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Optical properties of multi-component arsenic-containing chalcogenide thin films

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Results from investigations on multi-component vacuum evaporated thin $As_{40}S_{60-x}Se_x$ (0<x<60) films are presented. The compositional dependence of the refractive index n and the absorption coefficient, α, have been studied. Linear dependences of n and the optical band gap, E_g, on the Se-content have been observed. In addition, in order to clarify the structure and to determine the interactions between the separate structural units, we have applied the single-oscillator model, proposed by Wemple and Di Domenico. Thus, the dispersion energy, E_d, single-oscillator energy, E_0, and effective coordination number per cation, N_c, have been calculated. In agreement with other publications, we have observed E_d and N_c increasing with Se-content. The influence of light on the dispersion parameters has been demonstrated. Some conclusions on the photo-induced changes in the optical properties and the structure of As-S-Se films have been drawn from IR spectra.

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1. Introduction

Chalcogenide glasses and particularly those from the system As-S-Se have been studied as focusing media materials - owing to the photo-induced refractive index and thickness changes, one could easily obtain graded-index, expansion or etched microlenses [1], as well as submicron diffraction gratings [2]. Moreover, a refractive index profile could be achieved simply by varying the chalcogenide film composition. Besides their interesting fundamental properties and significant linear response to low-intensity electromagnetic waves, chalcogenide glasses have been found to show a high third--order non-linearity under high-intensity electromagnetic irradiation. It has been demonstrated [3] that glasses from the ternary system As-S-Se possess a second-order nonlinear refractive index, n_2, up to 400 times that of silica. In order to adequately utilize chalcogenides' potentialities, it is of great importance that their structure and optical properties be thoroughly studied.

There are some reports on the structure and optical properties of bulk As-S-Se samples [3, 4], and few reported results from thin film studies, e.g. [5, 6].

This work is aimed at studying the influence of composition and light irradiation on the refractive index and optical band-gap of 1-μm thin $As_{40}S_{60-x}Se_x$ films. The results from the present study are complementary to our previous investigations [7] on the optical properties of the same compound films of thickness under 100 nm.

2. Experimental

2.1. Materials and sample preparation, measurements

Bulk glasses from the system $As_{40}S_{60-x}Se_x$ for x = 0 - 60 at.% were prepared by direct synthesis from elements of 5N purity, positioned in a quartz ampoule at 700°C for 12 hours. The thin films were deposited onto optical BK-7 glasses and graphite substrates by thermal evaporation under a vacuum of 3×10^{-3} Pa at room temperature. The evaporation rate was about 0.7-0.9 nm/s. The thickness desired was controlled by measuring the intrinsic frequency of a piezocrystal. The compositions of the bulk samples, as well as of the thin films, were determined by scanning electron microscopy with an X-ray microanalyser (Jeol Superprobe 733, Japan). The infrared spectra were taken using a FT-IR spectrometer (BRUKER FTS-40) in the range 400-150 cm^{-1} with 2 cm^{-1} resolution and 64 scans. Optical transmission and reflection measurements in the spectral range 350-2000 nm were carried out with a UV–VIS–NIR spectrophotometer (Cary 05E, USA). Thin films were exposed for 2-3 hours to halogen lamp irradiation (20 mW/cm^2).

2.2. Methods and models

From the transmission measurements, using a computer program, developed by Konstantinov [8] and based on the envelope method proposed by Swanepoel [9], the optical constants (refractive index, n and extinction coefficient, k) and thickness, d of the films were determined with an accuracy better than ± 1 %. Furthermore, the absorption coefficient, α ($1 \le \alpha d \le 10$) was calculated through the relation:

$$\alpha = \frac{1}{d}\ln\frac{(1-R)^2}{T} \qquad (1)$$

where R and T are the reflection and transmission of the film. Plotting $(\alpha\hbar\omega)^{1/2}$=f $(\alpha\hbar\omega)$ (where $\hbar\omega$ is the photon energy) for the high-absorption region ($\alpha \le 10^4$ cm^{-1}) and assuming Tauc's law [10], we determined the optical band-gap, E_g^{opt}.

The refractive index dispersion was analyzed, using the single-oscillator model, proposed by and named after Wemple & Di Domenico [11] (WDDM). According to the authors, the refractive index dispersion is given by the relation:

$$n^2(\hbar\omega) - 1 = \frac{E_d E_0}{E_0^{\,2} - \hbar^2\varpi^2} \qquad (2)$$

where E_d and E_0 are the dispersion and the single-oscillator energy, respectively. The main advantage of WDDM is that it relates E_d to some physical parameters of the material:

$$E_d = \beta N_c Z_a N_e \qquad (3)$$

where N_c is the coordination number of the cation, Z_a the anion's chemical valence, N_e the effective number of the electrons per anion; for covalent materials, β = 0.37 eV. Thus, the E_d values could be used for intermolecular interaction estimation.

