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OPTICAL PROPERTIES AND STRUCTURE OF AMORPHOUS $Ag_x(As_{0.33}S_{0.67})_{100-x}$ FILMS PREPARED BY OPTICALLY- INDUCED DIFFUSION AND DISSOLUTION OF SILVER INTO SPIN-COATED AMORPHOUS $As_{33}S_{67}$ FILMS

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The $As_{33}S_{67}$ amorphous films were prepared by standard spin-coating technique. Prepared films were stabilized in a vacuum and then annealed in inert argon atmosphere. Silver film was deposited on top of $As_{33}S_{67}$ film by vacuum thermal evaporation technique. The optically- and thermally-induced diffusion and dissolution of silver into chalcogenide was used to introduce silver in step-by-step regime into $As_{33}S_{67}$ amorphous films prepared by spin coating technique. Obtained films have composition $Ag_x(As_{0.33}S_{0.67})_{100-x}$, where x = 0 – 27.3 at.%. The composition was measured by X-ray energy dispersive microanalysis (EDX). Optical properties (linear and non-linear) has been measured and calculated. Raman spectroscopy has been used to measure the structure of prepared films.

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1. Introduction

Optically-and thermally-induced diffusion and dissolution (OIDD) of metals and amorphous chalcogenides has been widely studied e.g. [1-5]. Spin-coating technique as an inexpensive deposition technique for amorphous chalcogenides was studied by Chern and Lauks [6]. The OIDD of silver in As-S spin-coated films has been observed by Hajto [7]. The OIDD of metals in spin-coated films is not fully understood and potential applications are expected in optical and microoptical elements such as gratings [8] and as the optical recording media [9]. The technique of step-by-step optically-induced dissolution and diffusion (OIDD) of Ag into $As_{33}S_{67}$ amorphous films prepared by thermal evaporation allow to design films with exact silver concentration and thickness [5,10]. The OIDD process of silver has also its potential for spin-coated films with similar compositions. The spin coated amorphous films with the composition of $As_{33}S_{67}$ are favorable in combination with OIDD of silver, because it could yield an optically homogeneous films with broad range of silver content as in thermally evaporated films [11]. Our aim was to prepare suitable silver-doped amorphous films and study their optical properties and structure. Optical constants of Ag-As-S spin coated films are important for a variety reasons. For example they are essential to predict the performance of diffractive optical elements or fast optical switches made in these films. They could also be important to find the right wavelength of light for optical recording into these films. Also they could yield structural information on photodoped materials. There is a lack of information on optical constants of Ag-As-S spin-coated films in dependence on silver content.

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2. Experimental procedure

The bulk $As_{33}S_{67}$ material fragments (2 grams) were dissolved in 10 ml of n-butylamine. The obtained solution was used for spin-coating in inert gas atmosphere onto planar silica glass and quartz substrates. The $As_{33}S_{67}$ films were stabilized in vacuum furnace for 8 hours. Thickness of $As_{33}S_{67}$ films was ~ 700 nm, which is an appropriate value for the accurate evaluation of optical parameters. Subsequently, constant thickness (~ 10 nm) of silver was vacuum evaporated step-by-step on the top of the chalcogenide host and dissolved by OIDD process. The 11 different composition of $Ag_x(As_{0.33}S_{0.67})_{100-x}$ films were photodoped by consecutive dissolving of thin (~10 nm) layers of silver in $As_{33}S_{67}$ films. It resulted homogeneous films of very good optical quality. The OIDD process was carried out by illuminating with a house lamp equipped with large Fresnel lens, IR-cut filter and 500 W tungsten lamp, in case of step-by-step OIDD of silver.

Microanalysis of samples has been performed on an electron scanning microscope JEOL JSM-5500LV and energy-dispersive X-ray microanalyser IXRF Systems (detector GRESHAM Sirius 10, accelerating voltage of the primary electron beam 20 kV).

