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Optical characterization of Ag/As-S-Se thin films

J. TASSEVA, V. LOZANOVA, R. TODOROV, K. PETKOV*

Central Laboratory of Photoprocesses, Bulgarian Academy of Sciences, Acad. G. Bonchev St., b.l 109, 1113 Sofia, Bulgaria

Results of investigations of optically uniform thin $As_{33}S_{67-x}Se_x$ ($0 \le x \le 67$) films deposited by thermal evaporation on BK-7 optical glass substrates are presented. Bulk samples were prepared by melting pure elements As, S and Se in a quartz ampoule at 760°C for 12 hours. The changes in transmittance, reflectance, refractive index and optical band gap in the visible and NIR region of thin films (700 nm thick) depending on composition and exposure to light have been studied. The photo-induced diffusion of Ag into As-S-Se thin films was studied using glass substrates with initially deposited by RF sputtering Ag films with different thickness. It was shown that the refractive index increases with the increase in the Se and Ag content from 2.24 for $As_{33}S_{67}$ to 2.80 for $As_{33}Se_{67}$ and from 2.40 for $Ag/As_{33}S_{67}$ to 3.65 for $Ag/As_{33}Se_{67}$ at λ=1060 nm, while E_g decreases from 2.58 to 1.78 and from 2.25 to 1.5, respectively (the Ag thickness was 70 nm). Thus, the dispersion energy, E_d, single-oscillator energy, E_0 and the effective coordination number per cation, N_c, have been calculated. In agreement with other authors, we have observed E_d and N_c increasing with the Se-content in the films. The dependence of the surface microstructure and optical parameters of the quaternary system on the Ag concentration was demonstrated. Some conclusions about the mechanism of the photoinduced structural changes of the studied system were drawn.

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Keywords: Chalcogenide glasses, Thin films, Optical properties

1. Introduction

Chalcogenide glasses are one of the most widely known families of amorphous materials and have been extensively studied for several decades, partly because of their interesting fundamental properties and partly because of their many potential applications in optical imaging, optical recording, infrared optics, and more recently, optical communications [1-6]. Among chalcogenide glasses, these from the As-S-Se system are characterized by a large-formation domain [7-9] and very interesting linear and nonlinear properties. The interest in chalcogen-rich compositions is due to the high non-linearity found in $As_{24}S_{38}Se_{38}$, which possesses third-order nonlinearity 400 times higher than that of silica [9].

When a chalcogenide layer in contact with a layer of certain metals (Ag, Cu, Zn) is illuminated, metal ions dissolve in the glass and migrate through it in the direction of illumination, thereby altering the composition and structure of the glass and changing its physical properties, particularly its solubility and optical constants. This effect is termed “photodiffusion”, “photodoping” or “photodissolution” [10-13]. Amorphous films with a composition $As_{33}S_{67-x}Se_x$ are favourable in combination with optically-induced dissolution and diffusion of silver, because optically homogeneous films within a broad range of silver content can be obtained [14].

The present paper is focused on the determination of the optical parameters (n, k, E_g, E_o and E_d) of thin films from the system $Ag/As_{33}S_{67-x}Se_x$ ($0 \le x \le 67$) and their changes after exposure to light depending on the selenium concentration and the thickness of the Ag layer. The dependence of the microstructure and optical parameters of the quaternary system on the Ag concentration was demonstrated.

2. Experimental

Bulk samples from the system $As_{33}S_{67-x}Se_x$ ($0 \le x \le 67$) were prepared by direct synthesis from the elements with a purity of 99.999%. These were heated in an evacuated silica ampoule placed in an oven at 760°C for 12 hours with subsequent cooling in ice water. In order to achieve good homogenization of the chalcogenide glasses the oven was slowly rocked during the time the ampoule was at high temperature. Thin As-S-Se films were deposited at room temperature onto graphite and BK-7 optical glass substrates in a high vacuum of 10^{-4} Pa by thermal evaporation of previously weighed powdered glassy material. The photo-induced diffusion of Ag into $As_{33}S_{67-x}Se_x$ thin films was studied using glass substrates with initially deposited by RF sputtering Ag films with different thickness. The films were exposed to light from a halogen lamp (20 mW.cm^{-2}), for saturation time experimentally established for each composition. The surface microstructure of the layers was investigated by Scanning Electron Microscope (SEM) (Philips, Netherlands). The composition of both bulk glasses and of thin films was determined in SEM with an X-ray microanalyzer (Jeol Superprobe 733). The transmittance (T) and reflectance (R) were measured by a Cary 5E UV-VIS-NIR spectrophotometer (USA) in the wavelength range of 350 to 2500 nm.

