Optical and Raman Spectroscopy of $(As_4S_3Se_3)_{1-X}$: Sn_X Glasses

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Abstract: Chalcogenide glasses are important materials for a wide range of technical applications, such as infrared optical elements, acousto-optic and all-optical switching devices, holographic recording media, diffractive optics, photonic crystals, etc. Optical investigation such as infrared reflectance and Raman spectroscopy are efficient tools for obtaining information on the local structure of the disordered material, especially when the composition is varied. In this paper we present the Raman spectra of bulk and amorphous thin films as-deposited and after light irradiation of $(As_4S_3Se_3)_{1-x}$:Sn_x ($0 \le x \le 10$ at. % Sn) chalcogenide glasses. The Raman spectra of $(As_4S_3Se_3)_{1-x}$:Sn_x glasses consist of two broad bands located at around $\nu = 236$ cm^{-1} and $\nu = 345$ cm^{-1}, which corresponds to the main vibration modes of vitreous As_2Se_3 and As_2S_3. Tin impurities didn't change the shape of Raman spectra, but shift the both bands to low frequency region. The maximum situated at around $\nu = 236$ cm^{-1} and $\nu = 345$ cm^{-1} are characteristic for all investigated glass compositions and are attributed to the symmetric stretching vibration modes of $AsSe_{3/2}$ and $AsS_{3/2}$ pyramids, respectively. The light exposure of amorphous $(As_4S_3Se_3)_{1-x}$:Sn_x thin films shift the main maximums of Raman spectra toward the lower energies.

1. Introduction

Chalcogenide glassy As_2S_3, As_2Se_3 and As_2S_3-As_2Se_3 are promising candidates for optoelectronic applications due to high chemical stability, high transmission in the IR (up to 10 μm) region, high refractive index ($n \approx 2.4 \div 2.6$), and low phonon energy. Optical investigation such as infrared reflectance and Raman spectroscopy are efficient tools for obtaining information on the local structure of the disordered material, especially when the composition is varied [1, 2]. Analysis of Raman spectra of binary chalcogenide glasses As_xS_{100-x} have been evidenced the presence of phase separation effects for $x \le 25$ [3]. It was shown that doping of chalcogenide glasses with metal impurities shift the main bands to the high frequency region and lead to the appearance of the additional vibration bands in the low frequency spectral range [2, 4, 5]. It was demonstrated that doping of As_2Se_3 with 0.5 at. % Dy lead to appearance in the Raman spectra of a new additional band located at $\nu = 185$ cm^{-1}, which can be attributed to the formation of new structural units like $DySe/DySe_2$ [6]. In addition, the Raman spectroscopy was successfully used for investigation the photoinduced transformation and structural changes during the heat treatment in amorphous As-based thin films [4, 5]. In the present paper we report experimental results of Raman spectra of bulk and amorphous thin films of $(As_4S_3Se_3)_{1-x}$:Sn_x ($0 \le x \le 10$ at. % Sn) chalcogenide glasses. The light exposure of amorphous $(As_4S_3Se_3)_{1-x}$:Sn_x thin films shifts the main maxima of Raman spectra located at around $\nu = 236$ cm^{-1} and $\nu = 345$ cm^{-1} toward the lower energies. The experimental results are discussed in frame of the molecular structure of the investigated materials, as was demonstrated for amorphous thin films of As_2Se_3:Sn_x and As_2Se_3 doped with rare-earth ions by Modulated Differential Scanning Calorimetry (MDSC) and Mossbauer spectroscopy [7, 8].

