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Raman spectra of Ag- and Cu- photodoped chalcogenide films

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Abstract. Raman spectra of the chalcogenide vitreous layers ($\text{As}_40\text{S}_{60}$, $\text{As}_40\text{S}_{40}\text{Se}_{20}$, $\text{As}_40\text{Se}_{60}$) non-doped and photodoped by Ag, Cu were measured. The spectra were analyzed in terms of a molecular model. It was ascertained, that for the spectra of photodoped $\text{As}_40\text{S}_{60}$, $\text{As}_40\text{S}_{40}\text{Se}_{20}$ layers, the shift of the main bands to the high frequency side and the appearance of the additional scattering bands in the low frequency spectral range are characteristic features. For the spectra of photodoped $\text{As}_40\text{Se}_{60}$ layers, such shift and significant increase in scattering were not observed. Variations in the Raman spectra with photodoping by Ag or Cu are consistent with the supposition concerning normal covalent and coordinative bond formation between metal additives and chalcogen atoms.

Keywords: arsenic chalcogenides, thin films, photodoping, Raman spectroscopy.

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1. Introduction

Chalcogenide vitreous semiconductors (ChVS) have high transparency in the IR spectral range. This and other of their specific properties enable one to use them as a media for light waveguides in optoelectronics and also in the IR technique. Among the numerous photo- and radiation-stimulated phenomena exhibited by ChVS - the phenomenon of the photostimulated diffusion of metal [1] (mainly Ag or Cu) into ChVS is one of the most interesting. Under the illumination of the ChVS layer that was deposited on the metal layer (or metal-containing layer, the order of the layers can be reversed) the interaction between substances in the semiconductor and metal layers occurs with the creation of an interaction product layer (photodoped layer). The phenomenon has attracted the attention of numerous investigators, various practical application possibilities (this effect leads to substantial changes in solubility rates of chalcogenide layer, which makes possible the production of various relief images) were shown for microelectronics [2-3], optical memory [4], holography, diffractive optics [5-9], etc. Many publications were devoted to the investigation of the photodoping mechanism and the basic physical properties of this phenomenon [10-18]. However, the peculiarities of the interaction of metal atoms with the atoms of the

chalcogenide matrix, along with the local structure of such products, have been studied very little even for the most investigated As_3S_3 -Ag structure. This is associated with experimental difficulties while using the standard X-ray methods of investigations. Application of the optical non-destructive techniques (including the investigations of the Raman spectra) can bring information on the changing of chemical bonds and the molecular structure for the ChVS films as a result of photodoping.

It is known that some metals intensively undergo photodoping in the structures based on vitreous arsenic sulfide and arsenic selenide. Investigations of the local structure of photodoped As-S layers were carried out using Raman scattering [11-14]. It was found that, in general, Raman spectra in such films are analogous to those for the As-S-Ag massive glasses and indicate the presence of Ag-S bonds. The latter are analogous to those present in Ag_2S compounds [11-12]. Later studies [13-14] conducted gave more detailed features of the possible formation mechanisms involving metal-impurity chemical bonds with the As_2S_3 glass matrix, and of the influence of impurity on the glass structure, too. The structure of the photodoped As-Se layers is less investigated. In the present work, the results of the Raman spectra investigations of ChVS ($\text{As}_40\text{S}_{60}$, $\text{As}_40\text{Se}_{60}$, $\text{As}_40\text{S}_{40}\text{Se}_{20}$ compositions) and their modifications with photodoping by

Ag or Cu are presented and discussed. The peculiarities of the formation of the metal-chalcogenide bonds are discussed.

