Raman scattering of Ge-As-Se thin films

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***Abstract* — Raman and infrared spectroscopy are efficient methods for obtaining information on the local structure of the disordered material, especially when the composition is varied. In particular, Micro-Raman spectroscopy have been used for study of the ternary glass system $Ge_xAs_xSe_{1-2x}$, for which different composition in dependence of it mean coordination number Z exists in different phases - *floppy*, *intermediate* and *stressed rigid*. In this paper we report experimental results and analysis of Micro-Raman spectra for both thermally as-deposited and laser irradiated amorphous $Ge_xAs_xSe_{1-2x}$ (x=0.07; 0.09 and 0.14, Z=2.21; 2.27 and 2.42, respectively) thin films, of which glassy system situated in the region of *floppy* and *intermediate* phases. It was shown that for all investigated samples the measured Micro-Raman spectra consists from three vibrational modes located around ν=193 cm^{-1}, ν=255 cm^{-1} and ν=475 cm^{-1}. It was shown that position and intensity of these vibrational bands slightly depend on the composition and method of preparation. It was established that for $Ge_{0.14}As_{0.14}Se_{0.72}$ composition with the mean coordination number Z=2.42, situated in the region of *intermediate phase*, the probability of existence of the tetragonal (pyramids $As(Se_{1/2})_3$ and tetrahedral structural units $Ge(Se_{1/2})_4$ is the same. For all samples of the glass composition $Ge_{0.14}As_{0.14}Se_{0.72}$ the ratio of the intensity of both main vibration peaks centered around ν=193 cm^{-1} and ν=255 cm^{-1} remain unchanged.**

***Keywords* — amorphous thin films, Raman spectra, vibration modes, light irradiation.**

I. INTRODUCION

Amorphous films of $Ge_xAs_xSe_{1-2x}$ represent a great interests, both for investigation of physical phenomena and its dependence of composition, as well as for practical application. It is well know that Ge-As-Se glassy and amorphous films exhibit enough high chemical stability, good transmission in the IR region, high refractive index, excellent linear and non-linear properties, low phonon energy, and photo-induced effects etc. [1-4]. Recently Ge-As-Se chalcogenide glasses have found its application as core materials for high-efficiency fiber amplifiers, Raman-parametric laser, wavelength converter and temperature sensors [5-7]. Other applications include its use as registration media of optical information due to their various photostructural transformations under the action of laser irradiation, X-ray, e-beam, γ-radiation, etc. It was established that the physical properties of such covalently-bonded glasses are determined by the mean coordination number Z (average number of covalent bonds per atom) [8]. Recently it was established, that in the disordered network of glassy system $Ge_xAs_xSe_{1-2x}$ exists three distinct phases: *floppy*, *intermediate* and *stressed rigid*, and the dependence of physical properties on average coordination number Z [9-11].

Introduction of the IV group metals of the Periodic Table (Sn or Ge) in arsenic selenide base glass, beside the existence of pyramidal structural units ($AsSe_{3/2}$), and leads to formation of new tetrahedral structural units $(GeSe_{1/2})_4$ and Sn(Se1/2)4, the concentration which increases with the increasing of metals content in the host chalcogenide material. Metallic bonds formation and phase separation in the investigated $Ge_xAs_xSe_{1-2x}$ glasses can explain some its physical and chemical properties [8].

Raman scattering was also successfully used for investigation the photo-induced transformation and structural changes during the heat treatment in amorphous As-based thin films [12-14].

In the present paper we report the experimental results of Micro-Raman measurements of thermally deposited amorphous $Ge_xAs_xSe_{1-2x}$ (x=0.07, 0.09 and 0.14, Z=2.21; 2.27 and 2.42) thin films. For these range compositions are identified two phases: *floppy* and *intermediate*. The influence of light exposure on Micro-Raman spectra of amorphous $Ge_xAs_xSe_{1-2x}$ thin films also was investigated.