2. Experimental results and discussion

The noncrystalline semiconductors preserve a short range order (SRO) in a range of 0.3-0.5 nm and are characterized by the existence of a correlation in the first atomic coordination sphere. In the case of dominantly covalently bounded amorphous solids, the SRO is described by local coordination polygons, e.g., pyramidal AsS_3 in As_2S_3. In many amorphous semiconductors, such as chalcogenide glasses, this order is shown at longer distances, the so-called medium range order (MRO) which extends up to a range of 0.5-1.0 nm. The XRD measurements show that the Sn impurities in the $(As_4S_3Se_3)_{1-x}$:Sn_x do not significantly change the shape of the first sharp diffraction peak (FSDP) of the X-ray diffraction patterns either; the intensity and the position of the FSDP nonmonotonically depend on the Sn concentration [9]. The intensity of the FDSP shows a nonlinear behavior with the different amounts of doping with Sn. The maximum intensity is achieved at about 6 at. % Sn in $(As_4S_3Se_3)_{1-x}$:Sn_x, while in the case of As_2Se_3:Sn_x the maximum intensity is situated at the tin concentration of about 2 at. % Sn. According to [10], when Sn is added in As_2Se_3 or As_2S_3 chalcogenide glasses, due to the tetrahedral disposal of the sp3 bonds in the chalcogens, the dopant atom implanted in the network increases the thickness of the layered configuration as revealed by a significant shift of the FSDP towards lower angles. This implantation corresponds to the introduction of the structural units of the $SnSe_2$ or SnS_2 type in the glass network, as was confirmed by the Mössbauer spectroscopy experiments [7].

The mid-IR transmission spectra of some $(As_4S_3Se_3)_{1-x}$:Sn_x bulk glasses also was investigated using a spectrophotometer PerkinElmer Spectrum 100. The mid-IR transmission spectra for the glasses under study are characterized by several well-resolved absorption bands. For vitreous As_2S_3, these bands are located at frequencies of $\nu = 5190$ cm^{-1} (S-H), $\nu = 3617$-3522 cm^{-1} (H_2O), $\nu = 2482$ cm^{-1} (S-H), $\nu = 1857$ cm^{-1} (As-H), $\nu = 1597$ cm^{-1} (H_2O), and $\nu = 1003$ cm^{-1} (As_2O_3). The characteristic absorption bands for pure As_2S_3 at $\nu = 5190$, 3617, 3522, 1857, and 1597 cm^{-1} are significantly reduced upon doping with Sn. At the same time, for the $(As_4S_3Se_3)_{0.98}$:$Sn_{0.02}$ glass, additional absorption bands appear at $\nu = 5190$, 3194, 2026, and 1493, 1500 cm^{-1} (Fig.1) [11].

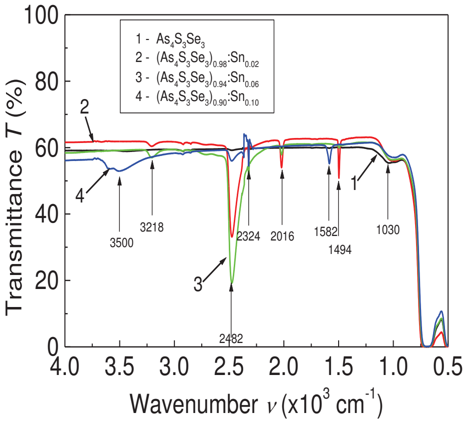

Fig.1. The transmission spectra of some bulk samples of bulk $(As_4S_3Se_3)_{1-x}$:Sn_x chalcogenide glasses.

The observed changes upon doping in the mid-IR region are most likely related to interactions of a portion of the introduced metal ion impurities with the inherent impurities of the host glass, such as hydrogen and oxygen atoms. These interactions result in the reduction of the relative intensity of bands associated with O-H, S-H, As-O, and As-H bonds in the parent glass. For the $(As_4S_3Se_3)_{1-x}$:Sn_x bulk glasses with the composition x = 0; 0.03; 0.04 no absorption bands were observed.