2. Experiment

The bulk materials ($\text{As}_{40}\text{S}_{60-x}\text{Se}_x$, $x = 0; 20; 60$) were prepared by the direct synthesis from 5N purity elements in evacuated quartz ampoules at 700 - 750 °C for 8 - 24 hrs. After synthesis, the ampoules were quenched in cold water. Thin ChVS films ($d = 0.4\text{-}5 \mu\text{m}$) and metal (Ag, Cu with $d = 0.01\text{-}0.2 \mu\text{m}$) were sequentially deposited by the vacuum thermal evaporation ($p = 1.33 \times 10^{-3}$ Pa) from the resistance-heated quartz or Mo boats onto clean glass substrates (microscopic slides) kept under room temperature. Deposition rate was continuously measured using the quartz microbalance technique, and in the present study it was within 1 - 6.0 nm/s. The prepared two-layer ChVS-metal structures were exposed to light in order to photodissolve and uniformly spread the metal in the ChVS film. An incandescent lamp was used for exposure. The concentrations of the metal in the photodoped samples were determined by the mass proportion of the deposited metal and ChVS. The metal concentration intervals for the investigated samples were chosen by taking into account the photodoping peculiarities in such structures.

The Raman spectroscopy investigations were carried out by using BRUKER IFS55 IR spectrophotometer with a FRA 106 accessory. The laser irradiation on the wavelength 1,06 μm was used for the excitation of the Raman spectra. In our case, this wavelength value was very essential because irradiation of samples in this range causes no detectable photostructural transformations or photodoping processes.

3. Results

Raman spectra of the investigated materials are presented in Fig.1-3. For each of the investigated compositions ($\text{As}_{40}\text{S}_{60}$, $\text{As}_{40}\text{Se}_{60}$, and $\text{As}_{40}\text{S}_{40}\text{Se}_{20}$) the spectra of the massive glass, the thermally- evaporated film and the photodoped film are presented. While normalizing on the intensity maximum, a correlation is observed in the spectral position and form of the most intense main bands of the thermally deposited film and the corresponding massive glass. This indicates the presence of the same structural elements in them, which determines the scattering characteristics in the spectra of both the massive glass and the film. However, at the same time, differences are also observed between these two types of spectra. In general, they are characterized by the appearance of the additional weak bands in the spectra of the films. This difference is more pronounced for $\text{As}_{40}\text{S}_{60}$ and less for $\text{As}_{40}\text{Se}_{60}$.

In the spectrum of the thermally evaporated $\text{As}_{40}\text{S}_{60}$ film the number of bands is equal to 14 (see Fig.1, curve 3), which corresponds to the results obtained in an earlier investigation [19]. In the region of the main maximum at 345 cm^{-1} the splitting can be seen, which is absent in the spectrum of the massive glass. From the results of previously carried out investigations [20-21], it is known that these differences as well as the numerous weak bands in the 50-250 cm^{-1} range, and also the band near 495 cm^{-1} , are due to the presence of non-stoichiometric structural units of As_4S_4 and S_2 in the structural network of the thermally-evaporated $\text{As}_{40}\text{S}_{60}$ film.

The main maximum in the spectrum of the photodoped layer in relation to the maximum for the initial nondoped layer is shifted to higher wavenumber, namely to 373 cm^{-1} (see Fig.1, curve 4). The spectrum of the photodoped layer is also characterized by the presence of a second intensive