The refractive index, n, and the film thickness were calculated using Swanepoel’s method [15] and a computer program developed by Konstantinov [16]. The method allows calculation of *n* when both the refractive index of the substrate and the position of the interference extrema are known. The refractive index, *s*, of the substrate was determined independently at various wavelengths by measuring the transmittance, T_s, of the substrate alone and using the equation [16]:

$$s = 1/T_s + 1/(T_s^2 - 1)^{1/2}. \qquad (1)$$

For BK-7 glass substrates it was found that $91 \le T_s \le 92$ and $89 \le T_s \le 91$ over the wavelength range 350-1400 nm and 1400-2500 nm, respectively. The program used to calculate *n* will determine it to an accuracy of ± 0.5 % for an error in the transmittance of ± 0.1 %.

In the case of chalcogenide semiconductors, for the highest values of the absorption coefficient ($\alpha \ge 10^4$ cm^{-1}) which corresponds to transitions between extended states in both valence and conduction bands, the Tauc's power law [17] is valid:

$$\alpha h\nu = B\,(h\nu - E_g)^2. \qquad (2)$$

B is the slope of the Tauc's edge, which reflects some disorder of the sample, *h* is Planck's constant and ν is the frequency. Usually this constant depends on the width of the localized states in the band-gap, which are attributed to the homopolar bonds in the chalcogenide glasses. Thus, Tauc's plots of $(\alpha h\nu)^{1/2}$ *versus* $(h\nu)$ should be linear and extrapolate to values of the optical gap, E_g. The refractive index dispersion was analyzed, using the single-oscillator model, proposed by Wemple & Di Domenico (WDDM) [18].

3. Results and discussion

The results from the X-ray microanalysis of bulk samples and thin films from the system $As_{33}S_{67-x}Se_x$ for x = 0, 17, 34, 51, 68 at. % are shown in Table 1. It is seen that the element content of the films differs from the expected compositions and the system seems to be closer to the $As_{30}S_{70-x}Se_x$ one.

Table 1. Data for the element content of the bulk and thin film chalcogenide samples.

Composition	Bulk samples	Thin films
$As_{33}S_{67}$	$As_{33.3}S_{66.7}$	$As_{26.8}S_{73.2}$
$As_{32}S_{51}Se_{17}$	$As_{30.7}S_{53}Se_{16.3}$	$As_{28}S_{52.2}Se_{19.8}$
$As_{32}S_{34}Se_{34}$	$As_{31.2}S_{37.2}Se_{31.6}$	$As_{28.4}S_{34.7}Se_{36.9}$
$As_{32}S_{17}Se_{51}$	$As_{31.2}S_{19.7}Se_{49.1}$	$As_{28.6}S_{20.6}Se_{50.8}$
$As_{33}Se_{67}$	$As_{35.7}Se_{64.3}$	$As_{29.8}Se_{70.2}$

3.1. System $As_{33}S_{67-x}Se_x$

In Fig. 1 the plots of the optical transmission of thin As-S-Se films versus wavelength, before and after exposure to light are presented. The absorption edge is shifted to the higher wavelengths with the increase of the Se-content in the films and the effect of photodarkening is negligibly small, except for the $As_{33}Se_{67}$ films. The refractive index dispersion for three compositions of the system is plotted in Fig. 2. As shown, in the whole spectral region, the refractive index increases with increasing the Se-content. The calculated values of *n* at λ = 632.8 nm increase from 2.32 to 2.95 for $As_{33}S_{67}$ and $As_{33}Se_{67}$, respectively.