The optical transmission spectra of the films were recorded with Jasco V-570 UV/VIS/NIR spectrophotometer. In order to calculate the thickness, *d*, the refractive index, *n*, and absorption coefficient, α, from the thin film transmission spectra, an evaluation method described by Swanepoel [12] was used. Maximum possible error varies in n ±0.005; in d ±5 nm. The optical gap, $E_{g,\,opt}$, was determined from intercept on the energy axis of the linear fit of the high-energy data, in a plot of $(\alpha\hbar\omega)^{1/2}$ versus $\hbar\omega$, which is widely accepted procedure (Tauc extrapolation [13]). The optical transmission data were also analyzed on the basis of a single-effective-oscillator model proposed by Wemple and DiDomenico [14]. These authors found that dispersion data can be described to good approximation by the following formula:

$$n^2(\omega)-1 = E_0E_d/(E_0^2 - (\hbar\omega)^2) \quad (1)$$

where $\hbar\omega$ is the proton energy, E_0 is the oscillator energy and E_d is the oscillator strength or dispersion energy. Plotting $(n^2-1)^{-1}$ against $(\hbar\omega)^2$ allows one to determine the oscillator parameters by fitting straight line to the points:

$$1 / n^2 - 1 = - (1 / E_d \,.\, E_0) \,.\, (\hbar\upsilon)^2 + E_0 / E_d \quad (2)$$

There were used energy up to proximity of band edge where linear fit is valid. Wemple and Di Domenico expression (1) could be also useful to estimate non-linear effect in chalcogenide glasses from linear optical index of refraction, n. According to Frumar [15] the Miller's rule is very convenient for visible and near-infrared frequencies, which equalize the third order of non-linear polarizability parameter, $\chi^{(3)}$ so called non-linear optical susceptibility and linear optical susceptibility, $\chi^{(1)}$, through equation (3):

$$\chi^{(3)} = A(\chi^{(1)})^4 = A\,[E_0E_d/4\pi\,(E_0^2 - (\hbar\omega)^2)]^4 \quad (3)$$

where $A = 1.7\times10^{-10}$ (for $\chi^{(3)}$ in esu). The covalency and ionicity of chemical bonds influence strongly the magnitude of non-linearity.

Raman spectroscopy has been carried in the $As_{33}S_{67}$ films, as silver was photo-doped into the host matrix. The Raman spectroscopy study was performed on a Fourier Transformation (FT) Raman spectrometer (Bruker, model IFS/FRA 106). Raman spectra were excited using a laser beam with λ = 1064 nm having an output power 50 mW. The wavelength of the laser beam was critical to avoid any photostructural changes in these chalcogenide glasses within the time scale of 100 scans. The resolution of the Raman spectrometer was 1 cm^{-1}. The spin-coated films ($As_{33}S_{67}$) and photodoped spin-coated films $Ag_x(As_{0.33}S_{0.67})_{100-x}$ were both mechanically peeled from the substrates, and immediately pressed into aluminum targets for the Raman measurements.

3. Results

Spin coating technique followed by OIDD of silver led to preparation of the set of 11 different samples of $Ag_x(As_{0.33}S_{0.67})_{100-x}$ films, where x varied from 0 to 27.3 at.%. The compositions were confirmed by EDX analysis. According to Kosa [11] the homogeneity of the doped thin film samples was clearly confirmed by the corresponding spectral dependence of transmission, where no shrinkage of the interference fringes was observed as it clear from Fig. 1. With increasing silver content the modulation depth of the interference fringes increased indicating that in the each case we measured a „new material". The absorption edges of the transmission curves for all prepared samples are displayed in Fig. 2 and the red shift of the absorption edge with increasing silver content at 40% of transmission is plotted in Fig. 3. Fig. 3 demonstrates also almost linear dependence of the red shift on silver content. Silver dissolution changes also other thin film characteristics e.g. optical band gap, $E_{g,opt}$, decreases and film thickness, d, increases both linearly with increasing silver content in films. These conclusions are drawn from Fig. 4. The dependence of the single-oscillator parameters, E_0 and E_d on silver content is shown in Fig. 5.

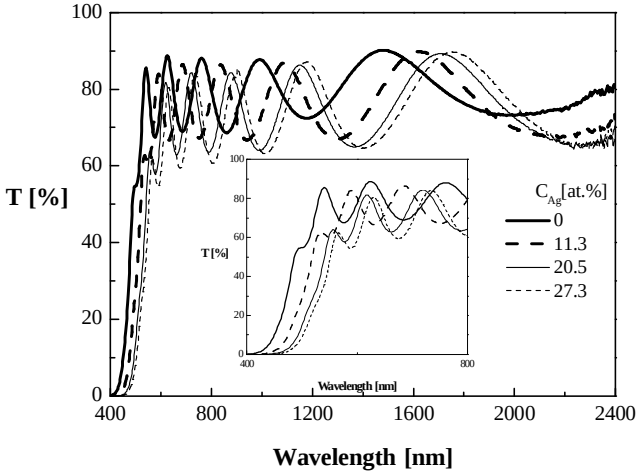


Fig. 1. Transmission spectra of $Ag_x(As_{0.33}S_{0.67})_{100-x}$ films prepared by OIDD of silver into spin-coated $As_{33}S_{67}$ amorphous films. Inserted figure shows the expanded part of the spectra close to absorption edge.

