

LIGHT-INDUCED CHANGES IN THE PHYSICO-CHEMICAL AND OPTICAL PROPERTIES OF THIN Ge-S-Se-As FILMS

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In this paper we report results from studying changes in the optical properties and the microhardness of vacuum deposited thin films from the systems As_xSe_{100-x} ($28 \leq x \leq 50$) and $(As_{50}S_{50})_x(Ge_{33}S_{67})_{100-x}$ ($0 \leq x \leq 100$) depending on the composition and conditions of evaporation and light illumination. Thin films with different compositions of the system As-Se-S-Ge were deposited by thermal evaporation of $As_{50}Se_{50}$ and $Ge_{33}S_{67}$ from two crucibles changing their evaporation rate. Chalcogenide glasses with compositions $As_{50}Se_{50}$ and $Ge_{33}S_{67}$ were chosen because they demonstrate the highest effects of photodarkening ($\Delta\lambda = +50$ nm at $T = 20\%$) and photobleaching ($\Delta\lambda = -25$ nm at $T = 20\%$), respectively. The exact element content of the films was determined by X-ray microanalysis. The optical transmission and reflection of thin films deposited on BK-7 optical glass substrates were measured in the spectral region of 350-2500 nm and their refractive index and optical band gap E_g were calculated. The photoinduced changes of the foregoing parameters, as well as the changes in their microhardness depending on the composition and the conditions of deposition were traced. Some conclusions about the origin of photoinduced changes in the optical properties of thin films from this multicomponent system are given.

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1. Introduction

Chalcogenide glasses are some of the promising materials for use in optical technology, which is due to their transparency in the visible, and IR region [1-3]. Depending on the exact composition, they can transmit up to 12 μ m [4]. These glasses exhibit a photodarkening effect when exposed to above band-gap light, and some of them demonstrate very large non-linear effects, which make them suitable for direct recording of waveguides and materials for compact all-optical switches and other non-linear devices [5-7].

The physicochemical and optical properties of chalcogenide glasses from the systems As-Se and Ge-S(Se) and their changes under exposure to light depend considerably on the composition and the conditions of deposition and illumination of the layers [8-11]. More complicated amorphous thin Ge-S-Se-As films were initially studied as possible material for microfiches [12] and recently - for planar channel waveguides with very low losses, gratings and for photonic integrated circuits [13, 14] due to the large refractive index changes depending on the film compositions and the high photosensitivity. The determination of the optical constants is of great importance for understanding the mechanism of the optical processing and for their practical application. When vacuum condensation is used for the preparation of films of complex chalcogenide glasses, some problems arise, associated with the stoichiometry and homogeneity of the coatings [15] and the phase and structural equilibrium of the condensates. This is the reason to study photoinduced changes in the properties of thin As-Se-S-Ge films deposited by co-evaporation of binary glasses.

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In this communication we report some experimental results related to photo-induced changes in the optical and mechanical properties of as-deposited and exposed As-Se-S-Ge films depending on the conditions of their deposition and light exposure.

2. Experimental

Bulk samples from the systems As_xSe_{100-x} ($28 \leq x \leq 50$) and Ge_xS_{100-x} ($20 \leq x \leq 40$) 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 700°C for 12 hours for As-containing and at 970°C for 24 hours for Ge-containing glasses with subsequent cooling in cold 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-Se-S-Ge films were deposited at room temperature onto graphite, Si and BK-7 optical glass substrates in a high vacuum of 10^{-4} Pa by thermal co-evaporation from two crucibles of previously weighed powdered glassy material. The films were exposed to light from a halogen lamp (20 mW.cm^{-2}), from an Ar laser ($\lambda=528 \text{ nm}$)(unfocussed beam – 20 mW.cm^{-2}) and from a Hg lamp HBO 200 (20 mW.cm^{-2}), until saturation time, experimentally established for each composition. The composition of both bulk glasses and thin films was determined in a Scanning electron microscope with an X-ray microanalyzer (Jeol Superprobe 733). Optical transmission to an accuracy better than $\pm 0.1\%$ and the absolute reflection from the film side were measured using a Carry 5E UV-VIS-NIR Spectrophotometer [16] in the spectral range 350 to 2500 nm. Infrared absorption spectra were recorded in the wave number range from 4000 to 150 cm^{-1} on films deposited onto double side polished Si wafers using a Bruker spectrometer.