II. EXPERIMENTAL

The bulk chalcogenide glasses $Ge_xAs_xSe_{1-2x}$ (x=0.07; 0.09 and 0.14) were synthesized from the elements of *6N* purity (Ge, As, Se) by conventional melt quenching method. The starting components were mixed in quartz ampoules and then evacuated to pressure of P~10^{-5} Torr, sealed and heated to temperature T=900 ºC at the rate of 1 ºC/min. The quartz tubes were held at this temperature for 48 hours for the homogenization and then quenched at the room temperature. The thin film samples of thickness L~2 μm were prepared by flash thermal evaporation in vacuum (P=10^{-5} Torr) of the synthesized initial glasses onto glass substrates held at T_{substr}=100 ºC. The surfaces of chalcogenide (CG) thin films were also optically examined using an Axio Observer Inverted Microscope (Zeiss). All images were obtained in reflection mode at different magnifications (5x, 10x, 20x). The Raman studies of the CG samples were carried out at room temperature by Confocal Micro - Raman Spectroscopy, using a LabRam HR800 system. All Raman spectra were generated by exposing the specimens during 300 s to a 0.03 mW, 532 nm wavelength green excitation laser and dispersing the emitted signal onto the CCD detector using a 600 lines/mm grating. The spectral resolution is around 0.6 cm^{-1}.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the Micro-Raman spectra of $Ge_{0.07}As_{0.07}Se_{0.86}$ samples with mean coordination number Z=2.21, prepared in the glass configuration (powder), and amorphous layers as-deposited and after laser irradiation. This composition with low concentration of Ge corresponds to the floppy phase region [9]. The obtained Micro-Raman spectra, for both glasses powder and amorphous layers, consist of three distinct bands centered around ν=193 cm^{-1}, ν=255 cm^{-1} and ν=475 cm^{-1}. The peak centered around ν=193 cm^{-1} is interpreted as existence of $Ge(Se_{1/2})_4$ structural units. The presence of the Raman peak around ν=255 cm^{-1} is due to the bond-stretching vibration of the disordered Se_8 chains and rings. A smaller a broad band located at higher frequency (ν=475 cm^{-1}) is presumed due to less associated clusters of As-Se bands and Se-Se chains.

It can be seen from Micro-Raman spectra (Fig.1) of $Ge_{0.07}As_{0.07}Se_{0.86}$ samples (powder, as-deposited layer and laser irradiated layer) the width and intensity of the main bands are slightly changed. For this composition the vibration bands situated at ν=193 cm^{-1} and ν=255 cm^{-1} slightly are shifted toward higher wavenumbers (the shift is about 2÷3 cm^{-1}) due to the shortening of Se_8 chains. Beside that the ratio of the peaks intensity situated at ν=193 cm-1 and at ν=255 cm-1 slightly increase from 0.34 for the powder samples up to 0.84 for the as-deposited amorphous films. This suggest that the number of tetrahedral bonds like $Ge(Se_{1/2})_4$ in amorphous films also increases. The same ratio for the laser irradiated layer with respect to the as-deposited layer also increases but is non-significant, what indicate that as a result of photostructural transformations in the investigated amorphous material some Se bonds are break and the Ge-like bonds increase [8, 15].

In the Fig.2 are illustrated the Micro-Raman spectra of $Ge_xAs_xSe_{1-2x}$ layers with different chemical composition (x=0.07, 0.09 and 0.14). It was observed that position of the vibrational mode situated around ν=193 cm^{-1} practically doesn't depend on film composition.

At the same time the peaks intensity ratio situated around ν=193 cm^{-1} and around ν=255 cm^{-1}, increase with increasing of the Ge concentration in the films, from 0.75 for x=0.07 up to 0.84 for x=0.14.

Figures 3 and 4 represent the Micro-Raman spectra of $Ge_xAs_xSe_{1-2x}$ compositions (x=0.09 and 0.14), powder glass (a), as-deposited amorphous layer (b) and laser irradiated layer (c). For the glass samples (powder) and amorphous layers presented in the Fig.3 the position of vibration modes centered around ν=193 cm^{-1} and ν=255 cm^{-1} practically are unchanged. As in the case of the glass composition $Ge_{0.07}As_{0.07}Se_{0.86}$, for the $Ge_{0.09}As_{0.09}Se_{0.82}$ thin films, the ratio of the intensity of the main vibrational bands located around ν=193 cm^{-1} and ν=255 cm^{-1}, increase, in comparison with a bulk glass.

