Raman spectra and optical properties of thin $As_{40}S_{60}$ and $As_{40}S_{50}Se_{10}$ films

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Abstract

Structure and optical properties of $As_{40}S_{60}$ and $As_{40}S_{50}Se_{10}$ glasses and thin films have been studied using the Raman spectroscopy. The structure of the films is suggested to be basically formed by triangular AsS_3 and $AsSe_3$ pyramids linked by two-fold coordinated sulphur or selenium atoms. A considerable amount of structural units with homopolar As-As and S(Se)-S(Se) bonds has been found in the matrix of investigated compounds. The influence of illumination and annealing on the structure and optical properties of $As_{40}S_{60}$ and $As_{40}S_{50}Se_{10}$ films has been studied. It has been shown that the mentioned actions lead to polymerization of molecular $As_4S(Se)_4$ groups and $S(Se)_n$ chains in the film matrix and formation of structural units with heteropolar As-S and As-Se bonds. This is accompanied by the absorption edge shift towards the long-wavelength region and the increase in the refractive index.

Introduction

Due to high-level photostructural transformations under the influence of UV or visible light, which bring about changes in the optical, chemical and mechanical properties, thin $As_{40}S_{60-x}Se_x$ layers are very promising for using as media for optical information recording [1–3]. Most investigations in this direction have been carried out on $As_{40}S_{60}$ and $As_{40}S_{60-x}Se_x$ layers with the increased selenium content ($x \geq 20$). The results of those studies have shown that photoresists on the basis of layers of As-S-Se system are characterized by rather high photosensitivity in the wavelength region of 476–532 nm and allow to obtain 200–300 nm sized pits. This fully satisfies the parameters of both the ordinary and DVD compact discs. However, as the studies for aging processes in

inorganic resists on the basis of $As_{40}S_{60-x}Se_x$ layers have shown [4], the films with the increased selenium content manifest some temporal instability of the parameters. The layers of $As_{40}S_{60}$ are better in this respect. Nonetheless, the glasses and thin films of As-S-Se system with the low content of selenium have not been practically studied up till now.

In the present paper, we report the results of both structural and optical researches for the glasses and films $As_{40}S_{60}$ and $As_{40}S_{60-x}Se_x$.

Experimental methods

Bulk samples of $As_{40}S_{60}$ and $As_{40}S_{50}Se_{10}$ were prepared by slow melting of the mixtures of high-purity components in the evacuated quartz ampoules at 900–970 K for 20–24 h, with subsequent quenching of the melt at the rates of ~10 K/s. The sealed ampoules were subsequently returned to the furnace for annealing at the temperature 20 K lower than the glass transition temperature.

Thin films were deposited onto cool silica glass substrates with the vacuum thermal evaporation technique. The deposition rate was continuously measured using the quartz microbalance technique. In the present studies it was within the range of 1–6 nm/s. The thicknesses of $As_{40}S_{60}$ and $As_{40}S_{50}Se_{10}$ films prepared for the structural and optical investigations were 500–1000 nm. The exposure was performed by means of a mercury lamp with an IR cut-off filter.

The Raman spectra for the bulk and thin film samples were studied at $T = 300$ K and the wavelength of 632.8 nm, with the resolution of about 1 cm^{-1}. The scattered light was analyzed using a standard DFS-24 spectrometer.

The optical transmission spectra of the films were recorded by means of diffractive monochromator. The spectral resolution was equal to less than 10^{-3} eV. Finally, the refractive index n of our thin films was determined from the optical transmission spectra.

Results and discussion

Raman spectra of $As_{40}S_{60}$ and $As_{40}Se_{60}$ glasses are shown in Fig. 1. Broad bands with the maxima located respectively at 343 and 227 cm^{-1} are dominant features of those spectra. The bands are caused by vibrations of arsenic and sulphur (selenium) atoms in the trigonal pyramids AsS_3 and $AsSe_3$, respectively. These structural groups are linked by two-fold coordinated sulphur or selenium atoms and form the matrices of $As_{40}S_{60}$ and $As_{40}Se_{60}$ glasses. In order to analyze the Raman spectra of $As_{40}S_{60}$ and $As_{40}Se_{60}$ glasses in a more detail, one has to take into account a presence of the other structural groups with homopolar bonds As-As and S-S (Se-Se), as well as the bridge complexes As-Se-As or As-Se-As.