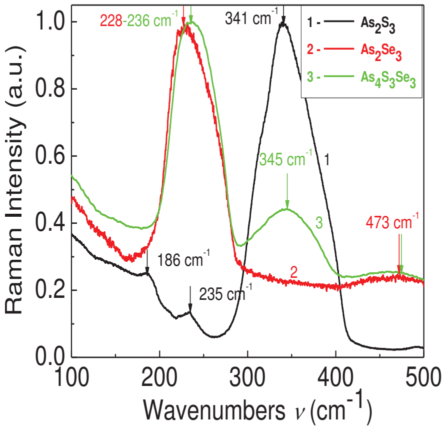

Fig.2. The Raman spectra of bulk As_2S_3 (1), As_2Se_3 (2), and $As_4S_3Se_3$ (3) chalcogenide glasses.

Raman spectroscopy of both bulk glasses and amorphous thin films of $(As_4S_3Se_3)_{1-x}$:Sn_x was performed using a Horiba LabRam 800 with an CW excitation wavelength of λ = 532 nm, in the spectral range ν = 100-2500 cm^{-1}. The light exposure of amorphous thin films was performed with halogen lamp, and the Raman spectra were measured for as-deposited and light exposed films. Fig.2 represents the Raman spectra of bulk As_2S_3 (1), As_2Se_3 (2), and $As_4S_3Se_3$ (3) chalcogenide glasses. The Raman spectra of $As_4S_3Se_3$ glasses (curve 3) consist of two broad bands located at around ν = 236 cm^{-1} and ν = 345 cm^{-1}, which corresponds to the main vibration modes of vitreous As_2Se_3 and As_2S_3 curves 1 and 2), and are attributed to the symmetric stretching vibration modes of $AsSe_{3/2}$ and $AsS_{3/2}$ pyramids, respectively [2, 5].

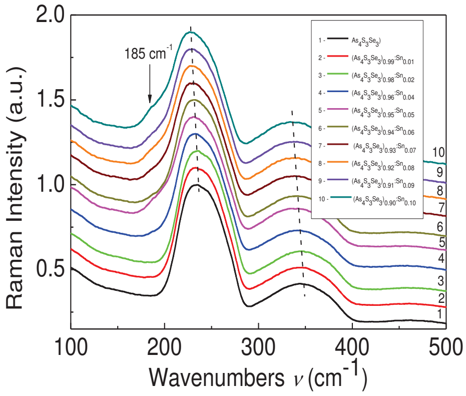

Fig.3. The Raman spectra of bulk $(As_4S_3Se_3)_{1-x}$:Sn_x chalcogenide glasses.

Tin impurities in the host glass shift the main bands situated at ν = 236 cm^{-1} and ν = 345 cm^{-1} towards the low frequency region of the spectra (Fig.3), and lead to the appearance of new vibration band located at around ν = 185 cm^{-1}, as was observed in the case of $As_{50}Se_{50}$ dope with 7.5 at. % Sn [6].

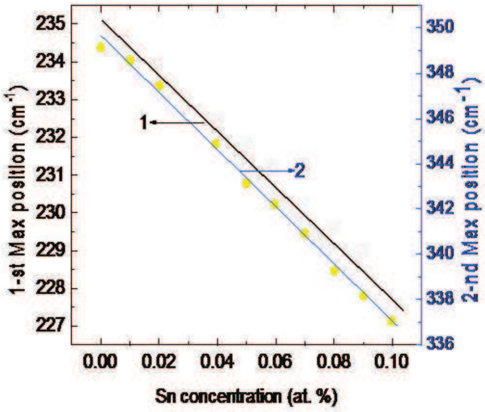

Fig.4. The dependence of the position of the 1-st peak (ν = 236 cm^{-1}, curve 1) and the 2-nd peak (ν = 345 cm^{-1}, curve 2) in the Raman spectra on the Sn concentration of bulk $(As_4S_3Se_3)_{1-x}$:Sn_x chalcogenide glasses.

