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Nano-sized phase inclusions in As₂S₃ glass, films and fibers based on this glass

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Abstract. In this report, the comparative analysis using Raman spectroscopy of the short-range order in amorphous As₂S₃ films deposited with different evaporation rates, volume glass and fiber based on this glass is presented. With increasing the film deposition rate, their structure becomes more non-uniform as compared to that of glass. Raman spectra excited by laser radiation with energy bigger than the width of the optical gap indicate photomodification of the structure of As₂S₃ glass and fiber based on it.

Keywords: Raman spectra; As₂S₃ films, glass and fiber; nano-sized phase inclusions.

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1. Introduction

Phase inclusions is the term that describes initially homogeneous system, in which two or more chemically or structurally different components or phases are distributed. Phase inclusions is the feature inherent to many vitreous systems that can exist in different scales from nanometers up to microns or even millimeters [1]. For practical application of glasses as optoelectronics materials, it is important to exclude or minimize phase inclusions up to the scale smaller than the operation light wavelength.

Raman spectroscopy deals with non-elastic light scattering by the substances exposed with intensive laser sources. The structure of amorphous materials is characterized by the wide distribution of bond lengths, angles between them and, respectively, different energies. Due to this, the Raman spectrum will be more "diffused" as compared to the crystalline one.

In the present report, presented is a comparative analysis of the short order in amorphous As₂S₃ (a-As₂S₃) films produced with different evaporation rates, volume glass and fiber on its base.

2. Experiment

Raman spectra of the films were excited by laser radiation with 632.8 nm wavelength, Raman spectra of the glasses and fibers by emission lines 785 and 488 nm (when using the first wavelength, the beam was directed into the fiber, in the second case – onto the surface).

Spectra were registered using the micro-Raman RENISHAW SYSTEM 1000 with the CCD (Charge Coupling Device) camera. The power of used laser radiation was limited by filters in order to avoid photoinduced transformations.

3. Results and discussion

At low deposition rates $V < 20 \text{ \AA/s}$, the difference of Raman spectra of a-As₂S₃ films and g-As₂S₃ (Fig. 2, curves 2 and 3) is in transformation of the shape of film spectrum and appearance of the intensive bands near 190 and 230 cm⁻¹, which are characteristic for vibrations of As-As bonds in As₂S_{4/2} structural units (s.u.). But the band near 230 cm⁻¹ is revealed also in the Raman spectrum of a-As (Fig. 1), that is, it is characteristic for the As-As bonds vibrations in As_{3/3} s.u. Consequently, unambiguous determination of the s.u. using the only Raman data is difficult. The growth of the film deposition rate results in appearance and growth of the intensity of the band peaking at 270 cm⁻¹, which is characteristic for As₄S₃ s.u. vibrations (Fig. 2).

Our structural interpretation of Raman spectra of As₂S₃ films has shown that with the growth of the deposition rate the film structure becomes more heterogeneous than that for glass, besides AsS_{3/2} pyramids, the As-As bonds in As₄S₄, As₄S₃, As_{3/3} "molecules" can be present.

Despite undertaken by us measures on the decrease of the share of nano-sized phase inclusions in g-As₂S₃ (change of the melt temperature from which the cooling

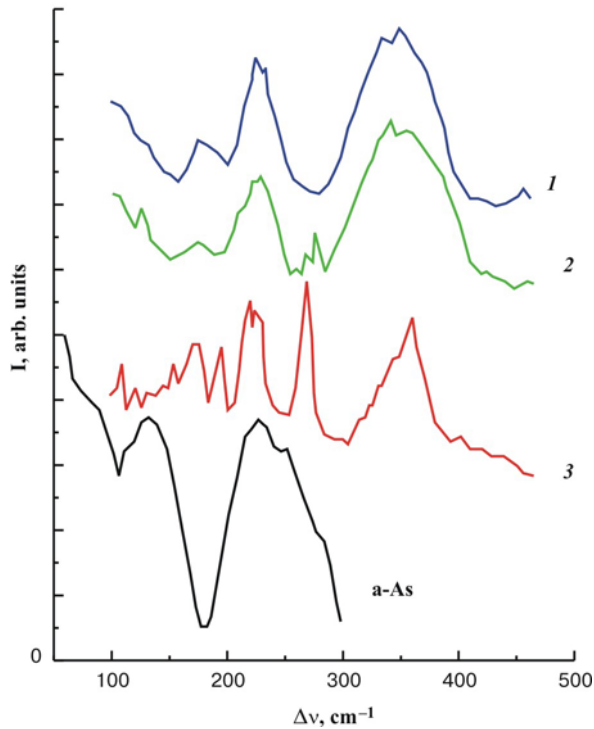


Fig. 1. Raman spectra of As_2S_3 films (1 – deposition rate $V < 20 \text{ \AA/s}$, 2 – $V = 20 \text{ \AA/s}$, 3 – $V > 20 \text{ \AA/s}$) and amorphous As (4). Spectra are vertically shifted for convenience.