The principal band for the $As_{40}S_{60}$ glass is asymmetrical and represents a result of several overlapped bands (see the peculiarities at 316, 330, 360 and 380–400 cm^{-1} – Fig. 1, curve 1). The shoulder at 316 cm^{-1} is related with deformation vibrations of S-As-S bonds in the trigonal AsS_3 pyramids, which take part in forming the glass network
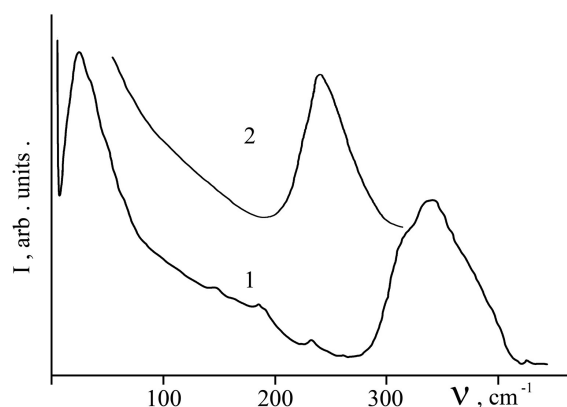
Fig. 1. Raman spectra of $As_{40}S_{60}$ (1) and $As_{40}Se_{60}$ (2) glasses.

[5]. The peculiarities at 330 and 363 cm^{-1} are attributed to the presence of structural groups As_4S_4 that contain homopolar As-As bonds. The wide shoulder in the region of 380–400 cm^{-1} could be referred to interaction between the AsS_3 pyramids. Weak bands at 146, 162 and 187 cm^{-1} detected for the vitreous $As_{40}S_{60}$ are also characteristic of crystalline β-As_4S_4 [6]. The bands located at 146 and 162 cm^{-1} are related to As-S-As vibrations and the band at 187 cm^{-1} is caused by As-As bonds. Rather intensive band at 231 cm^{-1} may be also attributed to homopolar bonds As-As, though a contribution of S-S bond vibrations is not excluded. The Raman spectrum of the glassy $As_{40}Se_{60}$ is simpler (see Fig. 1, curve 2). It contains the intense band with the maximum at 227 cm^{-1} and weak peculiarities in the regions of 110–150 and 250 cm^{-1}, associated with the presence of molecular fragments with homopolar As-As and Se-Se bonds in the glass matrix [7].

The Raman spectra of ternary $As_{40}S_{50}Se_{10}$ glasses manifest a two-mode character (see Fig. 2). Chiefly, they contain two intense bands, whose maxima correspond to almost the same frequencies as those for $As_{40}S_{60}$ and $As_{40}Se_{60}$. This testifies predominant role of structural units AsS_3 and $AsSe_3$ in the formation of $As_{40}S_{50}Se_{10}$ glass network. However, the Raman spectra depend substantially on the glass preparation conditions, as clearly seen from Fig. 2.
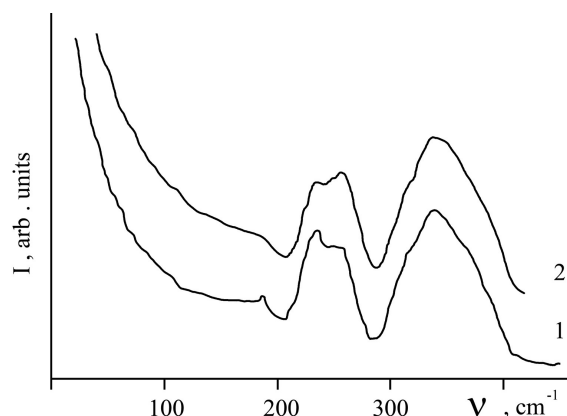

Fig. 2. Raman spectra of unannealed (1) and annealed (2) $As_{40}S_{50}Se_{10}$ glasses.