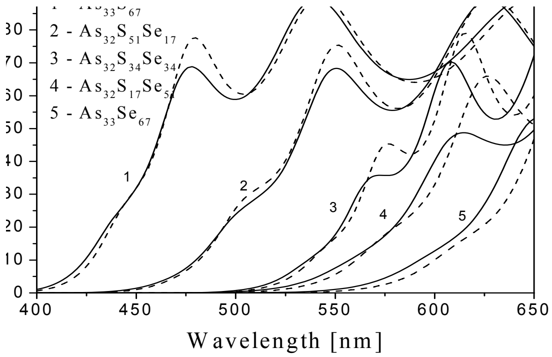

Fig. 1. Spectral dependence of the transmission of unexposed (—) and exposed (----) thin $As_{33}S_{67-x}Se_x$ films.

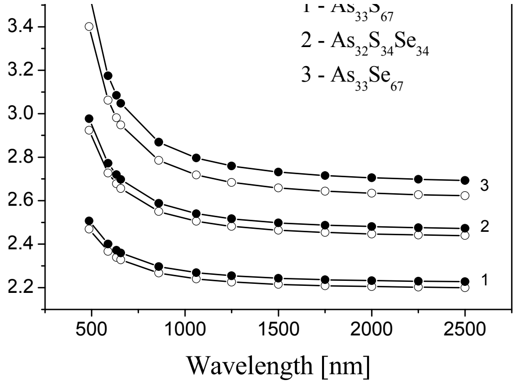

Fig. 2. Dispersion of the refractive index of As-S-Se thin films before (empty symbols) and after (filled symbols) light exposure.

The photo-induced increase in *n* depends on the Se-content in the films – up to a concentration of Se of 20 at. % it is ~ 1.35 - 1.7 % and after that it reaches 3.5 % for Se = 60 at. % as shown in Fig. 3,

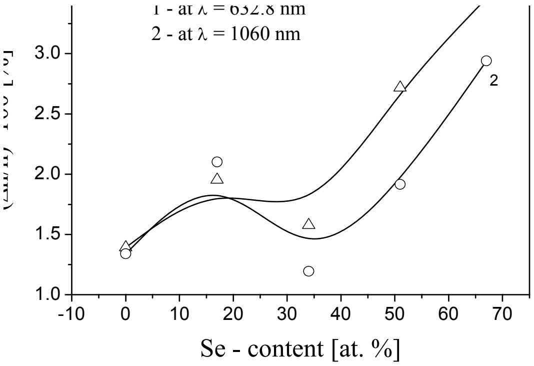

Fig. 3. Relative deviation of the refractive index (Δn/n) at two wavelengths vs. Se-content in thin films from the system $As_{33}S_{67-x}Se_x$.

where a comparison of the relative deviation $\Delta n/n = (n_{exp} - n_{unexp})/n_{un}$ of the refractive index for two values of the wavelength is given.

The shapes of the two curves (at λ = 632.8 and 1060 nm) are similar but there is a quantitative difference between the values of *Δn/n* for different wavelengths, which is a characteristic for the spectral region of their application. This effect could be explained by the difference in the optical band-gaps of thin As-S-Se films. These were determined from the Tauc's extrapolation of the $(\alpha h\nu)^{1/2} = f(h\nu)$ dependence (Fig. 4) for the same compositions as in Fig. 2.

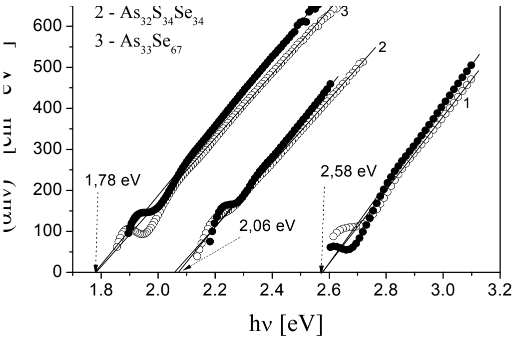

Fig. 4. Optical absorption edge $(\alpha h\nu)^{1/2}$ vs. photon energy (hν) for unexposed (○) and exposed (●) thin As-S-Se films.

