Optical properties and structure of As-Ge-Se thin films

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Abstract. Thin chalcogenide films with compositions $As_{10}Ge_{22.5}Se_{67.5}$ and $As_{12}Ge_{33}Se_{55}$ have been investigated. Optical constants and thicknesses of these films were obtained from transmission spectra. Structure of initial bulk glasses and films were investigated by Raman spectroscopy. Both films are estimated to have high values of the nonlinear refractive index.

Keywords: chalcogenide films, optical properties, nonlinearity, Raman spectra.

1. Introduction

Chalcogenide glassy semiconductors (ChGS) are attracting attention of many researches since the discovery of their semiconductor properties in the 1950s. This is due to their unique properties such as transparency in infrared region of spectrum, high stability and a number of photoinduced phenomena (photodarkening, photobleaching, photocrystallization, etc.). Recently, high attention has been paid to the nonlinear optical properties of ChGS. Measurements of nonlinear refractive index have shown that its value can range from 100 to 1000 times of that in silica glass. High nonlinear refractive index combined with moderate to low nonlinear absorption can be exploited in all optical signal processing devices to enhance performances of telecommunication systems. ChGS are very suitable for these kinds of applications, because they are compatible with well established silica-on-silicon and fiber drawing technologies. The nature of glassy state provides an opportunity to adjust the composition and therefore, to tune smoothly the properties of material. Photoinduced phenomena allow the local modification of the material properties by the exposure to suitable radiation which can be utilized in writing waveguide channels, diffraction gratings and so forth.

Quite complicated experimental techniques are exploited for determination of nonlinear refractive index. To avoid these difficulties several semiempirical relations have been proposed in literature to estimate the nonlinear refractive index or third order nonlinear susceptibility from other known parameters such as the linear refractive index, first order susceptibility, bandgap energy, etc.

The most simple of these relations is based on using the generalized Miller's rule [1]. According to this rule, third order nonlinear susceptibility can be estimated as

$$\chi^{(3)} \cong A\left(\chi^{(1)}\right)^4, \qquad (1)$$

where A stands for a constant, the value of which for chalcogenides appears to be $A = 1.7 \cdot 10^{-10}$ when $\chi^{(3)}$ value are obtained in esu units.

Authors of [1] also derived another formula that relates nonlinear refractive index to the bandgap of material:

$$n_2 \approx B / E_g^4, \qquad (2)$$

where $B = 1.26 \cdot 10^{-9}$ esu·eV^4.

Boling et al. [2] have derived several relations, the simplest of which is:

$$n_2(10^{-13}\text{esu}) \approx 391(n_d - 1)/\nu_d^{5/4}, \qquad (3)$$

where n_d stands for the refractive index at the d-line ($\lambda = 588$ nm) and ν_d stands for the Abbe number. This relation contains only these two linear macroscopic parameters, which can be easily evaluated. Accordingly, this formula has been frequently utilized for estimations

of n_2. It provides a good approximation for small n_d glasses with $n_d \leq 1.7$ [3]. For high n_d glasses, Lines [4] has proposed a relation that takes the atomic distance into consideration, too.

Since all the above mentioned formulas do not contain the wavelength, they cannot predict the dispersion dependence of nonlinear refraction, and all the obtained nonlinear parameters may be regarded as long-wavelength limit values.

Recently, Sanghera et al. [5] proposed to relate nonlinearity to the normalized bandgap that is a measure of how far the pump is from the band edge via the classical anharmonic oscillator model:

$$\chi^{(3)} \approx \frac{Ne^4}{3d^2m^3} \frac{1}{E_g^6}\left[1-\left(\frac{h\nu}{E_g}\right)^2\right]^{-4}, \qquad (4)$$

where $h\nu$ is the incident photon energy, N, d and m are constants (material properties), E_g is the bandgap. Values of n_2 were measured independently for silica glasses, some oxides and chalcogenides and plotted in the form of function

$$n_2 = f\left(\frac{1}{E_g^6}\left[1-\left(\frac{h\nu}{E_g}\right)\right]^{-4}\right) \qquad (5)$$

representing the results obtained by authors of the work as well as literature data at two wavelengths: 1250 and 1550 nm. All these values were fitted well by a straight line indicating the usability of Sanghera´s method.

Measurements of nonlinear refraction of different ChGS have shown that selenide glasses poses one of the highest values of n_2 among other chalcogenides. This is usually attributed to the high polarizability of Se atoms. Therefore, in this paper we studied Se-based chalcogenide glasses in the ternary As-Ge-Se system.

