Linear and non-linear optical properties of thin films from the system As-S-Se[*]

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Results from a study of the photodarkening effect in amorphous As-S-Se thin films, after exposure to light, are reported. Thin films with thicknesses of 50 to 1000 nm and of different compositions were deposited by thermal vacuum evaporation. Spectrophotometric measurements were carried out in the spectral region 400-2000 nm. An "envelope" method or a triple method (for very thin films) was used to determine the thickness, refractive index and extinction coefficient of the films. The optical constants of the films from the system As-S-Se were found to be thickness-independent. It was observed that an increase in the Se/(S+Se) ratio leads to a linear increase in the refractive index, n, at $\lambda = 1.55\ \mu m$, and to a linear decrease in the optical band-gap for the systems with As contents of 28, 33 and 40 at. %. After light exposure, an increase in n and a decrease in the film's thickness, d were observed. Predictions for the non-linear absorption and index of refraction were made.

1. Introduction

The possibility of obtaining micro-lenses and diffraction gratings, waveguides and non-linear switching devices from chalcogenides have been widely examined [1-4]. There are several systematic studies of the optical properties of glasses from the systems $As_{33}S_{67-x}Se_x$ and $As_{40}S_{60-x}Se_x$ [5-7], etc. It is interesting to compare the results for the triple system, depending on the concentration of As, but since the studies have not been implemented under the same experimental conditions, it will not be a just comparison.

Concerning the prediction of a nonlinear response of chalcogenides to light, one can use different models and formulae [8-11], the basic ones of which are Boling and Glass's [8] and Sheik-Bahae's [9]. The latter enables us to determine not only the magnitude at a certain wavelength, but the dispersion of the non-linear refractive index n_2, as well. Although it was originally developed for crystalline semiconductors, it has been shown [12] that it could be applied as a rough approximation to glasses and amorphous films.

We have previously reported results from our studies of thin films (with thicknesses between 0.05 and 1 μm) from the system $As_{40}S_{60-x}Se_x$ and $As_{33}S_{67-x}Se_x$ [13-15].

We report in this paper a comparative study of the optical properties of thin films from the systems $As_{28}S_{72-x}Se_x$, $As_{33}S_{67-x}Se_x$ and $As_{40}S_{60-x}Se_x$. Our aim was to determine the influence of the As content on the linear and non-linear optical properties of thin chalcogenide films. We also discuss the refractive index dependence on the thickness of the films.

2. Experimental

Bulk glasses of compositions $As_{28}S_{72-x}Se_x$ (x = 0, 36, 72 at. %), $As_{33}S_{67-x}Se_x$ (x = 0, 17, 34, 51, 67 at. %) and $As_{40}S_{60-x}Se_x$ (x = 0, 15, 30, 45, 60 at. %) were synthesized from 5N purity elements, evacuated in a quartz ampoule at 760 °C for 12 hours, with subsequent cooling in ice water. The thin films were deposited onto optical BK-7 glass and Si 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 desired thickness was controlled by measuring the intrinsic frequency of a piezocrystal. Optical transmission and reflection measurements in the spectral range 400-2000 nm were carried out by a UV–VIS–NIR spectrophotometer (Cary 05E, USA). The samples were exposed to a halogen lamp (20 mW/cm²) for 15 - 240 min, the duration being dependent on the composition and the thickness of the film.

From the spectrophotometric measurements the optical constants – linear refractive index, n and extinction

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coefficient, k – and thickness of the films, d were determined, using single, double or triple methods, as described elsewhere [13-15]. The program used to calculate n can determine it to an accuracy of $\pm$ 0.5 % for an error in the transmittance of $\pm$ 0.1 %.

The absorption coefficient, α, of the films was calculated from the relation $\alpha = 4\pi k/\lambda$, where λ is the wavelength. The optical band gap E_g^{opt} for non-direct transitions was derived by Tauc's law [16].