In the spectrum of unannealed $As_{40}S_{60-x}Se_x$ glass, the maxima referred to the principal bands are located at 235 and 339 cm^{-1} (see Fig. 2, curve 1). The difference in the positions of these maxima from those typical for the glassy $As_{40}S_{60}$ and $As_{40}Se_{60}$ testifies mutual influence of the structural groups AsS_3 and $AsSe_3$ and the appearance of mixed structural pyramidal units AsS_mSe_{3-m} (m = 1, 2). The both bands are asymmetrical. Here the frequency positions of the peculiarities available in the high-frequency spectrum region, which are responsible for sulphide subsystem, practically coincide (316, 363 and 380–400 cm^{-1}). The character of changes in the spectrum for the region responsible for selenide subsystem is somewhat more complicated. It is not surprising since in the region of the main peak for $As_{40}Se_{60}$ (227 cm^{-1}) there are some peculiarities characteristic of $As_{40}S_{60}$. As a result, the main low-frequency band of $As_{40}S_{50}Se_{10}$ glass has a complex character (see Fig. 2, curve 1).

The bands located at 186, 209, 228, 249 and 258 cm^{-1} are detected in the Raman spectrum of unannealed $As_{40}S_{50}Se_{10}$ glass. Furthermore, a shoulder is observed in the region of 277 cm^{-1}, which can be attributed to interactions between the $AsSe_3$ pyramids. As mentioned above, the 186 cm^{-1} band can be associated with the structural groups containing homopolar As-As bonds. The existence of shoulder in the region of 209 cm^{-1} may be caused by S-S bonds. The situation in the 230–260 cm^{-1} region is more complicated. In this region, the bonds characteristic of selenium chain and ring vibrations manifest themselves and the band at ~260 cm^{-1} associated with Se-Se vibrations in the As-Se-Se-As structures [8, 9] is available. The As-As bonds are active in this frequency region, too. The band in the 256–258 cm^{-1} region could be also attributed to presence of molecular As_4Se_4 fragments. Using the scaling coefficient 0.71 characteristic of $As_{40}S_{60}$ and $As_{40}Se_{60}$ glasses in the principal band region [10], we obtain its relationship with the 363 cm^{-1} band present in the Raman spectra of glassy $As_{40}S_{60}$. As shown above, this band is characteristic of vibrations of molecular As_4S_4 fragments. Finally, the band at 249 cm^{-1} can characterize mixed AsS_mSe_{3-m} (m = 1, 2) pyramids [11].

The Raman spectrum for the annealed $As_{40}S_{60-x}Se_x$ glass somewhat differs in the low-frequency region. The principal maximum is now located at 258 cm^{-1} and the intensity of band at 235 cm^{-1} becomes considerably lower. Likewise, the peculiarity present at 186 cm^{-1} and caused by As-As bonds is not so pronounced as for the spectrum of unannealed glass. The changes in the high-frequency range are minimal. Such behaviour of the Raman spectra suggests decreasing amount of homopolar bonds in the glass matrix after annealing, which leads to its ordering.

The Raman spectra change notably when the selenium content in the glass $As_{40}S_{60-x}Se_x$ composition increases [12, 13]. This concerns mainly the low-frequency spectral region, whereas the high-frequency one remains practically unchanged. In the region of low frequencies, the maximum centred at 253 cm^{-1} is principal for $As_{40}S_{45}Se_{15}$ and $As_{40}S_{40}S_{20}$ glasses. This confirms a growing role of Se-Se bonds in the glass structure occurring with increasing selenium content in the composition. The role of the band at 235 cm^{-1} is also considerable. The peculiarity at 209 cm^{-1} is absent and the shoulder at

228 cm^{-1} only slightly visible. However, the band at 187 cm^{-1} is still present in the spectrum of glasses with $x = 15$ and 20, thus testifying the existence of As-As bonds. Nonetheless, its intensity for the glasses mentioned above is significantly lower than that for the glass with $x = 10$.