2. Experimental

In this work, we have examined thin chalcogenide films of two compositions: $As_{10}Ge_{22.5}Se_{67.5}$ and $As_{12}Ge_{33}Se_{55}$.

Initial bulk glasses of the mentioned compositions were prepared by direct synthesis in evacuated silica ampoules. After the synthesis, ampoules were water-quenched. Thin films were obtained by thermal vacuum evaporation onto the glass substrate at room temperature.

Optical transmission spectra of these films were measured in the 0.4–2.5 μm range. Optical constants, optical bandgap, E_g, refractive index in the longwave limit, n_0, and thicknesses of these films were determined from transmission spectra using the method proposed by Swanepoel [6].

Raman spectra of initial bulk glasses and thin films were investigated using IR Fourier spectrophotometer Bruker IFS55 Equinox with FRA-106 attachment. Nd-YAG laser operating at the wavelength 1.064 μm was used as a pumping source.

3. Results and discussion

Fig. 1 shows the spectral dependence of refractive index of $As_{12}Ge_{33}Se_{55}$ thin film obtained by Swanepoel's method [6] from transmission spectrum. Solid line shows fitting of the dependence by the function:

$$n(\lambda) = \frac{a}{\lambda^2} + c. \qquad (6)$$

In Fig. 2, the energy dependence of $(\alpha E)^{\frac{1}{2}}$ parameter is plotted. Linear range in the region of high photon energies corresponds to the Tauc law that was used to determine optical bandgap, E_g. Its value is given by the point where this line intersects with abscissa (see Fig. 2).

Optical properties and thicknesses of the films obtained from transmission spectra are listed in Table, where E_g is the optical bandgap and n_0 is refractive index in the longwave limit.

Raman spectra of initial bulk glasses $As_{10}Ge_{22.5}Se_{67.5}$ and $As_{12}Ge_{33}Se_{55}$ are shown in Figs 3a and 3b, respectively. The main band in spectra of both glasses located near 200 cm^{-1} is a characteristic band of As-Ge-Se glasses. In the case of $As_{12}Ge_{33}Se_{55}$ glass it is centered at 192 cm^{-1} and contains two shoulders at 178 and 215 cm^{-1}. The mode at 216 cm^{-1} is also present in the $As_{10}Ge_{22.5}Se_{67.5}$ as a distinguished peak. In both glasses, there is a broad band near 250 cm^{-1} that has two maxima located at 241 and 254 cm^{-1} in the case of $As_{10}Ge_{22.5}Se_{67.5}$ glass and at 240 and 253 cm^{-1} in the case of $As_{12}Ge_{33}Se_{55}$ glass. In the low frequency region of both spectra, there are maxima near 80, 105, and 140 cm^{-1} that are more pronounced in the case of $As_{12}Ge_{33}Se_{55}$ glass.

In Fig. 4, Raman spectrum of $As_{10}Ge_{22.5}Se_{67.5}$ thin film is presented. As can be seen, it is very similar to the spectrum of corresponding bulk glass (Fig. 3a). The main difference between them lies in comparable intensities of the Raman modes. The modes near 145, 215, 240 and 250 cm^{-1} have larger intensity (in relation to the main band) in the spectrum of the film.
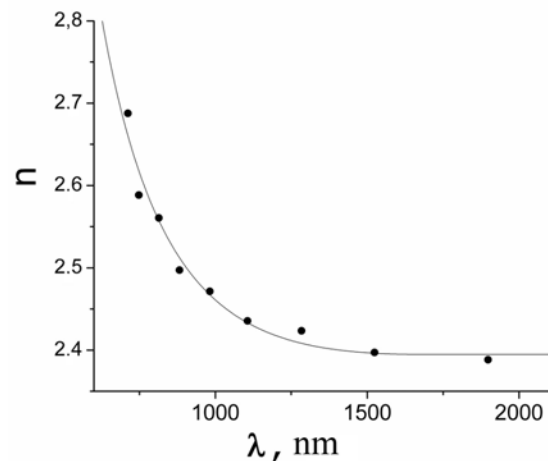

Fig. 1. Spectral dependence of the refractive index of $As_{12}Ge_{33}Se_{55}$ thin film.

Table. Films' parameters obtained from transmission spectra.