If we consider the non-linear response of the chalcogenide medium to intense light with photon energies $\hbar\omega < E_g^{opt}$, we know that two-photon absorption will be involved in the interband transitions [17]. One of the associated effects is the induction of a non-linear refractive index, n_2 [esu] or γ [m²/W].

It is known [18] that the intensity-dependent refractive index n' can be expressed as:

$$n' = n + \gamma I = n + \frac{n_2}{2}|E|^2 \qquad (1),$$

where n is the linear, weak-field refractive index, I denotes the intensity and E - the strength of the applied optical field and n_2 gives the rate at which the refractive index increases with increasing optical intensity.

For prediction of the non-linear refractive index, we have applied a formula developed by Sheik-Bahae et al. [9]. In the simple model, γ can be expressed as:

$$\gamma = K \frac{\hbar c \sqrt{E_p}}{2n^2 E_g^{opt4}} G_2(\hbar\omega/E_g^{opt}) \qquad (2),$$

where $E_p = 21$ eV, K is found to be 3.1×10^{-8} in units such that E_p and E_g^{opt} are measured in eV, and γ is measured in m²/W, $\hbar$ is the Dirac constant, c the speed of light in a vacuum and G_2 - a universal function:

$$G_2(x) = \frac{-2 + 6x - 3x^2 - x^3 - \frac{3}{4}x^4 - \frac{3}{4}x^5 + 2(1-2x)^{3/2}\Theta(1-2x)}{64x^6} \qquad (3),$$

where Θ is the Heaviside step function. n_2 and γ are related by:

$$n_2[esu] = \frac{cn}{40\pi}\gamma[SI] \qquad (4).$$

3. Results and discussion

The dependence of n at a certain wavelength on the Se/(S+Se) ratio, for the three series of studied materials, is plotted in Fig. 1. The refractive index linearly increases with increasing Se-content. For the system $As_{28}(S+Se)_{72}$, it varies from 2.23 ($As_{28}S_{72}$) to 2.64 ($As_{28}Se_{72}$). The values for $As_{33}(S+Se)_{67}$ and $As_{40}(S+Se)_{60}$ were published in [14, 15].
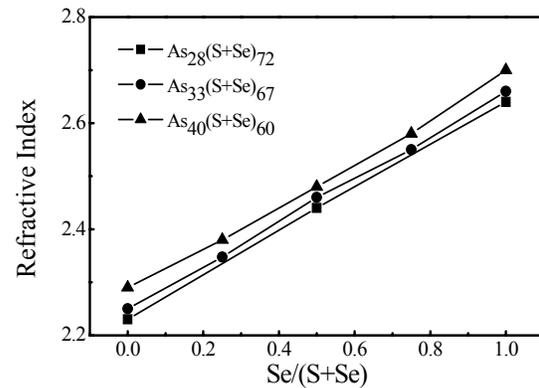
Fig. 1. Refractive index of thin As-S-Se films at $\lambda = 1.55$ μm, vs. Se/(S+Se) ratio.

Using the dispersion parameters published in [6, 7], we derived the dispersion of n for those films and found that the refractive index values of our layers are very close to theirs. Compared to the results published in [5], our films possess lower refractive indices. It is seen that the dependence of n on the As-content is not very strong, although a tendency for an increasing refractive index with increasing As-content in the layers' composition is observed.

In Fig. 2, the compositional dependence of the relative photoinduced increase ($\Delta n/n$) of n is plotted. It is defined as ($n_{exp}-n_{un}$)/n_{un}, where "un" and "exp" denote the as-deposited and exposed films, respectively. It is observed that the photosensitivity of the chalcogenide films is determined by the As rather than the Se content. The highest values of $\Delta n/n$ (4-4.2 %) are obtained for the system $As_{40}(S+Se)_{60}$, around the compositions Se/(S+Se) = 0.25 – 0.5. A decreasing As-content in the films leads to a decrease in their sensitivity to light irradiation - $\Delta n/n$ = 2.6 % ($As_{33}Se_{67}$) and 1.9 % ($As_{28}Se_{72}$).