The Raman spectrum of As_2S_3 film evaporated onto a glass substrate contains much more peculiarities (see Fig. 3, curve 1) than the spectrum for As_2S_3 glass (Fig. 1, curve 1). First of all, it is a considerable intensity of the bands at 231 and 187 cm^{-1} that draws attention, as well as a presence of weak bands at 102, 120, 134 and 221 cm^{-1}. The high-frequency spectral region does not practically change when passing from the glass to film, though the shoulder located at 316 cm^{-1} is expressed very weakly in the Raman spectrum of the film. Such the behaviour of the Raman spectra could be evidence of greater structural disordering for the amorphous film. At the same time, the bands centred at 102, 120, 134 and 221 cm^{-1} unambiguously point out at the presence of film condensate of the structural groups, with homopolar bonds in the matrix. Such structural groups should be molecular As_4S_4 units [14].

The presence of two cluster types of As_4S_4 must be allowed for here. In the monomer form, the two As-As bonds are connected by four bridging sulphur atoms in such a way that a closed cage-like structural unit is formed. At that, the valence requirements for all the atoms are satisfied. In the second model, the monomer cage is opened and two more sulphur atoms are added. These clusters allow formation of specially branched structural network of the glass or film and so determine to a large extent character of the vibrational spectra.

The Raman spectra of the mixed $As_{40}S_{60-x}Se_x$ films manifest a two-mode character, like the spectra of the corresponding glasses. The spectral peculiarities typical for both the glasses and films are generally preserved. This witnesses conservation of short-range and middle-range order in the structure of material [13,15]. The frequency positions of principal bands available in the regions of 230–260 and $310–400 \text{ cm}^{-1}$ practically do not change, though redistribution of the band intensities takes place. It especially concerns the $230–260 \text{ cm}^{-1}$ region. For the as-evaporated $As_{40}S_{50}Se_{10}$ film (Fig. 4, curve 1), the
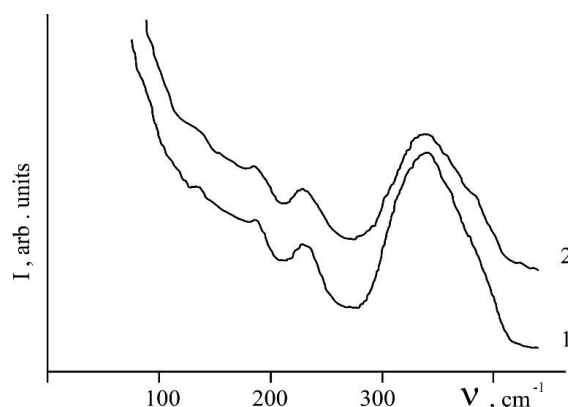

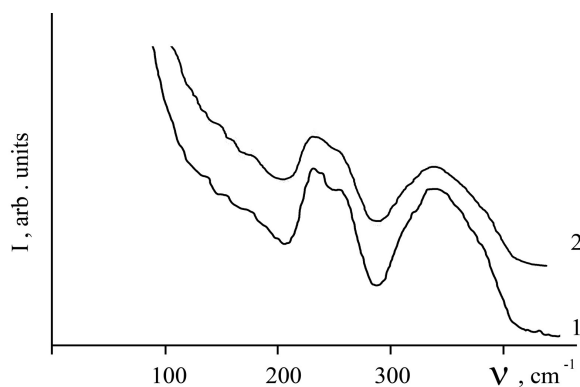**Fig. 3.** Raman spectra of as-evaporated (1) and exposed (2) $As_{40}S_{60}$ films.

