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Glassy $As_{40}Se_{25}Te_{35}$ films with high refractive index

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Some optical properties (transmission spectra, spectra of refractive index and absorption coefficient), photoinduced structural transformations, conductivity and photoconductivity are investigated in the As-Se-Te glassy films with increased amount of Te. High values of refractive index and keeping of property of photostructural transformations allow the recommendation of the $As_{40}Se_{25}Te_{35}$ films as the candidates for application in IR electro-optical devices.

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1. Introduction

Chalcogenide glassy As-Se films have been studied by many authors due to interesting physical phenomena observed in them and also in consequence of some prospects for application of such films in electro-optics as photoresists and photorecording media of very high resolution. One of important parameters of such films is their high refractive index, permitting the use of these films in planar optics as efficient waveguides [1,2], in micro-optics as the base for IR micro-lens and micro-prisms arrays [3-5] and in the photonic-band-gap structures [6-8] having many applications in modern photonics. Introduction of 10 at % of tellurium in the As-Se film was shown to increase the value of refractive index (up to ~ 3.2 at 850 nm), keeping the photoresist properties of the film and increasing the photosensitivity in the red and infrared ranges [9].

For various chalcogenide films applications in the IR micro-optics it is important to understand to what value the refractive index can be increased with keeping the effect of photostructural transformations at the growth of the tellurium content in the film. We did not find in the literature any information about the optical properties of As-Se-Te glassy films with increased amount of tellurium although for the bulk chalcogenide glasses of the Ge-As-Se-Te system with large tellurium content very high values of refractive index were reported [10].

In this paper, we report about the fabrication and study of glassy As-Se-Te films with larger Te content: $As_{40}Se_{40}Te_{20}$, $As_{40}Se_{25}Te_{35}$, $As_{40}Se_{15}Te_{45}$ and $As_{40}Se_{12}Te_{48}$ films. Main study was made with $As_{40}Se_{25}Te_{35}$ films (35 at.% of Te) which are characterized by high values of refractive index and kept the photoresist properties.

2. Experimental

All films were fabricated by thermal evaporation of starting crushed three-component glassy chalcogenide materials from usual quartz crucibles onto suitably cleaned Corning glass substrates in vacuum of (1-3) × 10^{-6} Torr. Thickness of the films was in the range of 0.1-1.0 μm. X-ray study confirmed that all films are amorphous. Spectra of refractive index and absorption coefficient in the films were calculated by the Swanepoel method [11], while a Hitachi U-1100 Spectrophotometer was used in order to measure the transmission spectra in the non-irradiated, irradiated and Ag-photodoped regions of the films. Photostructural transformations in the films were excited by the He-Ne laser light irradiation and taking into account the very strong absorption of the visible light in thick films, investigation of both photodarkening and photoinduced dissolution was performed using very thin (0.1 μm) samples. In the study of photodarkening, the two-beam installation [12] was used, and in investigation of photoinduced dissolution, the times of total dissolution of non-irradiated and irradiated areas of the film were measured.

Volt-ampere characteristics of dark conductivity and photoconductivity were measured using 610C Keithley Electrometer in the samples having the "gap type" gold electrodes with distance ~ 1 mm between them. The inter-electrode space was irradiated by the He-Ne laser light with intensity 2.75 W/cm^2.

For the study of Ag-photodoping, the ~ 2 μm As-Se-Te films were covered by 100 Å layer of silver by evaporation in the vacuum of 3×10^{-7} Torr, and such two-layer samples were irradiated by the light of Xe-lamp.

3. Experimental results

In the following part, mainly the results obtained at study of $As_{40}Se_{25}Te_{35}$ films will be described.

3.1 Optical properties

Typical transmission spectrum of the $As_{40}Se_{25}Te_{35}$ film having thickness 1.0 μm in the range 500 –2500 nm is shown in Fig. 1. It is seen that the film starts to transmit the light only after 900 nm, practically all visible light is absorbing in the film of this thickness. Figs. 2 and 3 demonstrate the spectra of refractive index and absorption coefficient obtained on the base of analysis of the transmission spectrum. We see that the refractive index has sufficiently large values between 2.7 and 3.6 in this spectral range. At shorter wave-lengths refractive index has vary large values but simultaneously the absorption coefficient also increases strongly enough. As it is seen in Fig. 3, absorption coefficient in the studied spectral range has values (1–4) × 10^3 cm^1.