The shift of the of the vibration bands situated at ν = 236 cm^{-1} and ν = 345 cm^{-1} with increasing of tin concentration up to 10.0 at. % Sn takes a values of $\Delta\nu_1$ = 7.69 cm^{-1} and $\Delta\nu_2$ = 10.71 cm^{-1}, respectively (Fig.4). At the same time the half width peak (HWP) increase ($\Delta\nu_{HWP}$ = 23.42 cm^{-1}) with increasing of Sn concentration up to x = 10.0 at. % Sn (Fig.5). The Raman spectra of amorphous $(As_4S_3Se_3)_{1-x}$:Sn_x thin films are presented in Fig. 6. From the comparison of Fig.3 and Fig.6 we can observe, that the Raman spectra of amorphous films are similar to those of bulk glasses and have the same features.

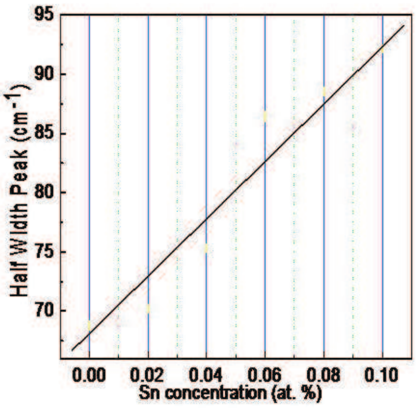

Fig.5. The dependence of the half width peak (HWP) Raman spectra (ν = 236 cm^{-1}) of bulk $(As_4S_3Se_3)_{1-x}$:Sn_x chalcogenide glasses.

Doping of amorphous $As_4S_3Se_3$:Sn_x thin films with Sn impurities shifts the vibration bands situated at ν = 236 cm^{-1} and ν = 345 cm^{-1} in the low frequency region of the spectra, similar to that was demonstrated for other chalcogenide glasses photodoped with Ag and Cu atoms [4]. This behavior is due to the formation of the normal metal-chalcogene covalent bonds which occurs by means of metal diffusion on the sites of defects of the amorphous matrix. Another explanation is the formation of new Sn-based structural units, such as $Sn(Se_{1/2})_4$ tetrahedral [2].

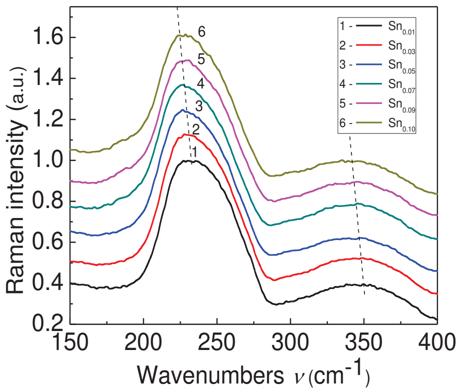

Fig.6. The Raman spectra of as-deposited amorphous $(As_4S_3Se_3)_{1-x}$:Sn_x thin films.

In the previous papers [2, 5] the Raman spectra shown that in As_2S_3 and As_2S_3 are presented structural units containing As—As bonds, —Se—Se—Se chains and Se_8 rings. Although the Raman spectra vibration bands $AsS_{3/2}$ and $AsSe_{3/2}$ are dominated, in the glasses also are included As_4S_4(As_4Se_4) and S_8(Se_8) structural units [15].

The Raman spectra of amorphous $(As_4S_3Se_3)_{1-x}$:Sn_x thin films were measured before and after light exposure with halogen lamp (λ = 400÷700 nm). As an example, in Fig.7 are presented the Raman spectra for as-deposited amorphous $(As_4S_3Se_3)_{0.93}$:$Sn_{0.07}$ thin films (curve 1), illuminated during t = 5 min (curve 2), and during t = 15 min (curve 3). The registered Raman spectra are similar to that reported for amorphous $As_{40}S_{20}Se_{20}$ thin films with light exposure [13].