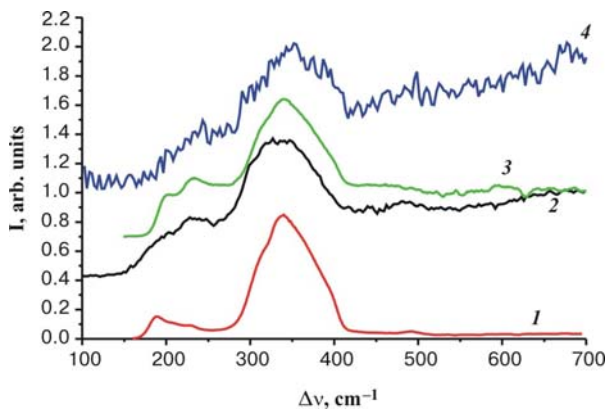


Fig. 2. Raman spectra: 1 – As_2S_3 glass ($\lambda = 785 \text{ nm}$), 2 – As_2S_3 glass ($\lambda = 488 \text{ nm}$), 3 – As_2S_3 fiber ($\lambda = 785 \text{ nm}$), 4 – As_2S_3 fiber ($\lambda = 488 \text{ nm}$).

started, cooling rate), in Raman spectra bands near 189 , 230 , and 360 cm^{-1} are always present, which can testify on the presence of $\text{As}_2\text{S}_{4/2}$ s.u. in the glass.

The Raman spectrum of the core of As_2S_3 fiber measured using 785 nm laser excitation wavelength has more intensive band near 230 cm^{-1} than the similar Raman band of the glass measured using the same excitation wavelength. In the Raman spectrum of the fiber core (Fig. 2) the peak near 190 cm^{-1} almost disappears, that is, $\text{As}_{2/3}$ s.u. are dominant in the structure of the fiber surface and not the $\text{As}_2\text{S}_{4/2}$ ones as

in the case of the glass. The Raman spectrum of the fiber in the region $\nu > 400 \text{ cm}^{-1}$ (Fig. 2, curves 3, 4) has more intensive bands than those of the glass (Fig. 2, curves 1, 2), which points to the enrichment of the fiber surface by sulfur.

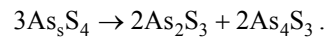
If chalcogenides are exposed by a laser radiation from the region of intrinsic absorption edge, incident photons are absorbed by the glass. That is, at exposure with photons of the energy bigger than the bandgap width (bandgap width of As_2S_3 , $E_g \sim 2.4 \text{ eV}$), the activation of the photoinduced phenomena on the surface and in subsurface layers occurs [2].

Let us analyze the spectra of As_2S_3 glasses and fibers excited by the laser emission of a bigger energy (shorter light wavelength).

It can be seen from Fig. 2 that, at excitation of Raman spectra of As_2S_3 glasses with the energy bigger than the bandgap width ($\lambda = 488 \text{ nm}$, $E = 2.54 \text{ eV}$), widening all the bands is observed, the intensity increase of the band near 230 cm^{-1} and Raman bands in the region $\nu > 400 \text{ cm}^{-1}$. The intensity growth of the band near 230 cm^{-1} with a simultaneous decrease of the maximum near 190 cm^{-1} can testify on the presence of free arsenic clusters as a result of the photodecomposition reaction [3]:



Besides that, under the influence of laser radiation the following reaction is possible [4]:



The presence of the kinks in the region $400 \dots 500 \text{ cm}^{-1}$ similar to those in the spectrum of As_2S_3 glass as well as in the spectrum of fibers on its base testifies on the sulfur formation in various forms in the matrix of the glass structure. It is necessary to note that the penetration depth of the laser radiation with $E = 2.54 \text{ eV}$ is about $\sim 1 \mu\text{m}$, that is photomodification of the structure proceeds at the surface.

4. Conclusions

1. Our structural interpretation of the Raman spectra of As_2S_3 films (Fig. 2) has shown that with the increase of the deposition rate the film structure is more heterogeneous than that of the glass. Besides $\text{AsS}_{3/2}$ pyramids, in the film As-As bonds in As_4S_4 , As_4S_3 , $\text{As}_{3/3}$ "molecules" can be present.
2. The Raman spectrum of the core surface of As_2S_3 fiber in comparison to the structure of As_2S_3 glass testifies on the presence of bigger $\text{As}_{3/3}$ concentration and not the $\text{As}_2\text{S}_{4/2}$ s.u. Raman spectra excited by the laser with the photon energy higher than the bandgap width, testify on the photomodification of the surface of As_2S_3 glass and fiber made on its base.

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