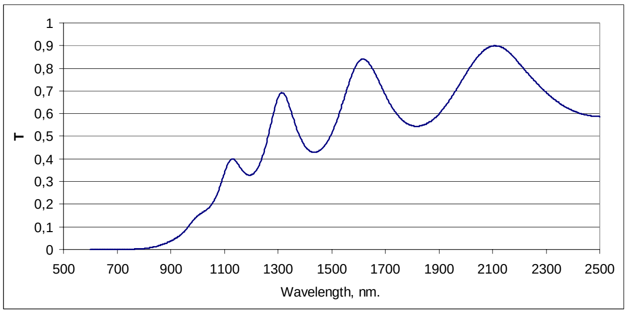

Fig. 1. Transmission spectrum of the $As_{40}Se_{25}Te_{35}$ film with thickness 1.0 µm.

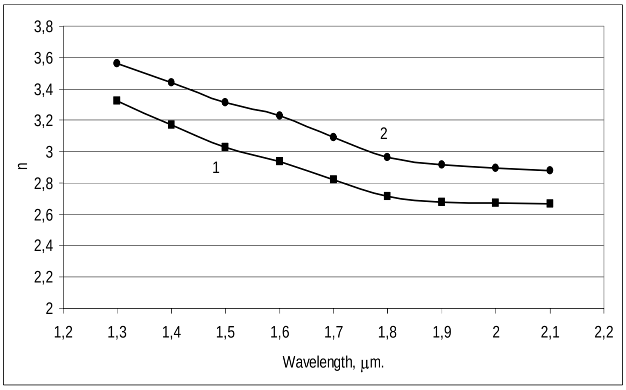

Fig. 2. Refractive index spectrum for the non-irradiated (1) and from Xe-lamp irradiated (2) $As_{40}Se_{25}Te_{35}$ film.

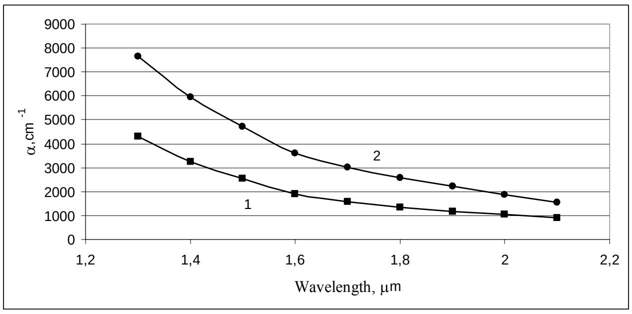

Fig. 3. Absorption coefficient spectrum for the non-irradiated (1) and from Xe - lamp irradiated (2) $As_{40}Se_{25}Te_{35}$ film.

Both the refractive index and absorption coefficient in the whole spectral range studied are increased after light irradiation.

3.2. Photoinduced phenomena

We usually study the photoinduced phenomena under action of different gas lasers. In our case, even for the most long wave-length He-Ne laser (λ = 632 nm) absorption in $As_{40}Se_{25}Te_{35}$ films is so large that we could investigate only very thin (100 nm) samples. In Fig. 4 the photodarkening of thin $As_{40}Se_{25}Te_{35}$ film induced by the He-Ne laser beam with energy 2.75 W/cm^2 is shown. Of course, the value of photodarkening in this film is essentially smaller than that in the $As_{45}Se_{45}Te_{10}$ film, as it is seen from the figure.

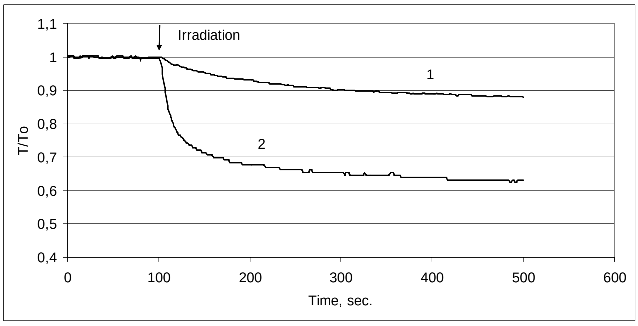

Fig. 4. Kinetics of photodarkening of thin $As_{40}Se_{25}Te_{35}$ (1) and $As_{45}Se_{45}Te_{10}$ (2) films.

In the next Table, the data about the photoinduced dissolution of thin $As_{40}Se_{25}Te_{35}$ and $As_{45}Se_{45}Te_{10}$ films, induced by irradiation with the light beams of different lasers, are shown.

Table. Dissolution contrast values observed in the $As_{40}Se_{25}Te_{35}$ and $As_{45}Se_{45}Te_{10}$ films irradiated by the light of different sources.