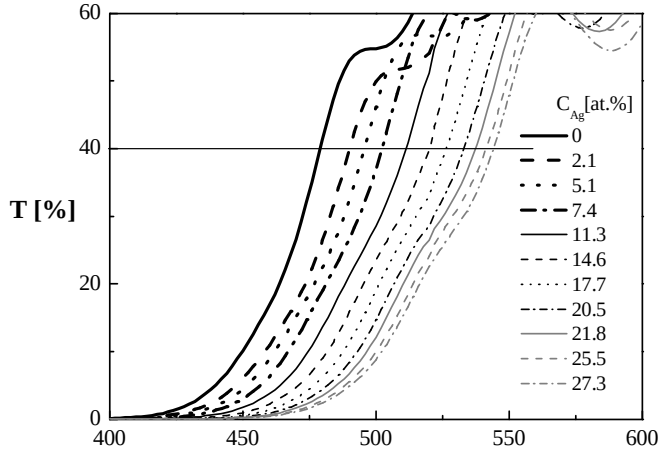


Fig. 2. Transmission spectra of all prepared $Ag_x(As_{0.33}S_{0.67})_{100-x}$ films in absorption edge spectral region.

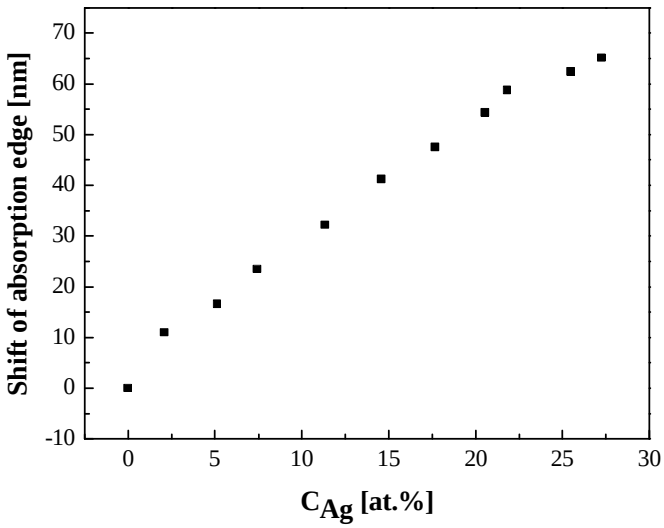


Fig. 3. Absorption edge shift vs. silver content in prepared films taken from the Fig. 2 at transmission value 40%.

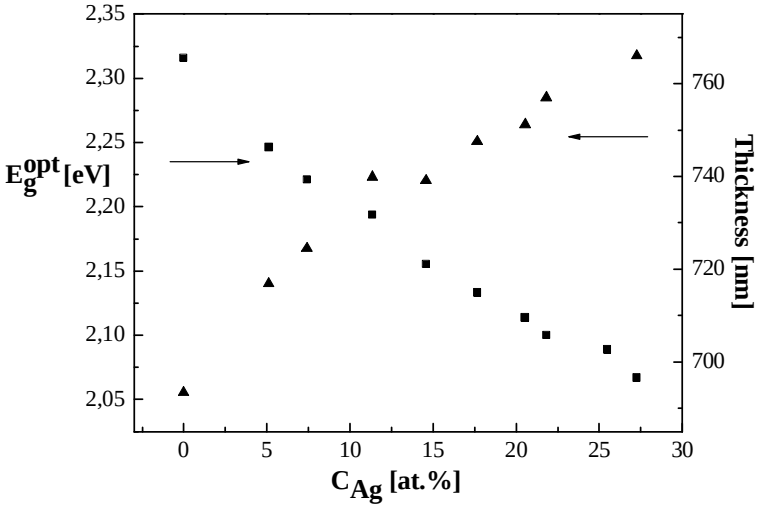


Fig. 4. Optical gap and film thickness versus silver content in the $Ag_x(As_{0.33}S_{0.67})_{100-x}$ films.

The index of refraction of spin coated $As_{33}S_{67}$ films increases significantly by OIDD of silver (Fig. 6). Also calculations of non-linear optical susceptibility, $\chi^{(3)}$, according to (Eq. 3) show in Fig. 7 increasing value of with silver built into spin coated films.