3. Results and discussion

The X-ray microanalysis of the system $As_{40}S_{60-x}Se_x$ for x = 0, 15, 20, 30, 45, 60 at.% showed good agreement (± 1 at. %) between the bulk and thin film compositions. This indicates that no chemical decomposition occured during the vacuum deposition process.

The IR spectra of unexposed thin $As_{40}S_{60}$, $As_{40}S_{30}Se_{30}$ and $As_{40}Se_{60}$ films had two bands - one located between 180 and 280 cm^{-1} and another between 280 and 400 cm^{-1} (Fig. 1a).

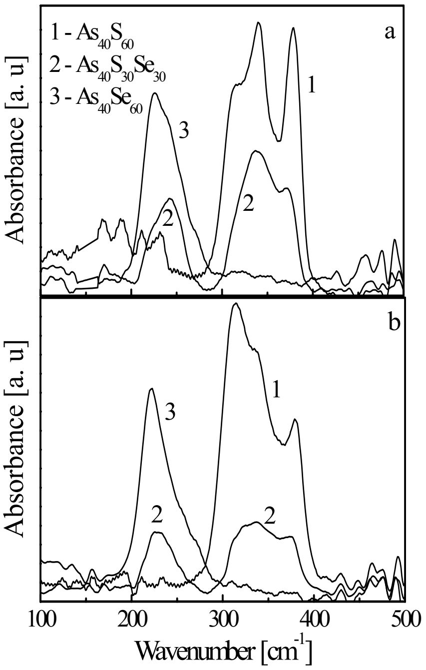

Fig. 1.IR spectra of unexposed (a) and exposed (b) thin As-S-Se films.

As-deposited $As_{40}S_{60}$ clearly shows peaks at 380, 340 and 315 cm^{-1}. The higher intensity of the first two peaks compared to the peak at 315 cm^{-1} (asymmetric stretching vibration of $AsS_{3/2}$ structural units) indicates that many As_4S_4 molecules are present in the films immediately after evaporation. The evaporated $As_{40}S_{30}Se_{30}$ film shows three peaks - at 372, 338 (with lower intensity compared to those from $As_{40}S_{60}$) and 242 cm^{-1}, while a typical (for As-Se vibrations in $AsSe_3$ pyramids) peak at 225 cm^{-1} exists in the $As_{40}Se_{60}$ absorption spectrum. After exposure to light of the $As_{40}S_{60}$ film, the intensity of the peaks at 380 and 340 cm^{-1} drastically decreases, while that at 315 cm^{-1} increases, which can be attributed to an increased number of As-S bonds. This suggests that the molecular species, which have peaks at 380 and 340 cm^{-1}, are polymerized to form As_2S_3 networks [12]. The spectrum of the film becomes similar to that of the bulk glasses. The peaks at 372 and 338 cm^{-1} from the unexposed $As_{40}S_{30}Se_{30}$ film get less intense after exposure, and the peak at 242 cm^{-1} shifts to lower wavenumbers (230 cm^{-1}). After exposure to light, the shoulders at 271 and 238 cm^{-1}, observed in the spectrum of the as-deposited $As_{40}Se_{60}$ film, disappear. This fact suggests that the formation of $AsS_{3/2}$ and $AsSe_{3/2}$ occurs simultaneously, and this is consistent with the formation of $AsSSe_2$, AsS_2Se hetero-pyramids in the glassy network of thin As-S-Se films [13].

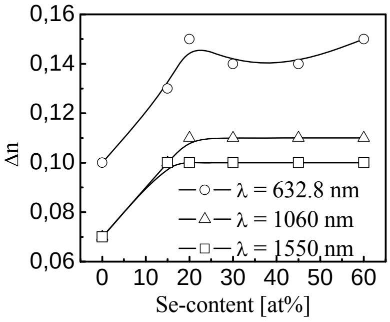

Fig. 2. Refractive index dispersion before (empty symbols) and after (filled symbols) light exposure; in the inset, the compositional dependence of the refractive index (at λ=633 nm) is given.

The refractive index dispersion for three specific compositions is plotted in fig. 2. As shown, in the whole spectral region the refractive index increases with increasing Se-content. More, the compositional dependence of n at a certain wavelength (the inset of fig. 2) is linear. The calculated values of n at λ = 633 nm increase from 2.43 to 3.03 for a Se-content 0-60 at. %, respectively. After light irradiation, thin films of all compositions exhibit the photo-darkening effect, which (in terms of refractive index dispersion) consists of a refractive index increase. After exposure to light, *n* increases by about 4-5% from its initial values, reaching 2.53 for $As_{40}S_{60}$ and 3.18 for $As_{40}Se_{60}$.

The photo-induced increase in *n* is also Se-content dependent. Fig.3 shows $\Delta n = n_{exp}-n_{unexp}$ (where ‘unexp’ and ‘exp’ indicate the as-deposited and illuminated layers, respectively) vs. Se-content for three fixed wavelengths (λ = 633, 1060 and 1550 nm).