It is shown that the calculated values of the optical band-gap, E_g^{opt}, decrease from 2.58 eV for $As_{33}S_{67}$ up to 1.78 eV for $As_{33}Se_{67}$ films. As expected, enriching the thin $As_{33}S_{67}$ films with Se leads to a certain increase of the $AsSe_{3/2}$ pyramidal structural units and therefore to the obtained compositional dependence of E_g^{opt}. The photoinduced changes in the refractive index increase with decreasing E_g^{opt} of thin films due to the lower binding energy between As and Se atoms compared with that between As and S atoms. It seems that there are no changes in the values of the optical band-gap after films illumination. The values of B for exposed films increase which could be connected with its ordering.

Finally, the dispersion energy, E_d, single-oscillator energy, E_0, and coordination number of the cation (As), N_c, were calculated by WDDM. The calculated values are presented in Table 2. With the increase in the Se-content and after light exposure, the dispersion energy, E_d and the cation coordination number (As), N_c increase. This increase may be due to strengthening of the interaction of the individual structural layers. It is suggested that along with triple-coordinated As atoms, fourfold-coordinated As atom also exists, which explains why $N_c > 3$.

Table 2. Dispersion parameters for unexposed and exposed $As_{33}S_{67-}Se_x$ films.

Composition		B cm$^{-1/2}$ eV$^{-1/2}$	E_g^{opt} eV	E_0 eV	E_d eV	N_c
$As_{33}S_{67}$	un	896	2.58	5.07	19.27	3.1
	ex	965	2.58	5.02	19.70	3.1
$As_{32}S_{51}Se_{17}$	un	763	2.22	4.62	20.19	3.2
	ex	849	2.25	4.68	21.48	3.4
$As_{32}S_{34}Se_{34}$	un	778	2.06	4.29	20.97	3.3
	ex	851	2.07	4.26	21.49	3.4
$As_{32}S_{17}Se_{51}$	un	775	1.91	4.01	21.24	3.4
	ex	856	1.92	3.93	21.84	3.5
$As_{33}Se_{67}$	un	782	1.78	3.79	21.90	3.5
	ex	844	1.78	3.71	22.79	3.6

3.2. System $Ag/As_{33}S_{67-x}Se_x$

The next step in our investigation was to study the effect of photoinduced dissolution of Ag into as-characterized thin $As_{33}S_{67-x}Se_x$ films (see 3.1). Thin films with the same compositions were deposited on the optical substrates BK-7 without and with silver films with different thickness (30-100 nm) deposited by RF sputtering for determination of the optimal concentration of Ag (expected to be around 10 % from the thickness of the chalcogenide film according to data published in the literature)[10, 19]. The data from X-ray microanalysis of exposed to saturation thin As-S-Se films deposited on Ag layer ~ 70 nm thick showed that the silver content in the films was around 12-13 at. %.

Fig. 5 compares the transmission spectra of $As_{32}S_{34}Se_{34}$ layers, evaporated on silver with two different metal thicknesses – 40 nm (a) and 85 nm (b). The chalcogenide layer thickness is 625 nm. Prior to light-exposure, the transmission of the two layered system is negligible. The transmission coefficient of the thicker silver is close to 0 % in the whole spectral range (curve 1, b), and the transmission coefficient measured for the thinner silver does not exceed 20 % (curve 1, a). After light-exposure for 3 hours, we obtain a homogeneous silver-doped layer of the examined system (judging by the equal amplitudes of the interference extrema in the spectral range of interest) for which the transmission coefficient in the interference maxima is close to 90 % (curves 2). Thus, the homogeneity and the high transmission coefficient made possible the application of the method of determination of the optical constants (n, k) and thickness (d) developed by Konstantinov [16].

