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Optical properties of thin Ag/As-S-Ge films

R. Todorov*, A. Lalova, V. Lozanova

Acad. J. Malinowski Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences
Acad. G. Bonchev Str., BG-1113 Sofia, Bulgaria

Subject of study of the present work are the optical properties of thin films of the system As-S-Ge and their changes after photo-diffusion of silver. For this purpose, thin chalcogenide layers were deposited on substrates of optical glass BK-7 and thin silver film was evaporated after by thermal evaporation. The dependence of the changes in the transmittance spectra, refractive index and optical band gap of the films on the time of illumination are traced. From the resulting dependencies conclusions are drawn about the mechanism of diffusion of silver in thin films of As-S-Ge. It was shown, that significant changes in their optical properties are observed after diffusion of the silver. For a thin film with a composition $As_{30}Ge_{10}S_{60}$ the refractive index increases from 2.64 to 2.98 at a wavelength of 488 nm after silver photo-doping. The possibility of relief diffraction grating recording with 0.7 *mu*m line width s is shown.

Key words: chalcogenide glass, silver diffusion coefficient, optical properties, refractive index, diffraction

INTRODUCTION

Diffusion of silver into thin chacogenide films is an interesting phenomenon resulting in a significant change in the films' optical band gap and, respectively, of their physical properties [1]. The compositional dependences of the photo-dissolved Ag in Ge_xS_{1-x} system were studied thoroughly by Kawaguchi and Maruno [2]. Their data show a high photo-diffusion rate of Ag in both S and Ge-rich glasses, with the minimum for the composition GeS_2. The authors found that the S and Ge-rich glasses adopt a relatively low amount of Ag, with the maximum being adopted namely by GeS_2.

How the mixed glassy network, consisting of different types of structural units (pyramids, tetrahedral or octahedral units), influences the ion mobility and particularly – the photo-diffusion of the silver, is an interesting problem [3]. The photo-diffusion in the ternary system As–S–Se, consisting from AsS_3 and $AsSe_3$ pyramids, has been a subject of numerous papers [4–6]. The silver photo-diffusion in mixed glassy network of the thin films built from different tetrahedral units of Ge-S-Ge system is investigated in [7]. The glassy network of thin As–S–Ge films is built from $AsS_{3/2}$ pyramidal and $GeS_{4/2}$ tetrahedral units [8]. The kinetics of the photo-dissolution of Ag into S-rich As–S–Ge glassy films of various compositions along the tie-line $(GeS_4)x(AsS_3)_{1-x}$ $(0 \leq x \leq 1)$ was studied in [9]. The authors found that the photo-dissolution rate and the amount of adopted Ag (except for GeS_4) do not depend on the glass composition.

* To whom all correspondence should be sent:
rossen@iomt.bas.bg

The aim of the present paper is to investigate the optical properties of thin films of the system $As_{40-x}Ge_xS_{60}$ at constant sulfur content (60 at%) and their changes after photo-diffusion of silver.

EXPERIMENTAL DETAILS

Thin As–S–Ge films were deposited on optical BK-7 glass substrates, in a high vacuum of 10^{-3} Pa by thermal evaporation of previously weighted quantities of the bulk materials. Thin films of compositions $As_{30}S_{60}Ge_{10}$ and $As_5S_{60}Ge_{35}$, and thickness of about 1.0 μm were deposited. To obtain thin films with uniform thickness, the substrates were rotated continuously during the processes of the thermal evaporation. The substrate holder is a dome-shaped calotte that can be considered as a segment of a sphere. The evaporation sources are located approximately at the geometric centre of that sphere. The ready chalcogenide coatings were immediately placed under vacuum and thin silver film with 50 nm thickness was evaporated on top of them.

The films were exposed to monochromatic light at $\lambda = 488$ nm (Ar^+-laser – 120 mW/cm^2). The transmittance, T and reflectance, R, were measured by UV-VIS-NIR spectrophotometer Cary 5E (Australia) in the region 400–2000 nm with an accuracy of $\pm 0.1\%$ and $\pm 0.5\%$, respectively. To prevent samples from oxidation and influence of dark mobility of silver in chalcogenide films the spectrophotomeric measurements were done immediately after film's deposition. The time for collecting of the spectrphotomeric measurements of virgin samples was approximately 20 minutes. A suitable lithographic mask was used for the diffraction gratings recording.

RESULTS AND DISCUSSION

The time dependence of the transmittance for $As_{30}Ge_{10}S_{60}$/Ag coating at $\lambda = 488$ nm is shown in Fig. 1. Prior to illumination of the samples the value of T is low $\sim 0\%$. As silver progresses into the chalcogenide film, the transmittance increases reaching maximal values of 5–6% after 15 minutes.