The non-linear refractive index n_2, according to Eqs. (2-4), as a function of the normalized photon energy $\hbar\omega/E_g^{opt}$ for three compositions of the system $As_{40}(S+Se)_{60}$ is plotted in Fig. 3. It is seen that the non-linear refractive index at low photon energy to band gap ratios displays small positive values. Then, n_2 gradually rises, giving a broad peak at $\hbar\omega$~$0.55E_g^{opt}$, after which it decreases, becoming negative for energies $\hbar\omega > 0.7E_g^{opt}$.

In other words, the nonlinear refractive index is strongly dependent on the optical band-gap and reaches maximum values at the edges of the two-
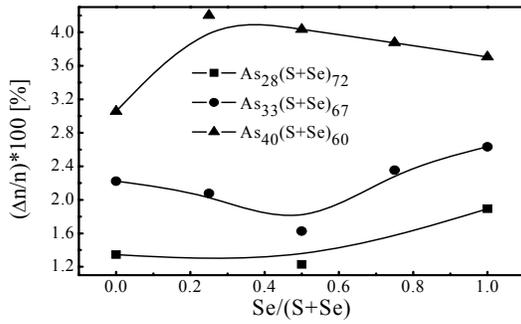
Fig. 2. Relative photoinduced change of the refractive index at λ = 1.55 μm vs. Se/(S+Se) ratio.
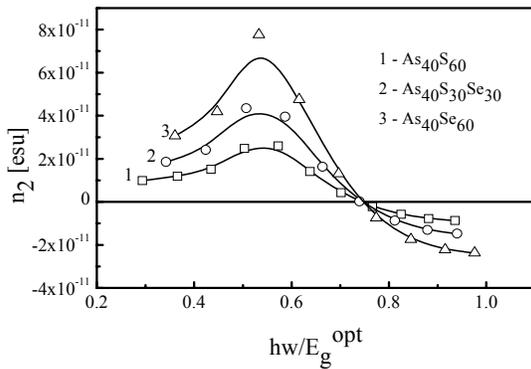
Fig. 3. Non-linear refractive index of thin $As_{40}S_{60}$, $As_{40}S_{30}Se_{30}$, $As_{40}Se_{60}$ films vs. $\hbar\omega/E_g^{opt}$.

Table 1 Optical properties of as-deposited films

Composition	E_g [eV]	at 1.55 μm		γ/γ fused silica
		γ [m²/W] x10^{-18}	n_2 [esu] x10^{-11}	
$As_{28}S_{72}$	2.55	1.58	0.84	58
$As_{28}S_{36}Se_{36}$	2.07	3.73	2.18	136
$As_{28}Se_{72}$	1.82	6.58	4.14	240
$As_{33}S_{67}$	2.55	1.55	0.83	57
$As_{32}S_{34}Se_{34}$	2.06	3.77	2.21	138
$As_{33}Se_{67}$	1.78	7.44	4.72	271
$As_{40}S_{60}$	2.40	1.96	1.08	71
$As_{40}S_{30}Se_{30}$	2.08	3.58	2.1	131
$As_{40}Se_{60}$	1.82	6.32	4.06	231

It is seen (Table 1) that the nonlinear refractive index of chalcogenides is more than 50 - 250 times higher than that of fused silica. In [20] the results from measurements of γ at λ = 1.55 μm for As-S-Se bulk glasses are reported. The nonlinear refractive indices of As_2S_3 and As_2Se_3 are calculated to be respectively 73 and 295 times higher than that of silica.

Finally, we have investigated the dependence of the optical constants on the thickness of the films, regarding their potential application in photonic integrated circuits.
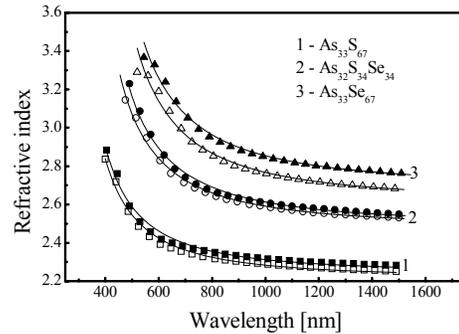
Fig. 4. Refractive index dispersion of as-deposited (empty symbols) and exposed (filled symbols) 70 - 80 nm thick As-S-Se films.