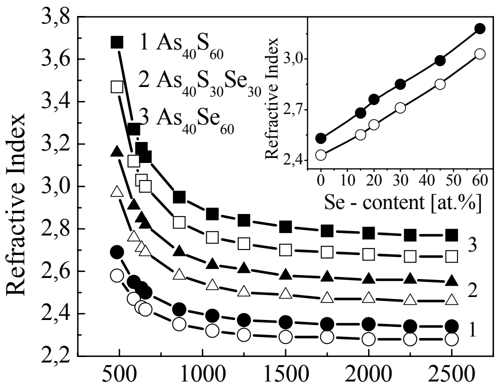

Fig. 3.Photoinduced refractive index change vs. Se-content in layers from the system $As_{40}S_{60-x}Se_x$

Increasing the Se-content in the system $As_{40}S_{60-x}Se_x$ to more than 15 at. % leads to no significant change in Δ*n* with composition. It is clearly shown that the photoinduced changes at λ = 633 nm are greater than those at 1060 and 1550 nm, which is reasonable as the energy corresponding to 633 nm is in the area of strong dispersion of *n*. Optical band-gap calculations presented below confirm this suggestion.

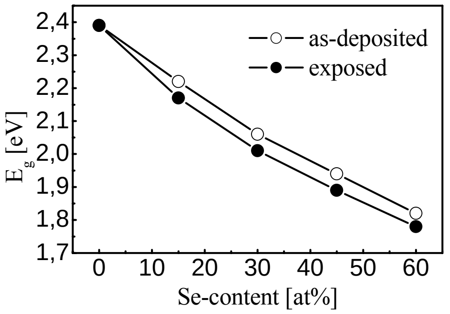

Fig. 4. Compositional dependence of the optical band-gap for the system $As_{40}S_{60-x}Se_x$

The compositional dependence of optical band-gap, E_g^{opt}, is plotted on fig. 4. When increasing Se content in the unexposed films from 0 to 60 at. %, E_g^{opt} linearly decreases from 2.38 to 1.82 eV. Indeed, the optical band-gap of As_2Se_3 (1.81 eV) was reported to be smaller than that of As_2S_3 (2.37 eV) [14]. As expected, enriching the thin films from the system $As_{40}S_{60-x}Se_x$ with Se leads to a certain increase of $AsSe_{3/2}$ pyramidal structures and therefore the obtained compositional dependence of E_g^{opt} appears to be quite reasonable.

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 1.

Table 1. Dispersion parameters for the system $As_{40}S_{60-x}Se_x$; the “unexp” and “exp” indices refer to the as-deposited and exposed films.

composition		E_0 [eV]	E_d [eV]	N_c
$As_{40}S_{60}$	unexp	4.94	20.7	3
	exp	4.76	22.7	3.3
$As_{40}S_{45}Se_{15}$	unexp	4.64	21	3
	exp	4.45	22.1	3.2
$As_{40}S_{40}Se_{20}$	unexp	4.59	21.8	3.2
	exp	4.28	22.3	3.2
$As_{40}S_{30}Se_{30}$	unexp	4.23	21.1	3.1
	exp	4.05	22	3.2
$As_{40}S_{15}Se_{45}$	unexp	4.07	22.2	3.2
	exp	3.90	23	3.3
$As_{40}Se_{60}$	unexp	3.86	22.7	3.3
	exp	3.64	23.5	3.4

Inasmuch as E_0 is considered to vary in proportion to E_g^{opt} [15], it is expected that the compositional dependence of E_0 will be similar to that of E_g^{opt}. Indeed, as shown in Table 1, E_0 decreases with increasing Se-content and also after exposure. At the same time, E_d increases and according to Eq.(3) (and assuming $\beta = 0.37$ eV, $N_e = 28/3$

and $Z_a = 2$ to be appropriate for all compositions from the system As_2Ch_3), that is due to the increase of N_c. The overall increase in E_d (respectively, N_c) with increasing Se-content is a probable indicator of a greater interaction between the separate structural layers (consisting of $AsS_{3-m}Se_m$ for m = 1 or 2 pyramidal units and interacting through As atoms). The results from the IR-spectra, as discussed above, are consistent with this suggestion. Moreover, the dispersion parameters values, obtained from the present study (Table 1), are close to those reported in [5].

4. Conclusions

The optimal conditions for direct synthesis of bulk samples and for vacuum thermal evaporation of thin films from the system $As_{40}S_{60-x}Se_x$ 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. The linear compositional dependence of the optical band-gap is a decreasing one. Discussions on the dispersion parameters were made and it was confirmed that an increase in the Se-content enhances the interactions between the separate structural layers in the amorphous matrix of the system $As_{40}S_{60-x}Se_x$.

Acknowledgements

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