Fig. 4. Raman spectra of as-evaporated (1) and exposed (2) $As_{40}S_{50}Se_{10}$ films.

bands in the low-frequency region of the Raman spectrum (i.e., 115, 136, 150, 174 and 200 cm^{-1}) appear, which are lacking in the glass spectrum (see Fig. 2). The existence of these bands is associated with the homopolar As-As and S(Se)-S(Se) bonds. It is necessary to point out that the peculiarities to be observed in the background of the main low-frequency Raman band for $As_{40}S_{50}Se_{10}$ glass, are shifted in the films of the same composition. Indeed, these peculiarities are detected at 223, 231, 239 and 256 cm^{-1} for the film, the band at 231 cm^{-1} being the most intense.

Thus, the analysis of the Raman spectra for $As_{40}S_{60-x}Se_x$ glasses and films enables us to draw conclusion about a micro-heterogeneous structure of the latter. Their structure may be given in the form of a matrix consisting of pyramidal $AsS_{3/2}$, $AsSe_{3/2}$ and AsS_mSe_{3-m} units. It also contains a considerable amount of molecular $As_4S(Se)_4$ and $S(Se)_n$ fragments characterized with homopolar bonds As-As, S-S and Se-Se.

The exposure of $As_{40}S_{60}$ and $As_{40}S_{50}Se_{10}$ films leads to substantial decrease in the amount of homopolar bonds, owing to severance and commutation of As-As and S(Se)-S(Se) bonds in the molecular As_4S_4 (As_4Se_4) fragments and the $S_n(Se)_n$ chains (see Fig. 3, curve 2 and Fig. 4, curve 2). The intensity decrease for some bands in the Raman spectrum of illuminated $As_{40}S_{50}Se_{10}$ film (136, 150, 174, 187, 239 and 256 cm^{-1}) and their disappearance (200 cm^{-1}) are the appropriate evidence. From the viewpoint of thermodynamics, the bond commutation accompanied by decreasing amount of homopolar bonds is preferable. The processes of polymerization of molecular groups in the main film matrix get stronger with increasing exposition dose. The film spectrum becomes similar to that of the glass. Moreover, the amount of homopolar bonds in the $As_{40}S_{60-x}Se_x$ films decreases when the exposure dose grows [13]. Thermal annealing also causes polymerization of molecular groups and, in some cases, it turns out to be much more efficient than the former factor [13,16].

Structural changes occurring in the films during their exposure or annealing are also accompanied by substantial changes in the optical properties. Fig. 5 and 6 display the optical transmission spectra of amorphous $As_{40}S_{50}Se_{10}$ film, which prove to be typical for all the materials under test. However, one should notice that 'washing out' of the spectra in the region of fundamental absorption edge is significantly lower for $As_{40}S_{60}$ and

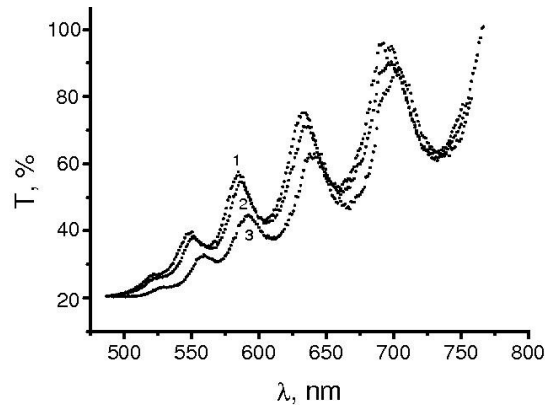**Fig. 5.** Transmission spectra of $As_{40}S_{50}Se_{10}$ films: 1 – as-evaporated, 2 and 3 – exposed for 40 (2) and 80 min (3), respectively.
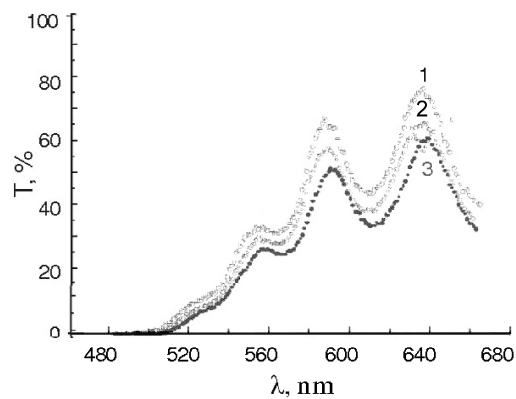

Fig. 6. Transmission spectra of $As_{40}S_{50}Se_{10}$ films detected at different temperatures: 1 – T = 293, 2 – 308, 3 – 358 K.