The Raman spectra measured in Ag-As-S films are shown in Fig. 8. The spectra were interpreted using references [16]. The illuminated $As_{33}S_{67}$ film (Fig. 8, $x_{Ag} = 0$) contains strong bands at 336 (units $AsS_{2/3}$) and 364 cm^{-1} (As_4S_4 units), and also weak bands at 474 and 496 cm^{-1} (S_8 rings or S rings fragments), respectively. The consequent step-by-step OIDD process of silver in $As_{33}S_{67}$ films leads to an appearance of a new strong band at 376 cm^{-1} (AsS_3 pyramids or As_3S_6 unit [17] connected by S-Ag-S linkage or AgS_3 pyramids [18]). The decrease of intensities of main bands and weak bands described for $As_{33}S_{67}$ film (Fig. 8, curves from $x_{Ag} = 20.5$) with significant decrease of S_8 rings or S rings fragments vibrations. Raman intensity of silver doped spin coated films was affected by the

luminescence, which is added to the Raman signal bellow 200 cm^{-1} and so Raman spectrum is more noisy. Nevertheless the conclusions mentioned above are still valid.

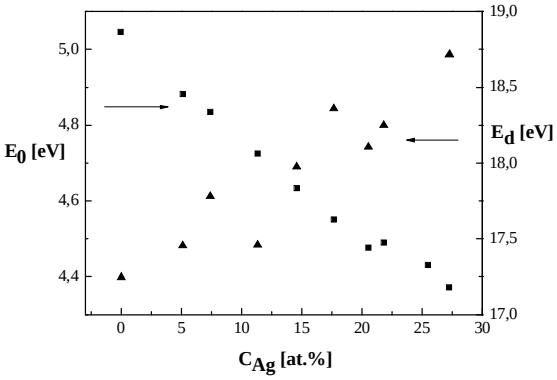


Fig. 5. Silver content dependence of single-effective-oscillator of parameters E_0 and E_d.

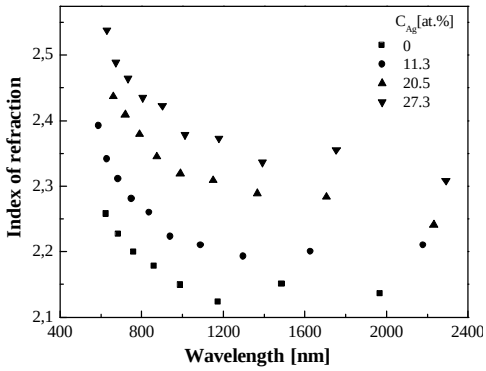


Fig. 6. The index of refraction dispersion n(λ) versus silver content in the $Ag_x(As_{0.33}S_{0.67})_{100-x}$ films.

4. Discussion

The decrease of the $E_{g,\,opt}$ value is in a good agreement with the results of similar experiments in thermally evaporated films [11]. The decrease of $E_{g,\,opt}$ value with increasing silver content is explained by the fact that Ag-S bonds have smaller binding energy than the As-S bonds, and this, therefore, leads to smaller energy splitting between the valence and conduction states. The oscillator energy i.e. E_0 parameter is the average energy gap and to a good approximation it varies in proportion to optical bandgap. with constant, C, ($C.E_0 = E_{g,\,opt}$, where $C \approx 2.1$). E_d serves as a measure of the strength of interband transitions.

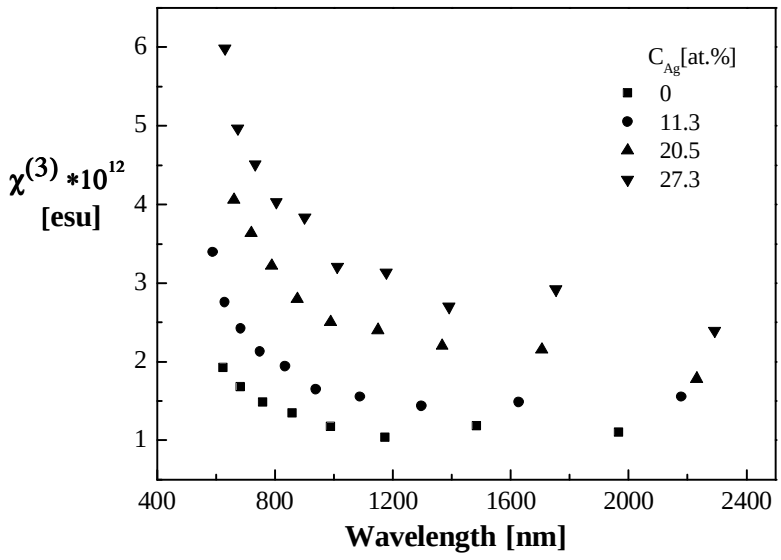


Fig. 7. The third order non-linear optical susceptibility dispersion $\chi^{(3)}(\lambda)$ versus silver content in the $Ag_x(As_{0.33}S_{0.67})_{100-x}$ films.