The Knoop hardness number (H_k) is the ratio of the load applied to the indenter, $P(\text{kgf})$ to the unrecovered projected area $A (\text{mm}^2)$

$$H_k = P/Cd^2, \quad (1)$$

where P is the applied load in kgf; d - measured length of long diagonal of indentation in mm, $C = 0.07028$ = constant of indenter relating projected area of the indentation to the square of the length of the long diagonal. We have used a Microhardness-measurement unit MHP 160 for a Vertival microscope (VEB Carl Zeiss, Germany) for the measurements with a standard loads of 3.75 and 2.5 g for producing impressions on Ge- or As-containing thin film ($\geq 1 \mu\text{m}$), respectively. Each observation was repeated at least ten times and the mean value of the hardness number was determined. The standard deviation was calculated and is shown as an error bar on the hardness bar.

The refractive index n and the film thickness were calculated using Swanepoel's method [17] and a computer program developed by Konstantinov [18]. The method allows calculation of n when both the refractive index of the substrate and the position of the interference extrema are known. In the present work 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 [18]:

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

For BK-7 glass substrates it was found that $91 \leq T_s \leq 92$ and $89 \leq T_s \leq 91$ 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 $\pm 0.5\%$ for an error in the transmittance of $\pm 0.1\%$.

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

$$\alpha h\nu = B (h\nu - E_g)^2. \quad (3)$$

Here B is the slope of the Tauc edge, which reflects some disorder of the sample, h is Planck's constant and ν is the frequency. Usually this constant (B) 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 .

3. Results and discussion

Table 1 shows the element content of bulks and thin films from the studied compositions. It is seen that the composition of the bulk glasses generally is within about 1-1.5 at.% of expected compositions, and only small deviations were observed for the quaternary thin films, deposited by co-evaporation of $\text{As}_{50}\text{Se}_{50}$ and $\text{Ge}_{33}\text{S}_{67}$.

Table 1. Composition obtained from X-ray microanalysis for bulk samples and thin films.

Composition	Expected composition (at. %)	Obtained compositions (at. %)	
		Bulk samples	Thin films
As_2Se_5	$\text{As}_{28}\text{Se}_{72}$	$\text{As}_{28}\text{Se}_{72}$	$\text{As}_{29}\text{Se}_{71}$
As_2Se_3	$\text{As}_{40}\text{Se}_{60}$	$\text{As}_{40}\text{Se}_{60}$	$\text{As}_{40}\text{Se}_{60}$
AsSe	$\text{As}_{50}\text{Se}_{50}$	$\text{As}_{50}\text{Se}_{50}$	$\text{As}_{49}\text{Se}_{51}$
$(\text{AsSe})_{75}(\text{GeS}_2)_{25}$	$\text{As}_{38}\text{Se}_{38}\text{Ge}_8\text{S}_{16}$		$\text{As}_{40}\text{Se}_{40}\text{Ge}_7\text{S}_{13}$
$(\text{AsSe})_{50}(\text{GeS}_2)_{50}$	$\text{As}_{25}\text{Se}_{25}\text{Ge}_{16}\text{S}_{34}$	$\text{As}_{24}\text{Se}_{26}\text{Ge}_{17}\text{S}_{33}$	$\text{As}_{28}\text{Se}_{33}\text{Ge}_{15}\text{S}_{24}$
$(\text{AsSe})_{25}(\text{GeS}_2)_{75}$	$\text{As}_{13}\text{Se}_{13}\text{Ge}_{25}\text{S}_{49}$		$\text{As}_{14}\text{Se}_{14}\text{Ge}_{25}\text{S}_{49}$
GeS_2	$\text{Ge}_{33}\text{S}_{67}$	$\text{Ge}_{33.2}\text{S}_{66.8}$	$\text{Ge}_{34}\text{S}_{66}$

As is known, photodarkening in thin As-Se films strongly depends on the composition [22]. We investigated changes in the optical constants of $\text{As}_x\text{Se}_{1-x}$ ($28 \leq x \leq 50$) and found that the effect of photobleaching is highest for the composition $\text{As}_{50}\text{Se}_{50}$ (Table 2). We believe that the red shift of the absorption edge (the effect of photodarkening) indicating narrowing of the optical gap of the films is due to changes in the polymeric structure of chalcogenide glasses and broadening of the valence band, the top of which is formed mainly by states of lone-pair electrons of the chalcogen atom [1]. The values of n and E_g of AsSe thin films do not depend on the thickness (in the range 100 - 1000 nm), either, confirming the data published in [23]. An increase of 6% in n was observed after exposure to light giving a possibility for grating production.