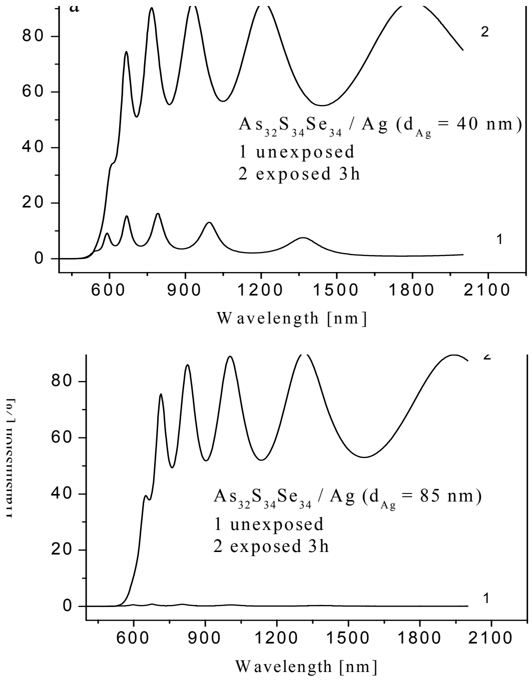

Fig. 5. Spectral dependence of the transmission of unexposed (1) and exposed (2) thin Ag/$As_{32}S_{34}Se_{34}$ films deposited on Ag films with different thicknesses – 40 nm (a) and 85 nm (b).

Fig. 6 shows the dispersion of *n* for the five compositions from the examined chalcogenide systems doped with silver. The results are compared for two source thicknesses – 35 nm (Fig. 6a) and ~70 nm (Fig. 6b).

The exact values of *n* (at two characteristic wavelengths, i.e. 633 and 1060 nm), E_g^{opt}, as well as the doped layers thickness for tin $As_{32}S_{34}Se_{34}$ films are shown in Table 3.

It is evident (Table 3) that the refractive indices of the doped layers are higher than that of the non-doped layer. Besides, the increase in the silver layer thickness also leads to an increase in *n* (i.e. the refractive index of the quaternary As-S-Se-Ag system is higher for the as-deposited thin films). Conversely, the addition of silver in the chalcogenide system results in a decrease in the optical band-gap width (Fig. 6b), which is probably due to an increase in the number of defect states in the band-gap of the material on doping it with silver.

It is remarkable that similar diminishing of optical band gap occurs in the case of the Se-S-AgI system, as reported by Monchev et al. [20].

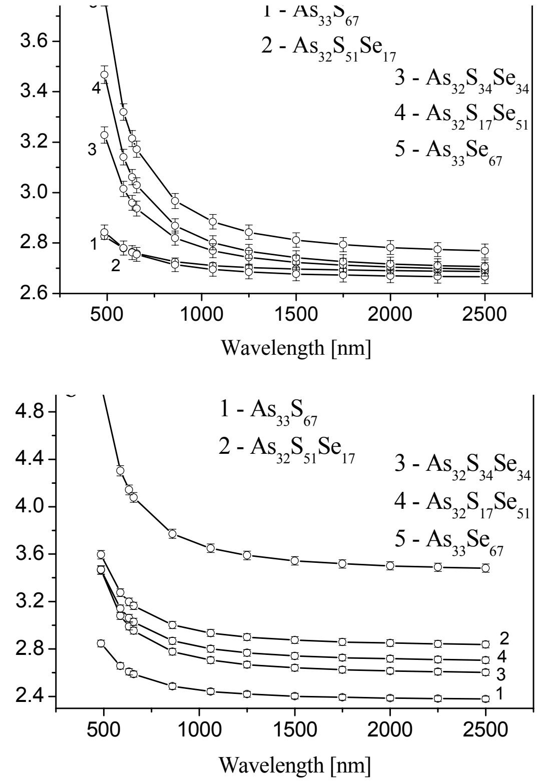

Fig. 6. Refractive index dispersion of exposed thin As-S-Se films deposited on Ag layers with two thicknesses – 35 nm (a) and 70 nm (b).

Table 3. Some physical parameters of doped chalcogenide layers from $As_{32}S_{34}Se_{34}$.

$As_{32}S_{34}Se_{34}$	d, nm	n 633 nm	n 1060 nm	B $cm^{-1/2}$ $eV^{-1/2}$	E_g^{opt} eV
As-deposited	625	2.73	2.56	766	2.05
d_{Ag}= 40 nm doped	681	2.93	2.70	786	1.87
d_{Ag}= 85 nm doped	714	3.05	2.80	764	1.79

Fig. 7a illustrates the compositional dependence of *n* at λ = 632.8 nm of the investigated silver-doped chalcogenide layers, whose thickness, prior to diffusion, is around 35 nm. The refractive index increases almost linearly from 2.76 ± 0.03 for $As_{33}S_{67}$ to 3.21 ± 0.03 for $As_{33}Se_{67}$.