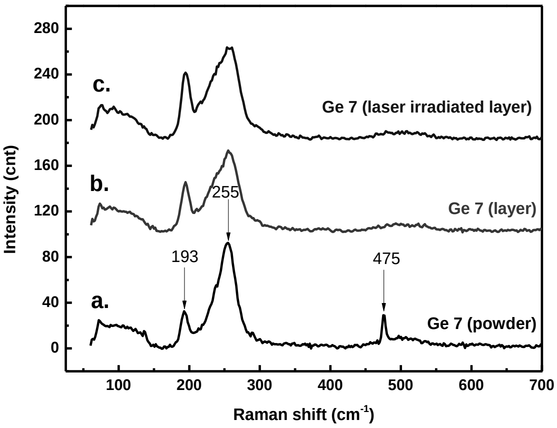

Fig.1. Micro-Raman spectra of $Ge_{0.07}As_{0.07}Se_{0.86}$ samples; powder (a), as-deposited layer (b), laser irradiated layer (c).

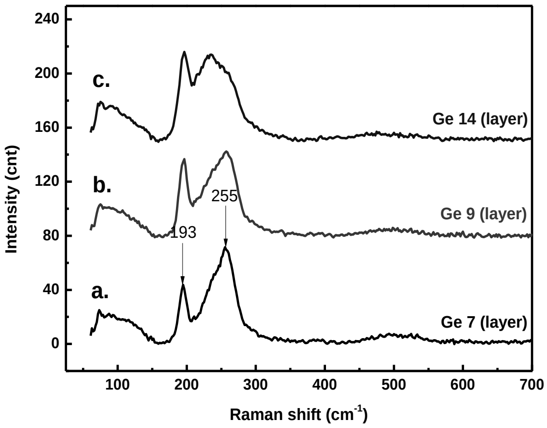

Fig.2. Micro-Raman spectra of $Ge_xAs_xSe_{1-2x}$ layers with different chemical composition: $Ge_{0.07}As_{0.07}Se_{0.86}$ (a), $Ge_{0.09}As_{0.09}Se_{0.82}$ (b), $Ge_{0.14}As_{0.14}Se_{0.72}$.

For the $Ge_{0.14}As_{0.14}Se_{0.72}$ glass composition, the peak situated around ν=193 cm^{-1} doesn't change its position after laser irradiation, but the peak situated at ν=255 cm^{-1} for the as-deposited and laser irradiated layers shifts toward lower wavenumbers (the shift is about 20 cm^{-1}). The ratio of the intensities of the both peaks remains unchanged. That means that for the $Ge_{0.14}As_{0.14}Se_{0.72}$ composition with the mean coordination number Z=2.42 and situated in the *intermediate phase* region, the probability of existence of the tetragonal structural units (pyramids $As(Se_{1/2})_3$) and tetrahedral structural units ($Ge(Se_{1/2})_4$) is the same.

The deconvolution method with Voigt profile was used to analyse the Raman spectra of unexposed and laser exposed Ge-As-Se thin films, and as an example is shown for $Ge_{0.09}As_{0.09}Se_{0.82}$ thin films in Fig.5 and Fig.6, respectively. The wavenumber position and the intensity of the vibrational mode situated around ν=194 cm^{-1}, which is responsible for Ge bonds ($Ge(Se_{1/2})_4$ tetrahedral structural units) remain unchanged in result of light exposure. At the same time, after the deconvolution process instead of 1 vibrational band siluated around ν=255 cm^{-1}, two vibrational modes appear, situated around ν=234 cm^{-1} and ν=260 cm^{-1} respectively. These two vibration modes correspond to As(Se$_{1/2}$)$_3$ pyramids [9] and the bond-stretching vibration of the disordered Se chains and rings. The vibrational mode situated around ν=234 cm^{-1} and ν=194 cm^{-1} shifts toward high frequencies after laser irradiation of the thin films while other one remain unchanged. These features indicate that the As-Se bonds are responsible for the photostructural transformation in amorphous $Ge_xAs_xSe_{1-2x}$ thin films.