It was found that after exposure to light the absorption edge of $\text{Ge}_{33}\text{S}_{67}$ thin films shifts to the higher photon energies and the band gap increases ($\Delta E_g = 0.38$ eV). These changes are most probably connected with the increase in the Ge-S bond density and the decrease in the randomness of the film structure [11]. The increase in the value of E_g is similar to this observed from Tichy [10].

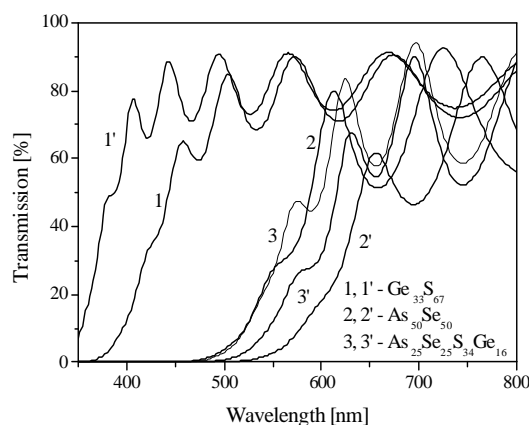


Fig. 1. Optical transmission, T , of thin films with different compositions, vs. wavelength, λ , before and after illumination by a halogen lamp ($20 \text{ mW}\cdot\text{cm}^{-2}$).

It is clear that a lot of combinations exist for deposition by co-evaporation process of thin As-Se-S-Ge films using compounds from the systems As-S(Se) and Ge-Se(S). Munzar and Tichy

[19] have investigated the bonding arrangement in bulk glasses synthesized by GeSe_2 and As_2S_3 glassy compounds. Our first experiments on studying As-Se-S-Ge films were made by co-evaporation of AsSe and GeS_2 with different ratios between the evaporation rates of the binary glassy substances. $\text{As}_{50}\text{Se}_{50}$ and $\text{Ge}_{33}\text{S}_{67}$ were chosen as we have previously shown that the maximum change in λ , n and E_g was observed in thin $\text{As}_{50}\text{Se}_{50}$ ($\Delta\lambda=+50$ nm at $T=20\%$) [20] and $\text{Ge}_{33}\text{S}_{67}$ ($\Delta\lambda= -25$ nm at $T=20\%$) [11] films. In Fig.1 the plots of the optical transmission of some thin chalcogenide films from the studied system vs. wavelength, before and after light exposure are presented. It is seen that a strong effect of photodarkening for thin $\text{As}_{50}\text{Se}_{50}$ films is observed after light exposure to a halogen lamp, while for $\text{Ge}_{33}\text{S}_{67}$ coatings the effect is opposite. The photodarkening effect decreases with the increase of GeS_2 in thin films and for compositions with higher content of GeS_2 (more than 50 at.%) the effect is of photobleaching.

From the transmission spectral dependence we calculated the dispersion of the refractive index n of $\text{As}_{50}\text{Se}_{50}$, $\text{Ge}_{33}\text{S}_{67}$, $(\text{AsSe})_{25}(\text{GeS}_2)_{75}$, $(\text{AsSe})_{50}(\text{GeS}_2)_{50}$ and $(\text{AsSe})_{75}(\text{GeS}_2)_{25}$ films (Fig. 2) and using Eq. 2 we determined from the plots $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ (Fig. 3) the optical band-gap of thin films. Their thickness was about 700 nm, and they were deposited with an evaporation rate about 1.0 nm/s including the quaternary compounds. The main data for the optical constants of thin As-Se-S-Ge films are summarized in Table 2 and they are very close to those published in [21]. It is seen that after light exposure, the shift of the absorption edge for As-Se films is to longer wavelengths, the refractive index increases, the thickness decreases and as we have already found [20], it is independent of their thickness.