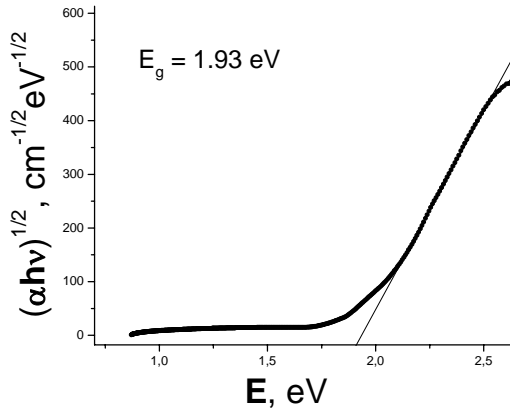| Composition	Film thickness, nm	E_g, eV	n_0
$As_{12}Ge_{33}Se_{55}$	788	1.67	2.34
$As_{10}Ge_{22.5}Se_{67.5}$	1070	1.93	2.28

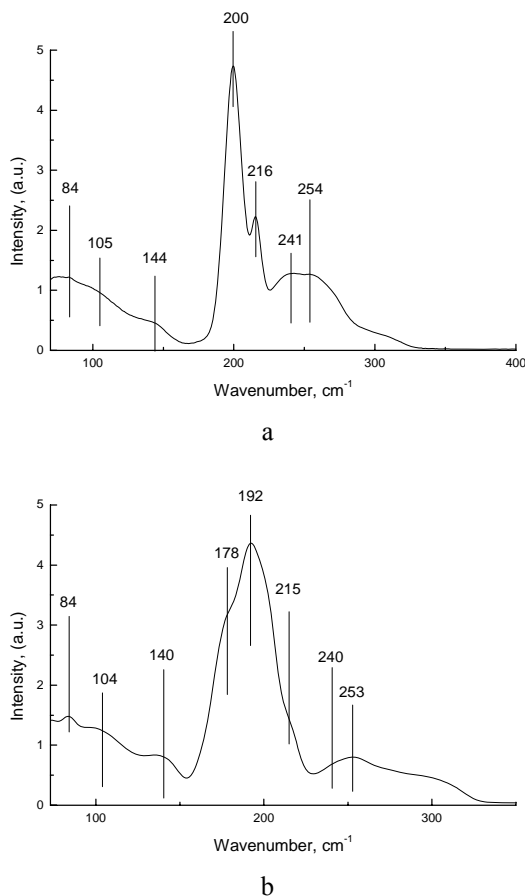**Fig. 2.** Tauc plot for $As_{10}Ge_{22.5}Se_{67.5}$ film.

a

b

Fig. 3. Raman spectra of initial bulk glasses $As_{10}Ge_{22.5}Se_{67.5}$ (a) and $As_{12}Ge_{33}Se_{55}$ (b).
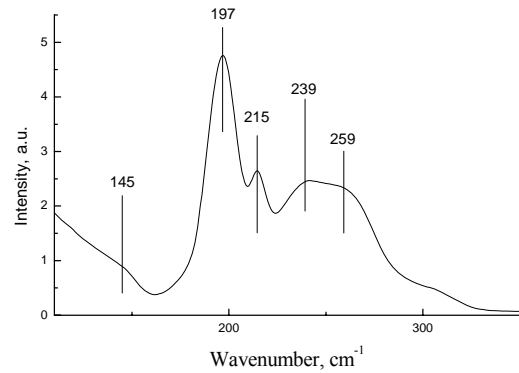

Fig. 4. Raman spectrum of $As_{10}Ge_{22.5}Se_{67.5}$ thin film.

The main band near 200 cm^{-1} and the mode at 215 cm^{-1} corresponds to the vibrations in corner-shared and edge-shared $Ge(Se_{1/2})_4$ tetrahedra [7], respectively, in both glasses. However, in the case of $As_{12}Ge_{33}Se_{55}$ glass, this band obviously possesses more complicated shape. The most distinguishable difference is the feature near 178 cm^{-1}. The latter can be ascribed to the presence of Ge-Ge bonds that are located in the $Ge_2(Se_{1/2})_6$ ethane-like structural units [7]. These structural units appear to be demixed from the network of the glass and form separate nanophase inclusions in the overall glass backbone [8]. Since the ethane-like phase has two Raman active modes located at 178 and 202 cm^{-1} [9], we can see that the main band of the spectrum of $As_{12}Ge_{33}Se_{55}$ glass is the superposition of these bands of corner-shared and edge-shared $Ge(Se_{1/2})_4$ tetrahedra and two bands of $Ge_2(Se_{1/2})_6$ ethane-like nanophase. The mentioned nanophase segregates from the backbone of the glass to accommodate Se deficiency in the $As_{12}Ge_{33}Se_{55}$ glass.