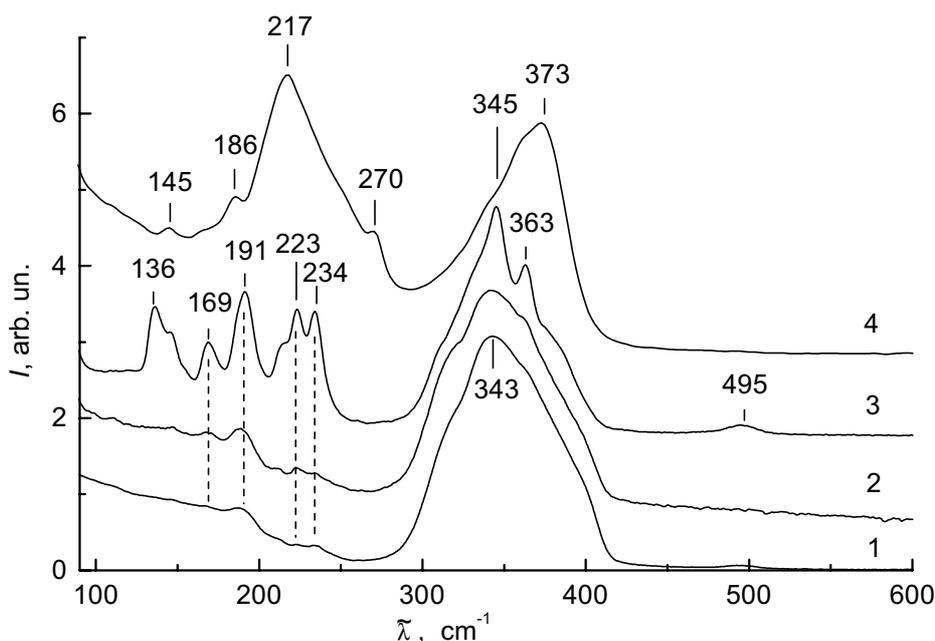


Fig. 1. Raman spectra of $\text{As}_{40}\text{S}_{60}$: 1 – bulk glass ; 2 – $\text{As}_{40}\text{S}_{60}$ layers annealed in Ar atmosphere; 3 – as-evaporated $\text{As}_{40}\text{S}_{60}$ layer; 4 – $\text{As}_{40}\text{S}_{60}$ layer photodoped with Ag ($\text{As}_2\text{S}_3\text{Ag}_{2,2}$).

band near 217 cm^{-1} . The wavenumber position of several bands and shoulders in this spectrum, in $50\text{-}190\text{ cm}^{-1}$ range is near to the position of the weak bands in the spectrum of the thermally-evaporated $\text{As}_4\text{S}_6\text{O}$ film. It is necessary to mention here that under the annealing (see Fig.1, curve 2) or the exposure processes of $\text{As}_4\text{S}_6\text{O}$ films there is no significant change of the main maxima position, and the corresponding spectra approach the spectrum of massive glass (see Fig.1, curve 1). The polymerization that proceeds under the exposure or annealing of $\text{As}_4\text{S}_6\text{O}$ films decreases the number of the nonstoichiometric structural units As_4S_4 and S_2 , that leads to the sufficient intensity decrease of corresponding to them weak bands in the $50\text{-}250\text{ cm}^{-1}$ range, and also of the band near 495 cm^{-1} . It can be seen from the comparison of curves 1-3 that the result involving only polymerization processes (see curve 2) is sufficiently different from the changes observed after photodoping processes (see curve 4), where the polymerization processes and photostimulated introduction of silver proceed simultaneously.

In the spectrum of thermally-evaporated $\text{As}_4\text{Se}_6\text{O}$ layer the band position of the most intense band is near 224 cm^{-1} (see Fig.2, curve 2), that practically coincides with the position of the maximum in spectrum for massive glass with the same composition. The maximum in the spectrum of the $\text{As}_4\text{Se}_6\text{O}$ layer photodoped by silver (see curve 3) is situated practically at the same wavenumber. In the spectrum of the thermally-evaporated $\text{As}_4\text{Se}_6\text{O}$ film the asymmetry of the main band and the presence of weak bands in the region $50\text{-}175\text{ cm}^{-1}$ can be seen. Such differences in spectra of the film and massive glass $\text{As}_4\text{Se}_6\text{O}$ are explained by the presence in the films network of the nonstoichiometric structural elements, similar to those that are present in the network of the arsenic sulfide layers [20]. As a result of the photodoping of $\text{As}_4\text{Se}_6\text{O}$ with silver, the intensity of the scattering in the wavenumber region less than 175 cm^{-1} is increased in a such way that the weak bands which are characteristic for the $\text{As}_4\text{Se}_6\text{O}$ film are not seen (see Fig. 2, curve 3), new maxima are not observed.