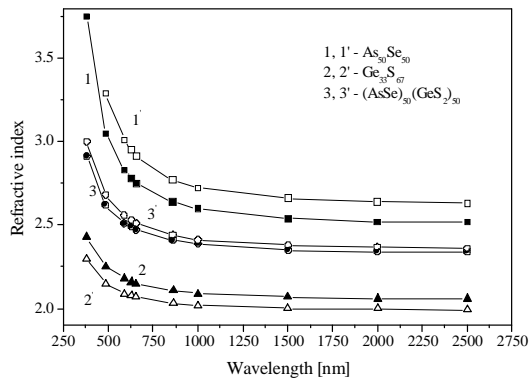


Fig. 2. Refractive index, n , vs. wavelength, λ , for thin As-Se-S-Ge film before and after light exposure from a halogen lamp.

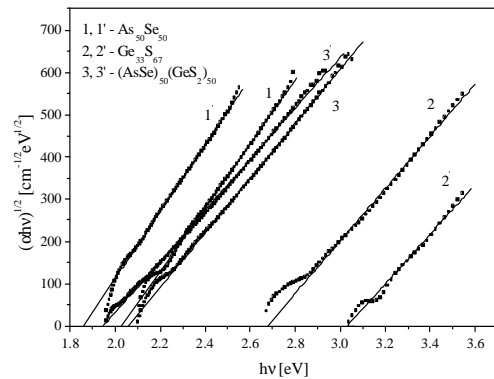


Fig. 3. Optical absorption edge $(\alpha h\nu)^{1/2}$ vs. energy of photon ($h\nu$) for unexposed and exposed thin As-Se-S-Ge films.

Table 2. Data for optical parameters of thin As-Se-S-Ge films depending on the film thickness.

Composition	$\Delta\lambda$ T=20%	Unexposed				Exposed			
		d (nm)	n (632.8 nm)	E_g (eV)	B $\text{cm}^{-1/2} \times$ $\text{eV}^{-1/2}$	d (nm)	n (632. 8 nm)	E_g (eV)	B $\text{cm}^{-1/2} \times$ $\text{eV}^{-1/2}$
$\text{As}_{28}\text{Se}_{72}$	+2	1267	2.99	1.83	859	1237	3.05	1.81	915
$\text{As}_{40}\text{Se}_{60}$	+19	1267	2.97	1.83	818	1249	3.14	1.78	872
$\text{As}_{50}\text{Se}_{50}$	+50	804	2.78	2.01	823	800	2.94	1.86	840
$\text{Ge}_{33}\text{S}_{67}$	-25	785	2.16	2.68	620	810	2.08	3.06	586
$\text{As}_{40}\text{Se}_{40}\text{Ge}_7\text{S}_{13}$	+41	840	2.65	2.12	685	830	2.83	1.94	680
$\text{As}_{28}\text{Se}_{33}\text{Ge}_{15}\text{S}_{24}$	-12	980	2.54	2.02	624	978	2.60	1.91	605
$\text{As}_{14}\text{Se}_{14}\text{Ge}_{25}\text{S}_{49}$	-20	975	2.36	2.22	540	958	2.41	2.08	480

As shown in Table 2 the values of $\Delta\lambda$, Δn and ΔE_g of thin $(\text{AsSe})_{50}(\text{GeS}_2)_{50}$ films are smaller than these of AsSe and GeS_2 which indicates that there is a compensation between the effects of

photodarkening and photobleaching. Since the system is so complicated we will continue with measuring the IR spectra and more details will be published in the near future.

The values of the refractive index of unexposed films monotonously decrease from 2.78 for $\text{As}_{50}\text{Se}_{50}$ to 2.16 for $\text{Ge}_{33}\text{S}_{67}$ films, and the relative deviation of the refractive index $\Delta n/n$ passes through a minimum (Fig. 4) at 50 at.% GeS_2 . That means that for films with higher AsSe-content the photoinduced changes are more pronounced.