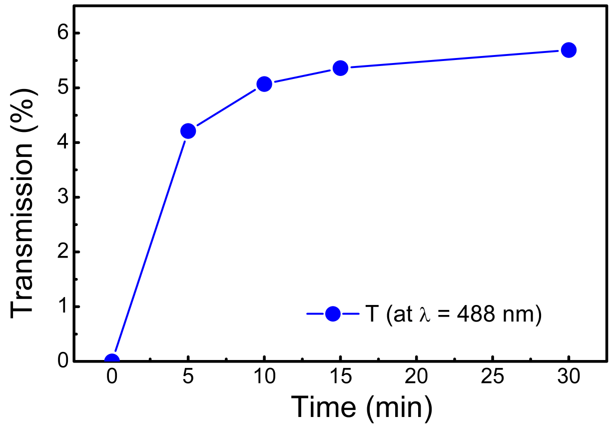

Fig. 1. Dependence of transmittance at $\lambda = 488$ nm of $As_{30}Ge_{10}S_{60}$/Ag coating on the time of irradiation with Ar-laser ($\lambda = 488$ nm).

The experimental results in Fig. 1 demonstrate that the transmittance changes more drastically in the first 10 minutes of the exposure to light. Bychkov et al. [10] found that the concentration profile of silver changes in time by the so called error function while in [11] it is demonstrated that the diffusion front possesses step-like profile due to the quick diffusion of mobile silver ions. Considering that the mass diffusion length is $L_d = 2\sqrt{Dt}$, we can make a rough calculation of the diffusion coefficient, D. Assuming that the time necessary for the silver to penetrate through a chalcogenide layer with thickness of 950 nm is approximately 600 s in this case, the silver diffusion coefficient is in the range of $D = 1.6 \times 10^{-14}$ cm^{2}s^{-1}. This value for the diffusion coefficient is lower in comparison with the one obtained in our previous work for As_2S_3 [12] and As–S–Se [5] films.

The refractive index, n and thickness, d of thin $As_{30}Ge_{10}S_{60}$ films were calculated from the interference extrema in the transmission spectra using Swanepoel's method [13, 14]. The program used to calculate n will determine it to an accuracy of $\pm 0.5\%$ for an error in the transmittance of $\pm 0.1\%$ [14]. The accuracy of the calculated thickness is 0.5-1%.

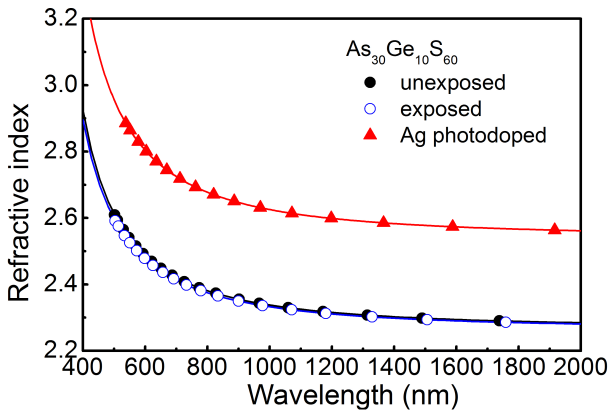

Fig. 2. Dispersion of the refractive index of the as-deposited thin $As_{30}Ge_{10}S_{60}$ film after illumination with Ar-laser and photo-doping with silver.

The calculated values for n were extrapolated by Sellmeier's equation:

$$n^2(\lambda) = 1 + \frac{A_1 \lambda^2}{\lambda^2 - A_2^2} \tag{1}$$

where A_1 and A_2 are Sellmeier's coefficients. The coefficients obtained from Eq. (1) with λ written in nm are presented in Table 1. The dispersion of calculated refractive indices of unexposed exposed and silver photo-doped thin films is shown in Fig. 2. It is seen that the refractive index of thin $As_{30}Ge_{10}S_{60}$ film drastically increases after photo-doping with silver while the changes of the values of n after illumination of the as-deposited thin silver-free film are negligible.

Table 1. Optical parameter of silver doped thin As-Ge-S films.

Composition		***d*** [nm]	***n*** at $\lambda = 488$ nm	A_1	A_2 [nm]	E_g^{opt} [eV]	***B*** cm$^{1/2}$eV$^{1/2}$
$As_{30}Ge_{10}S_{60}$	undoped	956	2.64	4.186	269.24	2.33	745
	Ag - doped	971	2.98	4.827	269.48	2.24	487
$As_5Ge_{35}S_{60}$	undoped	877	2.78	4.735	267.55	2.07	568
	Ag - doped	879	3.04	8.148	102.18	1.97	375