Fig. 7 b shows the change in the optical band-gap width with the Se-content in the doped layers. The investigated composition dependences of E_g^{opt} are for two silver thicknesses – 35 and 70 nm. For the lower thickness of Ag, the layers exhibit linear reduction of the optical band-gap width with the increase in the Se quantity in the glasses - E_g^{opt} diminishes from 2.43 eV ($As_{33}S_{67}$) down to 1.61 eV ($As_{33}Se_{67}$). The linear relationship for the silver-doped layers of 70 nm is violated at a composition of the chalcogenide layer $As_{32}S_{51}Se_{17}$. The values obtained for $As_{33}S_{67}$ and $As_{33}Se_{67}$ are 2.24 and 1.53 eV, respectively.

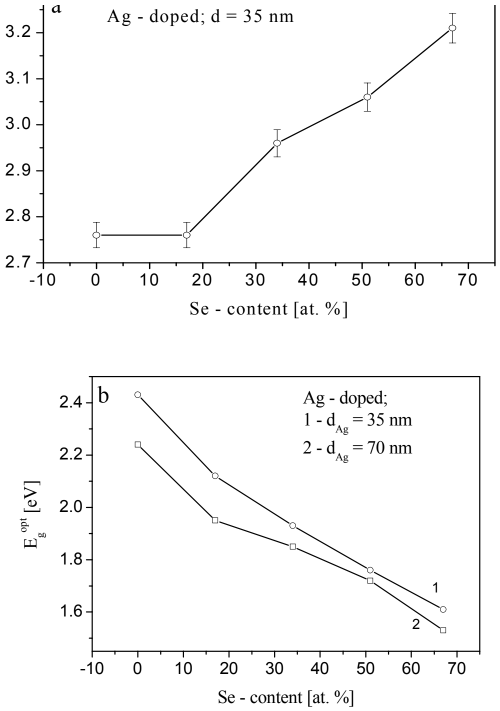

Fig. 7. Compositional dependence of the refractive index at λ = 632.8 nm (a) and the band-gap (b) for chalcogenide films deposited on Ag films with two thicknesses.

The surface microstructure of exposed thin $As_{33}S_{67}$, $As_{32}S_{34}Se_{34}$ and $As_{33}Se_{67}$ films deposited on 70 nm thick Ag layer and changes in the surface microstructure of exposed thin $As_{32}S_{34}Se_{34}$ films deposited on Ag layers with different thickness are shown in Figs. 9 and 10, respectively. As a reference picture, Fig. 8 shall be used where the surface of an undoped $As_{32}S_{34}Se_{34}$ layer is shown.

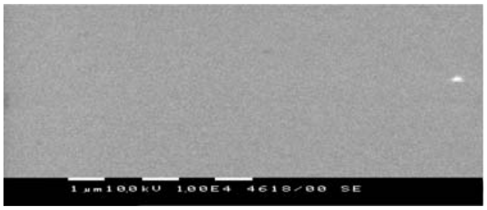

Fig. 8. SEM micrograph of an undoped $As_{32}S_{34}Se_{34}$ film; the marker corresponds to 1 μm and shall refer to Figs. 9, 10, as well.

It is seen that the surface of the undoped layer is smooth (Fig. 8), while well defined grains appear on the top of the doped films (Figs. 9, 10).

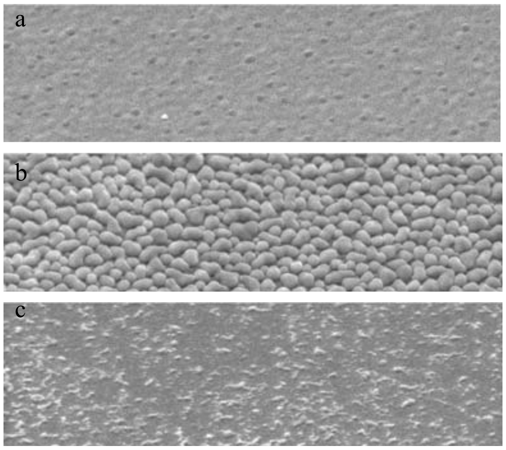

Fig. 9. SEM micrographs of Ag-doped films from $As_{33}S_{67}$ (a), $As_{32}S_{34}Se_{34}$ (b) and $As_{33}Se_{68}$ (c); the thickness of the metal layer is 70 nm.