$As_{40}S_{60}$. Considerable process of 'washing out' of the transmission spectra for $As_{40}S_{50}Se_{10}$ films, which are more complex in their composition, might be explained by influence of composition disordering on the replacement of sulphur atoms by selenium ones [17]. The transmission spectra shift towards the long-wavelength region with increasing selenium content in the $As_{40}S_{60-x}Se_x$ film composition, testifying a decrease in the pseudo-forbidden gap. The refractive index then increases, too. The values of n for the films measured at the wavelength of 632.8 nm are presented in Fig. 7. Similar to the case of glasses with the same compositions, the composition dependence of the refractive index for the films is virtually linear.

As seen from Fig. 5, the transmission spectra shift to the longwave region and a simultaneous transmission decrease takes place after illumination of films. Similar results have been obtained for $As_{40}S_{60-x}Se_x$ films with the large contents of Se [3]. The same situation is also observed in case of temperature investigations of the transmission spectra (Fig. 6). Darkening of the films and, correspondingly, decrease in their pseudo-forbidden gap width E_g^* take place during the illumination and heating. The refractive index of
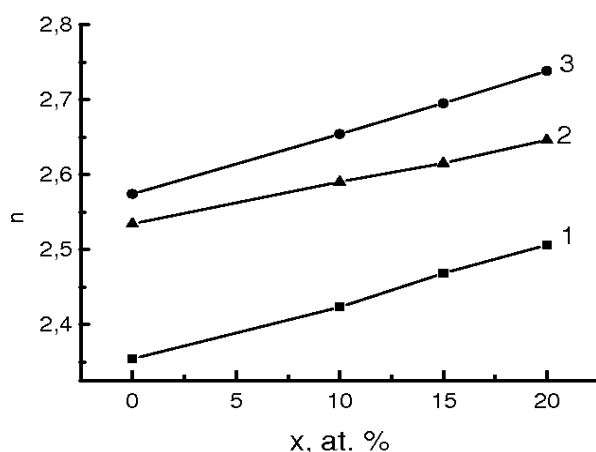
Fig. 7. Refractive index of $As_{40}S_{60-x}Se_x$ films referred to the wavelength of 630 nm versus Se content: 1 – as-evaporated, 2 – exposed, 3 – annealed films.

$As_{40}S_{60-x}Se_x$ films then increases (see Fig. 7). It is worth mentioning that the n values for the films annealed at $T \cong T_g - 20$ K during 1 h correspond to curve 3 in Fig. 7. It is seen that, in what the influence on the refractive index is concerned, thermal annealing is more efficient than the exposure of films.

Conclusions

Basing on the above analysis of the Raman spectra performed for $As_{40}S_{60}$ and $As_{40}S_{50}Se_{10}$ glasses and films, we arrive at the conclusion about their micro-heterogeneous structure. The structure of the materials under study could be represented in the form of matrix consisting of pyramidal units $As_2S_{3/2}$, $As_2Se_{3/2}$ and the mixed units AsS_mSe_{3-m}. These structural groups are linked by two-fold coordinated sulphur or selenium atoms. The structure contains also the molecular fragments $As_4S(Se_4)$ and $S(Se)_n$ with homopolar bonds As-As, S-S and Se-Se. Both the exposure and annealing lead to polymerization of the molecular groups As_4S_4 and As_4Se_4 and the chains of S_n and Se_n in the film matrix, with further formation of structural units characterized with heteropolar As-S and As-Se bonds. The latter is accompanied by the absorption edge shift towards the long-wavelength region and the refractive index increase.

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