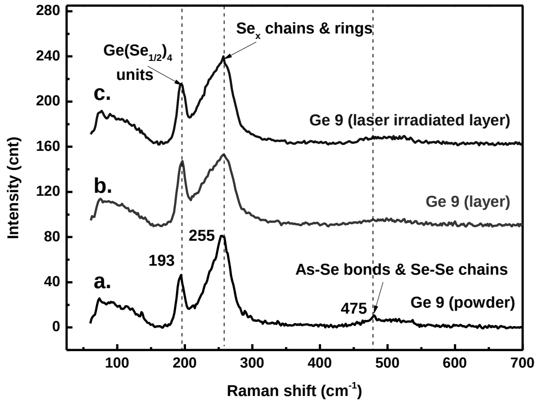

Fig.3. Micro-Raman spectra of $Ge_{0.09}As_{0.09}Se_{0.82}$ layers; powder (a), as-deposited layer (b), laser irradiated layer (c).

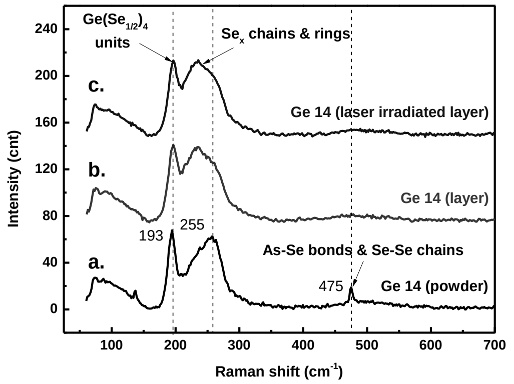

Fig.4. Micro-Raman spectra of $Ge_{0.14}As_{0.14}Se_{0.72}$ layers; powder (a), as-deposited layer (b), laser irradiated layer (c).

Figure 7 shows the compositional dependence of the Micro-Raman intensity of the peak located around ν=193 cm^{-1} for the un-exposed (1) and laser irradiated $Ge_xAs_xSe_{1-2x}$ layers (2).

It was observed that with increasing of Ge contents in $Ge_xAs_xSe_{1-2x}$ layers the intensity of these peak also increases. Some peculiarities occur for the composition with x=0.09, for which the tendency of metal-metal bonds formation is observed [8].

Figure 8 represents the ratio dependence *R* of the peaks intensity situated around ν=193 cm^{-1} and ν=255 cm^{-1} for the powder samples (1), un-exposed (2) and laser irradiated (3) in the $Ge_xAs_xSe_{1-2x}$ glass composition. Increasing of this ratio suggest that the concentration of the separate tetrahedral clusters also increase with increasing of Ge content in the alloys. According to experiments using a high-resolution X-ray photoelectron spectroscopy, the network of the $Ge_xAs_xSe_{1-2x}$ glasses consists from separate $GeSe_{4/2}$ tetrahedra and $AsSe_{3/2}$ pyramids interconnected through Se chains, and are formed from structural fragments based on Ge-As, As-As and Ge-Ge bonds.

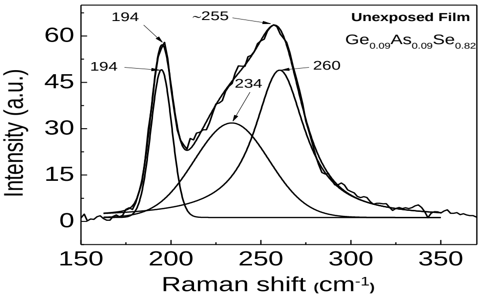

Fig.5. Deconvolution of the Micro-Raman spectra of unexposed amorphous $Ge_{0.09}As_{0.09}Se_{0.82}$ thin films.