A clear difference between the grain size of the surface depending on the quantity of Ag diffused into the chalcogenide layers is observed. The process of photodiffusion and photodissolution of silver is most pronounced for the films with composition $As_{32}As_{34}Se_{34}$ (Fig. 10). On the surface of the first layer (Fig. 10a), grains sized around 0.5-1 μm are clearly distinguished, which are closely stuck to each other. This proves that silver has been thick enough in order to come out on the layer surface. With the decrease in the silver layer thickness, the grain size also decreases, becoming around 300, 250, 200 nm, respectively, for the remaining three thicknesses of Ag (Fig. 10b, c, d).

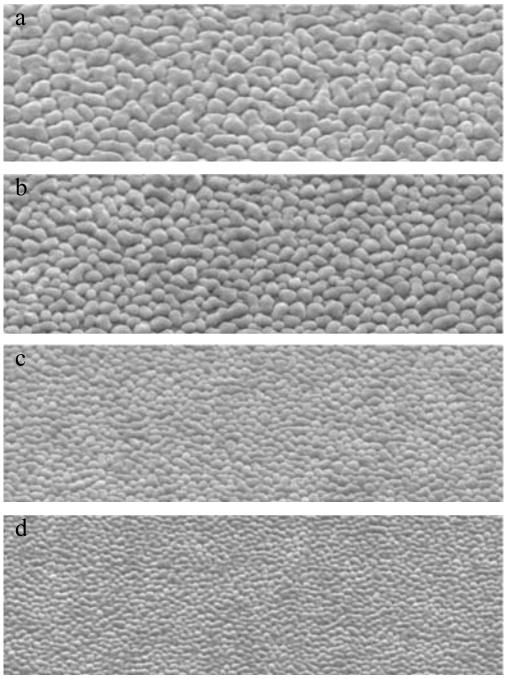

Fig. 10. SEM micrographs of Ag-doped films from $As_{32}S_{34}Se_{34}$ with various thickness of the metal layer – 85 nm (a), 65 nm (b), 40 nm (c) and 30 nm (d).

For some compositions, the surface of the silver layers doped with the thinnest silver layer, become smooth and no grains are observed. This probably means that silver is not sufficiently thick in order to reach the upper surface of the non-doped chalcogenide layer. We have not investigated the grain structure. Judging by literature data, however, [21], we can suggest that the layers remain glass-like after doping, if the Ag content in them does not exceed 25 at. % and, hence, the system does not tend to crystalise. The results of the more detailed investigation on the photo-diffusion process kinetics and changes of the surface microstructure of As-S-Se films will be published soon.

4. Conclusions

The conditions for direct synthesis of bulk samples and for vacuum thermal evaporation of thin films from the system $As_{33}S_{67-x}Se_x$ have been established. From spectrophotometric measurements, the optical constants n and k and the dispersion parameters, E_0 and E_d of the films were determined. It was found that the refractive index increases with increasing silver and Se concentration in the films. The difference of the refractive index between undoped and silver doped (70 nm Ag thickness) $As_{33}S_{67}$ and $As_{33}S_{67}$ films was 0.24 and 1.17, respectively. The value of E_g^{opt} of Ag doped thin films is strongly affected by Ag content in the films. The decrease in E_g^{opt} for doped $As_{33}S_{67}$ and $As_{33}S_{67}$ films compared with the as-deposited ones was 0.15 and 0.17 eV, respectively. This effect could be explained by the fact that Ag-S(Se) bonds have smaller binding energy than As-S(Se) bonds, and therefore this leads to smaller energy splitting between the valence and conductive states [14]. Discussions on the dispersion parameters were made and it was confirmed that the increasing of Se – content enhances the interactions between the separate structural layers in the amorphous matrix from the system $As_{33}S_{67-x}Se_x$. The maximum changes in the surface microstructure of doped chalcogenide films were found to become in $As_{32}S_{34}Se_{34}$ films which could be explained with the different rate of penetration of silver (and maybe different mechanism of photodissolution of Ag).

Acknowledgements

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*Corresponding author: kpetkov@clf.bas.bg