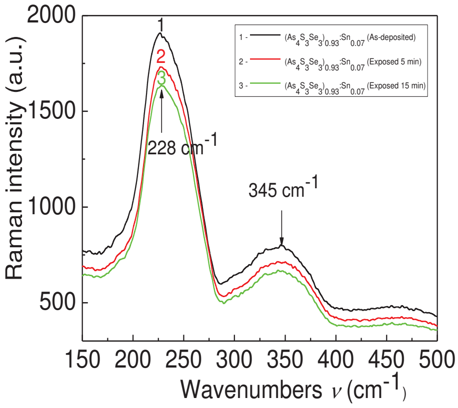

Fig.7. The Raman spectra of amorphous as-deposited $(As_4S_3Se_3)_{0.93}$:$Sn_{0.07}$ thin films (1), exposed during t = 5 min (2), and during t = 15 min (3).

The light exposure decrease the intensity of the main vibration peaks, and slightly shift it in the high frequency region. As was pointed out in [13], the Raman spectra structure of evaporated amorphous thin films differs from the glass one and the molecular structure can be presented in the form of matrix, which consists of pyramidal units $AsS_{3/2}$, $AsSe_{3/2}$ and $AsS(Se)_{2/2}$. This matrix also can contain considerable amount of $As_4S(Se)_4$ and $S(Se)_n$ fragments which contain As-S and S(Se)—S(Se) homopolar bonds. Beside that, in the structure of the amorphous $(As_4S_3Se_3)_{1-x}$:Sn_x thin films can be presented and other structural units like tetrahedral $Sn(Se_{1/2})_4$, quasi-octahedral SnSe, and clusters such as of $SnSe_2$, as was demonstrated for the amorphous As_2Se_3:Sn_x thin films from the X-Ray Diffraction, MDSC and Mössbauer spectroscopy measurements [14].

The presence of the structural units containing homopolar bonds in the structure of as-deposited amorphous As_2S_3, As_2Se_3 and $As_4S_3Se_3$ thin films can be explained by the thermal dissociation reaction during evaporation. For example of As_2S_3 this reaction can be presented as [15]:

$$(As_2S_3)_{liq} \xrightarrow{kT} (As_4S_4)_{vap} + (S_n)_{vap} \tag{1}$$

where the nonstoichiometric As_4S_4 units contain a homopolar As—As bonds. Due to fast condensation of vapor on the cold glass substrate, these structural units are frozen in the structure of as-deposited amorphous films, and they are responsible for the photosensitivity and for the photodarkening processes of these films [16]. The concentration of the homopolar bonds, which is higher in the structure of as-deposited amorphous films, is reduced by exposure to light, and the structure of the amorphous thin film becomes closer to the structure of the bulk glass, as was demonstrated in [13] for amorphous $As_{40}S_{60-x}Se_x$ thin films. After light exposure of the amorphous thin film take place the polymerization reaction:

$$As_4S_4 + S_n \xrightarrow{h\nu} As_2S_3 \tag{2}$$

This polymerization process seems to be reversed by thermal annealing, as was demonstrated for amorphous As_2S_3 [5, 17].

3. Conclusions

In this paper the results of X-ray diffraction patterns, mid-IR and Raman spectroscopy for characterization of $(As_4S_3Se_3)_{1-x}$:Sn_x glasses are presented. It was shown that Sn impurity influences the optical transmission spectra of the host glass, and shifts the main Raman spectra vibration bands in the low frequency region. The maxima situated at around $\nu = 236$ cm^{-1} and $\nu = 345$ cm^{-1} are characteristic for all investigated glass compositions and are attributed to the symmetric stretching vibration modes of $AsSe_{3/2}$ and $AsS_{3/2}$ pyramids, respectively. The light exposure of amorphous $(As_4S_3Se_3)_{1-x}$:Sn_x thin films also shifts the main maxima of Raman spectra in the high frequency region. The obtained experimental results are discussed in framework of the molecular structure model of chalcogenide glasses.

Acknowledgement

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