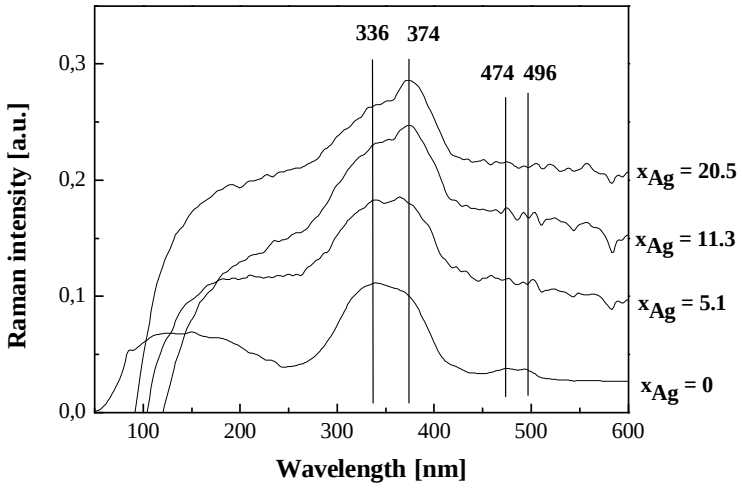


Fig. 8. The Raman spectra versus silver content in the $Ag_x(As_{0.33}S_{0.67})_{100-x}$ films.

An important achievement of the Wemple-DiDomenico model is that it relates the dispersion energy to other physical parameters of materials through an empirical formula:

$$E_d = \beta N_c Z_a N_e \text{ (eV)} \tag{4}$$

where β is a constant with either ionic or covalent value (β = 0.37 eV), N_c is coordination of cationts, Z_a is formal valency of the anion and N_e is effective number of valence electrons per anion. The increase of E_d value means increase of average cation coordination number. The silver presence leads definitely to increase of silver coordination number as this was also proved in numerous studies in evaporated films and bulk glasses with values between 3 and 4 [11,19]. The silver bonding to binary As-S amorphous network of spin coated films is visible from Raman spectra. E_d value in ternary systems is according to Kim [20] related also to bond length, X, ($E_d \sim X^2$) and explains why film thickness expands during OIDD of silver. Clearly, OIDD produces a very significant change in linear refractive index compare to spin coated $As_{33}S_{67}$ films ~0.4 for highest silver concentration. The linear index of refraction is in reasonable approximation connected to non-linear one by $\chi^{(3)}$. The polarizable atoms with lone pairs as e.g. chalcogens influence the $\chi^{(3)}$ value but also presence of heavy atoms with easily polarizable electron clouds (e.g. Ag) are even more profitable. The $\chi^{(3)}$ value is increasing also due to the fact that silver improves polymerization and strength of bonds in amorphous network.

5. Conclusions

It was measured the optical bandgap $E_{g,opt}$, films thickness, the dispersion of the refractive index $n(\lambda)$ in $Ag_x(As_{0.33}S_{0.67})_{100-x}$ films, where x is from 0 to 27.3 at.%. The silver containing samples were prepared by OIDD of Ag process. Dissolution Ag into the matrix introduces new Ag-S bonds with smaller binding energy than the As-S bonds, which explains decrease of the optical bandgap with increasing Ag content. Raman spectra supported the interpretation of measured data in which dominated decrease of S-S bonds with silver content increase. The analysis of dispersion data on the basis Wemple-DiDomenico single-effective-oscillator model. The oscillator energy E_0 varied in proportion to $E_{g,opt.}$. Oscilator strength E_d increased with increasing Ag content as silver is highly coordinated in the matrix. The E_d value was related to bond length. Index of refraction, E_0 and E_d

value enabled calculation, according to Miller's rule, of non-linear optical susceptibility, $\chi^{(3)}$, which increases with increasing Ag content.

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