We have previously reported results for 50-80 nm and ~1 μm [13, 14] films from the system $As_{40}(S+Se)_{60}$, and found the refractive index to be thickness independent. In Fig. 4, the dispersion of n for 70-80 nm films from the system $As_{33}(S+Se)_{67}$ is plotted. The refractive index increases with increasing Se content and after exposure to light, though there is not a considerable photoinduced change for $As_{33}S_{67}$ and $As_{32}S_{34}Se_{34}$ films.

The calculated values at λ = 1.55 μm are 2.24 ($As_{33}S_{67}$) and 2.68 ($As_{33}Se_{67}$). These, within the accuracy

and single-photon absorption. According to Eq. (1), the positive values of n_2 lead to an increase in n'. Thus, a refractive index gradient is obtained within the material and it acts as a positive lens, which is known as the "self-focusing effect". It is also seen that increasing Se content in the system leads to an increase in the n_2 values. As shown in Table 1, the same tendencies for the other two systems - $As_{28}(S+Se)_{72}$ and $As_{33}(S+Se)_{67}$ - are observed. According to Eq. (2), the nonlinear refractive index is strongly dependent on the optical band-gap, and since enriching the film composition with Se narrows the band-gap (Table 1), the observance above is absolutely expected.

The values of n_2, calculated by Petkov and Ewen [10], by means of formulae developed for long wavelengths, are 0.97×10^{-11} esu for $As_{40}S_{60}$, 0.98×10^{-11} esu for $As_{32}S_{68}$ and 0.81×10^{-11} esu for $As_{28}S_{72}$. Tichá and Tichý, using a semi-empirical relation for n_2 [11], obtained three times higher values for $As_{40}S(Se)_{60}$ than we did. We also compared the predicted values for γ of the chalcogenide films to that measured for fused silica ($\gamma = 2.74\times10^{-20}$ m²/W at λ = 1.53 μm [19]).

of the method applied for their determination, coincide with the values obtained for ~1 μm films [15]. A substantial disparity, observed for $As_{40}(S+Se)_{60}$ films, is that the photoinduced change in the refractive index is greater in 50 nm films than in 1 μm ones. This is due to the penetration depth of the exposing irradiation, which is probably not sufficient to irradiate the whole 1 μm layer.

4. Conclusions

The conditions for the glass synthesis and evaporation of thin films (50-1000 nm) from the systems $As_{40}(S+Se)_{60}$, $As_{33}(S+Se)_{67}$ and $As_{28}(S+Se)_{72}$ were established. From spectrophotometric measurements, the optical constants and thicknesses of the layers were determined. For the three studied systems, it was found that the linear refractive index is a linearly growing function of Se-content. Our results are in a good agreement with those in [6, 7]. It was shown that the As content in the system does not significantly affect the refractive index values, but only the photoinduced change in it. The highest values of $\Delta n/n$ (4-4.2 %) were obtained for the system $As_{40}(S+Se)_{60}$ compared to 2.6 % for $As_{33}Se_{67}$ and 1.9 % for $As_{28}Se_{72}$. The dispersion of nonlinear refractive index γ (or n_2) was predicted, applying the model proposed by Sheik-Bahae et al. [9]. It was found that around 0.5 E_g^{opt} (at the two-photon absorption edge), n_2 reaches a maximum positive value. The fact that n_2 is > 0 in the energy interval 0.2 – 0.7 E_g^{opt}, and the resulting effects of self-focusing, self-trapping and laser beam filamentation [17], could be utilized in optical device fabrication – such as optical power limiters and switches. We have also found a certain agreement between the values of n_2, calculated according to the formulae of Sheik-Bahae [9] and the one developed by Petkov and Ewen [10]. Eventually, we have shown that the thickness of the films (within the interval 50 – 1000 nm) does not affect the calculated optical constants, but only the photoinduced changes in them.

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