Three lower frequency bands near 80, 105, and 140 cm^{-1} along with the bands near 240 and 253 cm^{-1} represent vibration modes of amorphous selenium [10]. The bands at 80, 112 and 250 cm^{-1} are characteristic of the Se_8 rings and their fragments with 5 and 6 atoms. The bands at 140 and 240 cm^{-1} are ascribed to the vibrations in Se_n polymeric chains. The broad band near 250 cm^{-1} also contains the overlapping contribution from the vibrations in $As(Se_{1/2})_3$ pyramidal units that are parts of the glass network.

The increase of the relative intensities of bands near 145, 240 and 250 cm^{-1} in the spectrum of $As_{10}Ge_{22.5}Se_{67.5}$ thin film can be attributed to the higher concentration of Se molecular units and/or polymeric chains. The mode at 215 cm^{-1} is increased due to augmentation of the number of edge-shared $Ge(Se_{1/2})_4$ tetrahedral units, which is necessary as the total amount of Se in this material remains the same as in the corresponding bulk glass.
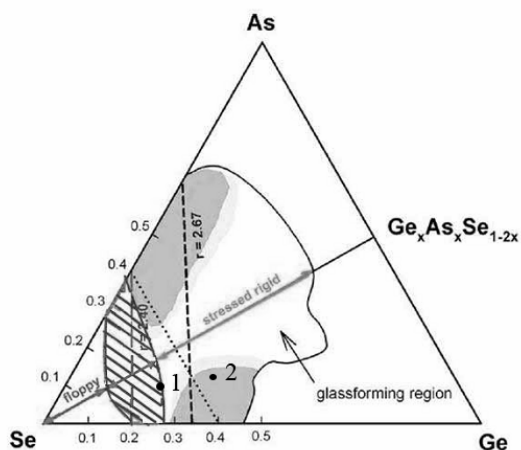
Fig. 5. Phase diagram of As-Ge-Se system [11]. The intermediate phase is shown by the hashed region between the floppy and stressed rigid phases. Nanoscale phase-separated alloys are shown by grey shading. Compositions under investigation are marked with the numbers: 1 for $As_{10}Ge_{22.5}Se_{67.5}$, and 2 for $As_{12}Ge_{33}Se_{55}$.

The phase diagram of As-Ge-Se system is presented in Fig. 5 [11]. According to the structure classification proposed by Phillips et al. [11], there exist three regions: (1) floppy phase, (2) intermediate phase (hashed region in Fig. 5), and (3) stressed-rigid phase. Compositions under investigation are shown in Fig. 5 as spots marked by numbers: 1 for $As_{10}Ge_{22.5}Se_{67.5}$, and 2 for $As_{12}Ge_{33}Se_{55}$. In the binary As-Se and Ge-Se systems, stressed rigid glasses are nanoscale phase-separated. However, the investigations of the ternary glasses $As_xGe_xSe_{1-2x}$ containing equal concentrations of As and Ge have shown that these glasses appear to be fully polymerized. Detection of the ethane-like nanophase in $As_{12}Ge_{33}Se_{55}$ proves that this glass falls into the region of nanoscale phase-separated alloys.

To characterize the nonlinear optical properties of the obtained films, we estimated nonlinear refractive indexes of the films at the telecommunication wavelength ($\lambda = 1550$ nm) using the formula (4). Estimation gave $n_2 = 3.7 \cdot 10^{-17}$ m^2/W for $As_{12}Ge_{33}Se_{55}$ film and $n_2 = 1.2 \cdot 10^{-17}$ m^2/W for $As_{10}Ge_{22.5}Se_{67.5}$ film. These results appeared to be in satisfactory agreement with another results published on As-Ge-Se glasses [12-14]. The obtained high values of third order nonlinearity make these glasses suitable to be considered as perspective materials for all-optical switching and other optical signal processing applications.

4. Conclusions

Thin chalcogenide films with compositions $As_{10}Ge_{22.5}Se_{67.5}$ and $As_{12}Ge_{33}Se_{55}$ have been investigated in this paper. Transmission spectra measurements allowed to determine optical constants of these films. Both glasses possess high values of the third order refractive index ($n_2 = 3.7 \cdot 10^{-17}$ m^2/W for $As_{12}Ge_{33}Se_{55}$ film and $n_2 = 1.2 \cdot 10^{-17}$ m^2/W for $As_{10}Ge_{22.5}Se_{67.5}$ film). It

makes them very promising materials for fabrication of all-optical signal processing devices.

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