The most intensive bands in the Raman spectra of thermally-evaporated $\text{As}_4\text{S}_4\text{Se}_2\text{O}$ layers are located near 222 and 343 cm^{-1} (see Fig. 3, curve 2) which are near to the band maxima positions in the spectra of the layers for the extreme compositions (As_2S_3 and As_2Se_3). The differences in the spectra of massive $\text{As}_4\text{S}_4\text{Se}_2\text{O}$ glass from the spectra of the layers in general are in agreement to those that were observed in the spectra of As_2S_3 and As_2Se_3 layers in relation to their corresponding massive glasses. As a result of photodoping of $\text{As}_4\text{S}_4\text{Se}_2\text{O}$ by silver up to the ~ 25 at% concentration the band maxima positions (222 and 343 cm^{-1}) are shifted to the high wavenumber region up to 234 and 353 cm^{-1} , respectively (see Fig. 3, curve 4). Curve 3 of the same figure corresponds to the sample involving photodoping of the $\text{As}_4\text{S}_4\text{Se}_2\text{O}$ film up to ~ 10 at% Photodoping of the $\text{As}_4\text{S}_4\text{Se}_2\text{O}$ layers by copper also causes the shift of the maxima to 232 and 352 cm^{-1} , respectively (see Fig. 3 curve 5). In all spectra for $\text{As}_4\text{S}_4\text{Se}_2\text{O}$ layers photodoped by metals, the wavenumber positions of the shoulders near 188 , 146 , 135 cm^{-1}

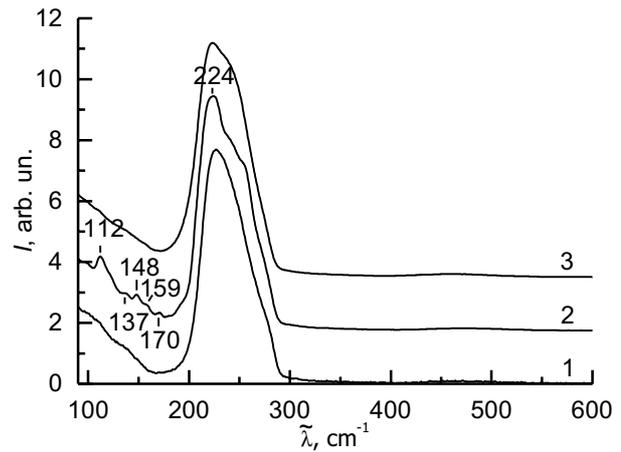


Fig. 2. Raman spectra of $\text{As}_4\text{Se}_6\text{O}$: 1 – bulk glass ; 2 – as-evaporated $\text{As}_4\text{Se}_6\text{O}$ layer; 3 – $\text{As}_4\text{Se}_6\text{O}$ layer photodoped with Ag (~ 10 at%).

coincide with the positions of the corresponding weak bands in the spectra of the initial layers.

4. Discussion

The vibrational spectra of the chalcogenide glasses show differences with respect to other amorphous materials. The influence of the matrix elements that modulate the density of the phonon states is more strongly pronounced. In this connection, the main peculiarities of the Raman spectra of the arsenic-containing ChVS are in agreement with the molecular selection rules for the AsX_3 ($X = \text{S}, \text{Se}$) pyramidal structural units in the glass [22-25]. The most intense bands in the Raman spectra of As_2S_3 and As_2Se_3 occur near 345 cm^{-1} and 224 cm^{-1} and correspond to the $\nu_1(\text{A})$ valence vibrations of the corresponding pyramidal structural units in the glass. The deformation vibrations $\nu_3(\text{E})$ near 310 cm^{-1} for As_2S_3 and 216 cm^{-1} for As_2Se_3 are pronounced weaker. The stretching and compression force constant K_r of As-X

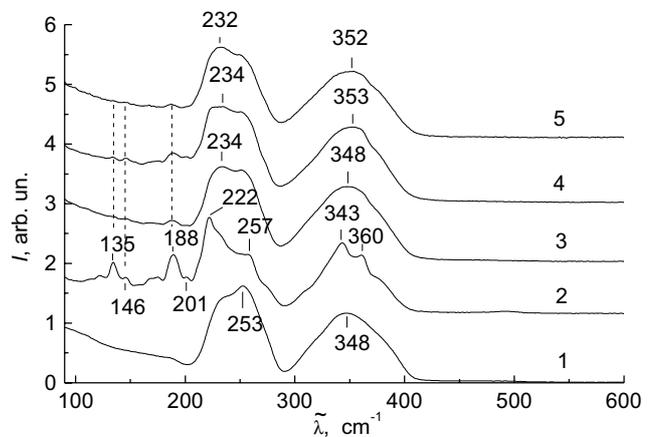


Fig. 3. Raman spectra of $\text{As}_4\text{S}_4\text{Se}_2\text{O}$ layers: 1 – bulk glass ; 2 – asevaporated $\text{As}_4\text{S}_4\text{Se}_2\text{O}$ layer; 3, 4 – photodoped with Ag ~ 10 and 25 at%, respectively; 5 – photodoped with Cu.

bond that determine the wavenumber of the valence vibrations can be calculated according to the Gordy rule [23, 26]:

$$K_r = aN(X_{As}X_x/d^2)^{3/4} + b, \quad (1)$$

where a and b are empirical constants, N is the order of the bond, X_{As} and X_x are the electronegativities of the corresponding elements, and d is the bond length.