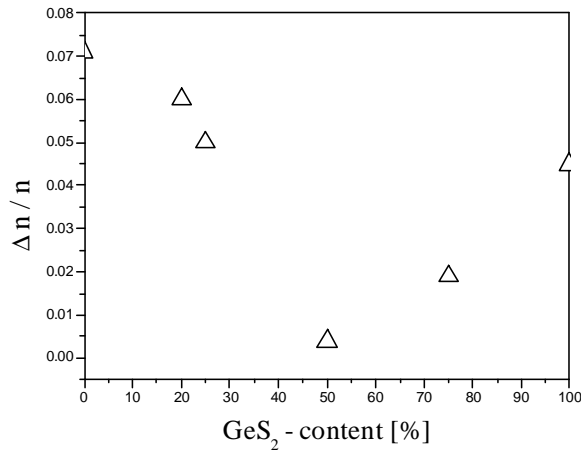


Fig. 4. Relative deviation of the refractive index ($\Delta n/n$) at $\lambda=632.8$ nm for thin AsSe- GeS_2 films.

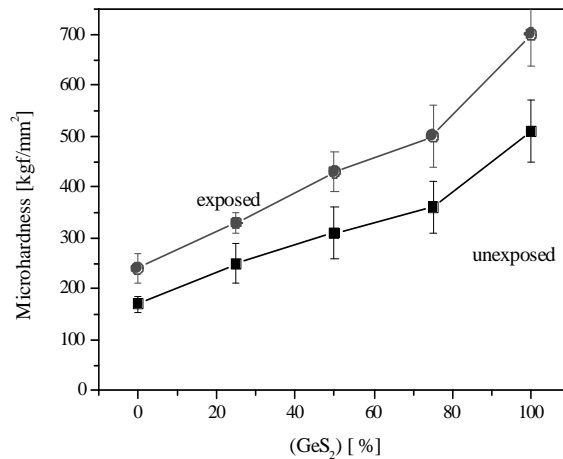


Fig. 5. Compositional dependence of the microhardness of unexposed and exposed thin As-Se-S-Ge films.

Studying the changes in the Knoop hardness (H_k) for As-Se thin films, we have found that it monotonously increases with increasing the As content from 120 kgf/mm^2 for $\text{As}_{28}\text{Se}_{72}$ films up to 170 kgf/mm^2 (for $\text{As}_{50}\text{Se}_{50}$ films). On comparison with data published in [24] for bulk samples, a difference is observed which is apparently due to the different conditions of glass synthesis and thin films preparation. Increasing the As content of As-Se layers increases the amount of cross-linking between the Se chains. Also, as arsenic is added, Se-Se bonds are broken in favour of formation of AsSe_3 units which consist of stronger As-Se bonds.

Fig. 5 shows the dependence of the Knoop hardness on the $\text{Ge}_{33}\text{S}_{67}$ content in the As-Se-S-Ge thin films. An effect of increasing the microhardness was obtained with the increase in the Ge content in the films because of the existence of stronger Ge-S bonds in the coatings. It is not clear if some exchanging between S and Se took place forming new compounds with Ge-Se and As-S

bonds. The IR spectra of the quaternary films showed only absorption peaks which characterize AsSe and GeSe₂ compounds. The results from our detailed investigation will be published elsewhere.

4. Conclusions

Conditions for glass synthesis of bulk samples from the system As-Se-S-Ge were established. Thin films with different content of GeS₂ were deposited by co-evaporation of AsSe and GeS₂ from two crucibles. From the transmission and reflection measurements, using the Swanepoel's method, the optical constants (n , k), E_g , and d of thin As-Se-S-Ge films was determined and the influence of the evaporation rate, thickness and light illumination has been demonstrated. It was found that the photoinduced changes in the refractive index after illumination for 120 min was 0.11 (4.4 %) and 0.16 (5.4 %) at 1500 nm for As₄₀Se₆₀ and As₅₀Se₅₀, respectively. Changes in the physicochemical and optical properties of the system As-Se-S-Ge films occurred. We claim that the increase in the AsSe-content in the system makes it more photosensitive, i.e. larger changes in the optical constants are observed. Films richer in AsSe show lower values of microhardness. The great changes in n obtained allow thin films of certain compositions to be used for production of Bragg gratings, as a media for irreversible recording as well as for anti-reflection coatings.

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