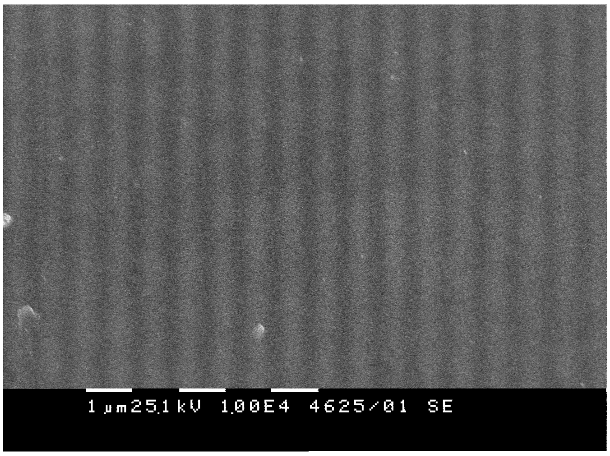

Fig. 3. SEM image of a diffraction grating recorded in thin $As_{30}Ge_{10}S_{60}$ film.

Comparison between the optical parameters of undoped and silver containing films with compositions $As_{30}Ge_{10}S_{60}$ and $As_5Ge_{35}S_{60}$ are given in Table 1. It is seen that the increase of the reflective index of the thin films after silver photo-diffusion in them is in the range of 0.26–0.34 at $\lambda = 488$ nm. The results for the thickness of the chalcogenide coatings show that the doping process leads to volume expansion.

The optical band gap of the thin films was determined from the absorption coefficient, α. It is known that at high values of the absorption coefficient, where the condition $\alpha d \geq 1$ is observed, α can be calculated from the equation:

$$T = (1-R)^2 \exp(-\alpha d), \quad (2)$$

where T is transmittance, R is reflectance and d is thin film's thickness. Analysis of the strong absorption region ($10^4 \leq \alpha \leq 10^5$ cm^{-1}) has been carried out using the following well-known quadratic equation, often called Tauc's law [15]:

$$(\alpha h\nu)^{1/2} = B(h\nu - E_g^{\mathrm{opt}}), \quad (3)$$

where B is a substance parameter, which depends on the electronic transition probability, $(h\nu)$ is the photon energy and E_g^{opt} is the so-called Tauc's gap. The results for the optical gap of the thin films, E_g^{opt} and the slope parameter, B before and after silver photo-doping are given in Table 1. It is seen that the value of E_g decreases after photo-doping for both chalcogenide films. The slope parameter B in Eq. (3) is assumed to be an indicator for the degree of the structural randomness in the amorphous semiconductors and could be related to the localized-states tail width, ΔE ($B \sim 1/\Delta E$) [16]. The observed decrease of B for thin As–Ge–S films after photo-doping (see Table 1) suggests an increase of the localized-states tail in the band gap.

We used the results for the thickness changes to examine the possibility for thin As–Ge–S film to be used for recording of relief diffraction grating. We applied a simple copy technique of lithographic masks with 700 nm period to obtain a diffraction pattern in the thin film. The experiments were performed on thin films with composition $As_{30}Ge_{10}S_{60}$. The scanning electron microscopy image of the recorded diffraction pattern is clearly seen in Fig. 3.

CONCLUSIONS

The optical properties of thin films from the system As-S-Ge and their changes after photo-diffusion of silver were investigated in the present work. It was established that the silver doping of thin films from As-Ge-S system leads to a significant increase of the refractive index - 0.26–0.34 at $\lambda = 488$ nm. Due to the incorporation of silver atoms in the glassy network of the thin films, expansion of their thickness was observed. The obtained results were applied for recording of a relief diffraction gratings with 0.7 μm line width.

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ОПТИЧНИ СВОЙСТВА НА ТЪНКИ Ag/As-S-Ge СЛОЕВЕ

Р. Тодоров, А. Лалова, В. Лозанова

Институт по оптически материали и технологии "Акад. Йордан Малиновски", Българска академия на науките, ул. "Акад. Г. Бончев", бл. 109, 1113 София, България

(Резюме)

Обект на изследване на настоящата работа са оптичните свойства на тънки слоеве от системата As-S-Ge и техните промени след фотодифузия на сребро в тях. За тази цел тънките халкогенидни слоеве бяха отложени върху подложки от оптично стъкло BK-7 с предварително нанесен чрез радио-честотно разпрашване сребърен филм. Проследени са в зависимост от времето на осветяване промените в спектрите на пропускане, показателя на пречупване и оптичната забранена зона на тънкослойните покрития. От получените зависимости са направени заключения за механизма на дифузия на сребро в тънки слоеве от As-S-Ge. Установено е, че след фотодифузия на сребро, в тънките слоеве се получават значителни промени в оптичните им свойства. За тънък слой със състав $As_{30}Ge_{10}S_{60}$ показателят на пречупване нараства от 2.32 до 2.61 за дължина на вълната 1060 nm. Показана е, възможността да бъдат записани релефни дифракционни решетки с ширина линията 0.7μm.