As mentioned above, the introduction of metals into the $As_{40}S_{60}$ and $As_{40}S_{40}Se_{20}$ layers causes the shift of the Raman maxima to the region of higher wavenumbers. The wavenumber position for the maximum of the photodoped $As_{40}Se_{60}$ spectrum remains the same as for the initial nondoped layer.

It is important to note that such changes in the Raman spectra for the $As_{40}S_{60}$ and $As_{40}S_{40}Se_{20}$ layers or the absence of essential changes for the $As_{40}Se_{60}$ layers are characteristic for the photodoped ChVS layers with the substantial dopant concentration, when the number of the metal atoms is near to the number of chalcogene atoms and for some concentrations exceeds the number of pnictide atoms. For example, the optimal concentration of Ag during photodoping of the As_2S_3 layers is 30-32 at%, which correspond to the composition $As_2S_3Ag_{2.2-2.4}$ [27]. Thus, the given set of experimental results can be explained by the formation of specific bonds between the metal and the chalcogen atoms. In the given case, the same principle acts, which explains the weak influence of some dopants on the ChVS electrophysical properties and when the valence demands of the dopant are satisfied at the cost of lone pair electrons [28].

It was shown that the metal with V valence in the ChVS melt forms V normal covalent bonds in the place of broken bonds and 4 - V coordinative bonds formed with the participation of the lone pair electrons from chalcogene atoms [29-30]. In the network structure of the thermally-evaporated film of $As_2S_xSe_{3-x}$ composition, the number of broken bonds can exceed 7 at % [31]. Thus, a certain amount of metal atoms can be bonded by means of normal covalent bonds. The presence of the intense band in the spectrum of the photodoped layer near 217 cm^{-1} supports this suggestion. The presence of several shoulders in the region $50-260\text{ cm}^{-1}$ in the spectrum of thermally-evaporated $As_{40}S_{60}$ layers, whose wavenumber positions correspond to the positions of weak bands, which are connected to As-As vibrations, indicate that the covalent pnictide bonds (As-As) also contribute to this part of spectrum. The band near 495 cm^{-1} which indicate the presence of the non-stoichiometric structural units S_2 in the photodoped $As_{40}S_{60}$ layer is absent. This can be explained by sulfur bonding with metal during photodoping processes (normal covalent bonds) and also by the polymerization. Illumination induces polymerization processes between the S-rich and As-rich parts of the films, resulting in formation of As_2S_3 network structure. The content of these molecular fragments is decreased because of these reactions.

As said above, the polymerization processes and photo-stimulated introduction of silver proceed simultaneously. Nevertheless, the other metal atoms satisfy the demands of their chemical valency at the cost of coordinative bonds for-

mation. In accordance with the nature of such bonds after their formation there is no destruction of pyramidal structural units of As-S-Se glasses, that is in agreement with preservation of the main bands characteristic for the undoped samples in the Raman spectra of the investigated photodoped As-S-Se layers. Sulfur-silver coordinative bonds also contribute to the band at 217 cm^{-1} . Under formation of the coordinative bonds metal-chalcogene, partial redistribution of the charge density of the lone-pair electrons from the chalcogene to metal atom occurs. Due to this, the effective electronegativity of the chalcogene increases, which in accordance with the Gordy rule leads to an increase of the force constant K_r . This force constant change is observed in the Raman spectra of As_2S_3 as the shift of the maximum to the higher wavenumber side.

