержанием сурьмы ($x=0, 0.8, 1.6, 4.6$) 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 запрещенной зоны $E_d$ и показателя преломления $n$ пленок. Рассчитаны параметры одноосциляторной модели (энергия осциллятора $E_0$, дисперсионная энергия $E_d$ и эффективное координационное число). Максимальные изменения оптических характеристик наблюдались в пленках As$_{36}$Sb$_4$S$_{60}$. Изменения оптических параметров пленок обусловлены структурными превращениями, происходящими в них при облучении и отжиге.

Ключевые слова: халькогенидные аморфные пленки, спектры пропускания, фотон-дуцированные эффекты, оптические свойства, структурные превращения.

СПИСОК ВИКОРИСТАНОЇ ЛІТЕРАТУРИ

2. Семак, Д.Г., Різак, В.М., Різак, І.М. (1999), Фото-термоструктурні перетворення халькогенідів, Ужгород, Закарпаття, 392 с.


34. Шпотюк, О.И., Савитский, И.В. (1989), “Радиационно-термические эффекты в стеклообразных полупроводниках системы As$_2$S$_3$–Sb$_2$S$_3$”, Укр. Физ. Ж., Т.34, №6, сс. 894-898.


© Ужгородський національний університет