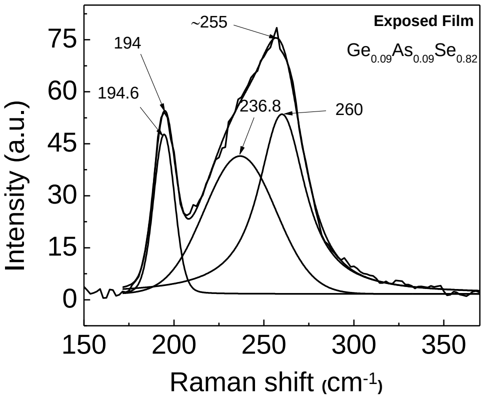

Fig.6. Deconvolution of the Micro-Raman spectra of laser exposed amorphous $Ge_{0.09}As_{0.09}Se_{0.82}$ thin films.

IV. SUMMARY

Chalcogenide $Ge_xAs_xSe_{1-2x}$ (x=0.07; 0.09 and 0.14, *Z*=2.21; 2.27 and 2.42) glasses, powders, as-deposited and laser irradiated thin films, situated in the *floppy* and *intermediate* phases region were investigated by Micro-Raman spectroscopy. It was shown that for all investigated samples the Micro-Raman spectra consists from two main vibration bands situated around ν=193 cm^{-1}, ν=255 cm^{-1} and ν=475 cm^{-1}. It was observed that the position of these vibration bands slightly depends on the composition and on the type of studied material (powder or thin film). Light irradiation of the $Ge_{0.07}As_{0.07}Se_{0.86}$ layer whose composition corresponds to the regime with *floppy* phase, leads to increasing of Ge-like bonds. For the composition $Ge_{0.14}As_{0.14}Se_{0.72}$ with the mean coordination number *Z*=2.42 and which corresponds to the region of *intermediate* phase, the probability of existence of the tetragonal structural units (pyramids As(Se$_{1/2}$)$_3$) and tetrahedral structural units (Ge(Se$_{1/2}$)$_4$) is the same. For all type of samples of the glass composition $Ge_{0.14}As_{0.14}Se_{0.72}$ the ratio of the intensity of both main vibration bands situated around ν=193 cm^{-1} and ν=255 cm^{-1} remain unchanged. The experimental results from the Micro-Raman spectra showed that the As-Se bonds are mainly responsible for the photostructural transformation in amorphous $Ge_xAs_xSe_{1-2x}$ thin films under laser exposure.

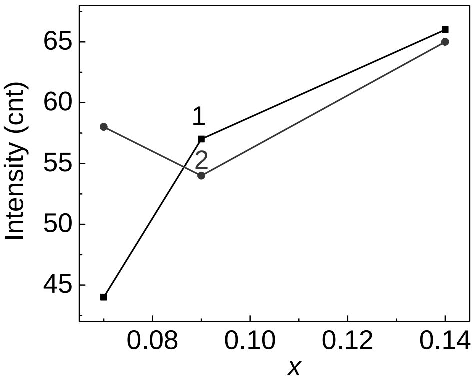

Fig.7. Compositional dependence of the Micro-Raman intensity of the peak located at ν=193 cm^{-1} for the un-exposed (1) and laser irradiated (2) $Ge_xAs_xSe_{1-2x}$ layers.

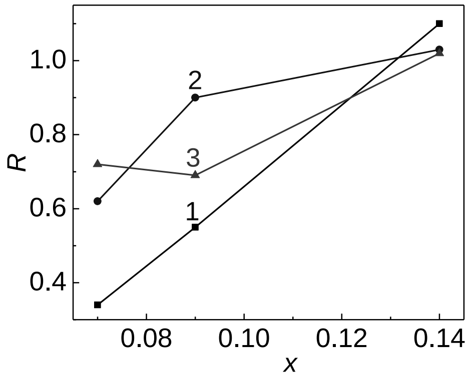

Fig.8. Dependence of the ratio R of the intensities of the peaks situated at ν=193 cm^{-1} and at ν=255 cm^{-1} for the powder samples (1), un-exposed (2) and laser irradiated (3) in the $Ge_xAs_xSe_{1-2x}$ glass composition.

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