Film composition	Developer composition	Nd:YAG laser 532 nm, 400 mW/cm^2	He-Ne laser 632 nm, 2.75 W/cm^2	Xe-lamp 12 mW/cm^2
$As_{40}Se_{25}Te_{35}$	60% EDA* 40% DMF**	9	11	6
$As_{45}Se_{45}Te_{10}$	10% EDA* 90% DMF**	30	60	16

In this table * Ethylenediamine, ** Dimethylformamide

The dissolution contrast is the ratio of the dissolution rates for the non-irradiated and irradiated areas of the chalcogenide film.

3.3. Conductivity and photoconductivity

The volt-ampere characteristics of the typical $As_{40}Se_{25}Te_{35}$ film in darkness and under laser light irradiation are shown in Fig. 5. For comparison, the similar volt-ampere characteristics of the $As_{45}Se_{45}Te_{10}$ films are also demonstrated. From these linear characteristics the values of conductivity $\sim 6 \times 10^{-4}$ $Om^{-1}\cdot cm^{-1}$ and photoconductivity $\sim 2\times10^{-4}$ $Om^{-1}\cdot cm^{-1}$ for $As_{40}Se_{25}Te_{35}$ film and $\sim 5\times10^{-7}$ $Om^{-1}\cdot cm^{-1}$ and $\sim 1\times10^{-6}$ $Om^{-1}\cdot cm^{-1}$ for $As_{45}Se_{45}Te_{10}$ film were determined.

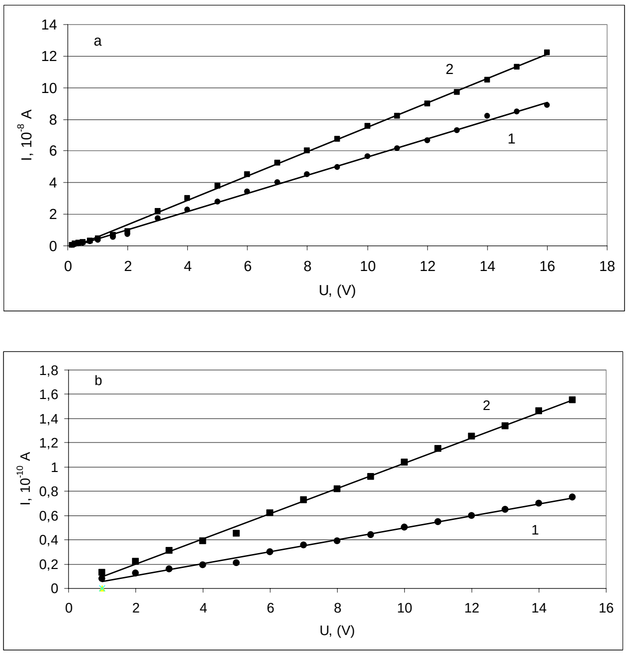

Fig. 5. Volt-ampere characteristics of $As_{40}Se_{25}Te_{35}$ (a) and $As_{45}Se_{45}Te_{10}$ (b) films in darkness (1) and under laser light irradiation (2).

3.4. Some additional data

Together with $As_{40}Se_{25}Te_{35}$ films, the films of other compositions: $As_{40}Se_{40}Te_{20}$, $As_{40}Se_{15}Te_{45}$ and $As_{40}Se_{12}Te_{48}$ were also investigated, but in $As_{40}Se_{15}Te_{45}$ and $As_{40}Se_{12}Te_{48}$ films we practically could not record the photostructural transformations, induced by the He-Ne laser light, and the $As_{40}Se_{40}Te_{20}$ films had smaller refractive index than the $As_{40}Se_{25}Te_{35}$ films and therefore they are not so interesting and prospective for the IR application.

In all films we recorded the process of Ag-photodoping, which was accompanied by the long wavelength shift of transmission spectra and stopping of dissolution in the amine-based developers.

5. Conclusion

This investigation shows that the increase of Te content in the As-Se-Te films keeps their amorphous state, increases the refractive index and keeps (at least up to 35 at.% of Te) the property of photostructural transformations. The conductivity of the films increases with increased amount of Te but the photoconductivity continues to be observable at least till $As_{40}Se_{25}Te_{35}$ films. Obtained data indicate that the As-Se-Te films with increased Te content are the interesting object for the study of various photoinduced processes. These data must also help to specialists who are busy with application of chalcogenide glassy films in the IR electro-optics and micro-optics.

In conclusion, the authors wish to take this opportunity to congratulate Professor Radu Grigorovici on his 95th birthday and to wish him a good health, optimism and activity.

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