The absence of shift of the maximum in the Raman spectra of photodoped As_2Se_3 can be explained in the following way. The atomic mass is more than two times bigger for selenium than for the sulphur. Thus, under the same relative increase of the force constant the effect of the redistribution of the density of phonon states must be less pronounced. One the essential reason more for the observed differences in the spectra of As_2S_3 and As_2Se_3 , can be the smaller metal concentration up to which the arsenic selenide is photodoped.

In the investigations of the IR spectra of $GeSe_2$ and As_2Se_3 photodoped by metals the displacement of the density of phonon states to the high wavenumber side (that was characteristic for As_2S_3 and GeS_2 [32]) was not observed. This experimental results shows that under the formation of the coordinative metal-selenium bonds, the charge transfer is less pronounced, then for the metal-sulphur bonds. Also, it is known, that Ag-S (Ag-Se) bonds which form the $Ag_2S(Se)$ structure have weak cross-sections of Raman scattering [12]. Therefore, a substantial amount of Ag-Se bonds in $As_2Se_3Ag_x$ products will be hardly observed in Raman spectra. Besides that, it can be seen from the comparison of the spectra of thermally evaporated As_2S_3 and As_2Se_3 films that the bands corresponding to the presence of the homopolar bonds are sufficiently weaker in the Raman spectrum of As_2Se_3 film. Thus, they are also hardly observed in the Raman spectrum of photodoped As_2Se_3 layer.

In the network structure of the As-S-Se glasses, the chaotic replacement of chalcogenes of one type by chalcogenes of another type takes place [33-34]. This can explain why the displacement value of the main maxima in the Raman spectra of the $As_{40}S_{40}Se_{20}$ layer photodoped by silver or copper has an intermediate magnitude between those observed for the two extreme stoichiometric compositions. It is necessary to note here that in the region of main band 234 cm^{-1} in the Raman spectra of the $As_{40}S_{40}Se_{20}$ layer photodoped by silver the weak bands, corresponding to the presence of the As_4S_4 and S_2 nonstoichiometric structural units within the films network (see Fig.1, curve 3) are also present. This circumstance makes clouds the interpretation of its evolution. In the spectrum of $As_{40}S_{40}Se_{20}$ layer photodoped by silver up to the 25 at% the intensity ratio between the bands at 234 and 353 cm^{-1} is preserved the same

as in the spectrum of the nondoped layer involving the bands at 222 and 343 cm^{-1} . Taking into account the results of the previous investigations of the IR absorption spectra of the photodoped As_2S_3 layers [35], we can consider these experimental data to be good evidence that during the photodoping of the $\text{As}_2\text{S}_x\text{Se}_{3-x}$ compositions, no destruction of the pyramidal structural units in films takes place.

The main mechanism, that enables the structural elements of chalcogenide glasses to remain indestructible under the photodoping by the metals is that the lone-pair electrons of the chalcogene atoms are not taking part in the formation of the AsX_3 pyramids. Usually, the coordinative bonds are weaker than covalent ones [36]. Thus, the formation of the coordinative metal-chalcogene bonds doesn't lead to the destruction of the structural units of the glass, and can influence only the dynamical characteristics of this structural elements. Under the formation of such bonds during the photodoping process or processes of the photostimulated mass transfer of metal through the photodoped layer, the ions of metal are diffuse along the sites of the lone-pair electrons belonging to the chalcogene atoms. The formation of the normal metal-chalcogene covalent bonds occurs by means of metal diffusion on the sites of defects of the amorphous matrix. Two types of metal photodiffusion channels correspond to two types of the structural centers [35], and presence of the different activation energy values for the silver photostimulated diffusion into ChVS during the various stages of the process [15, 37] supports this suggestion.

5. Conclusion

The study of Raman spectra of Ag- and Cu- photodoped chalcogenide films revealed that changes in the Raman spectra with photodoping by Ag or Cu are consistent with the suppositions concerning normal covalent and coordinative bond formation between metal additives and chalcogene atoms. Such behaviour is in accordance with the principle, which explains the slight influence of the additives on the electrical properties of chalcogenide glasses, when valence demands of additive atoms are satisfied at the cost of lone-pair electrons. The introduction of a high concentration (10-30 at%) of doping metal in $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$ does not lead to destruction of a large fraction of structural unit bonds.

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