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Thickness dependence of the optical properties of amorphous As-Ge-S thin films

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In this paper we present some results from the study of the optical properties of thin As - S - Ge films and their dependence on the composition and film thickness. The optical constants (refractive index, *n* and extinction coefficient, *k*) were calculated using both measured transmittance, T and reflectance, *R* spectra. The thickness dependence of the optical properties of thin As - S - Ge layers was investigated. The results for the refractive index showed that the optical constants of As - S - Ge films thicker than 80 nm are independent on the film's thickness. For the films thinner than 80 nm the refractive index is strongly influenced by the substrate and depends on the process of the thin films growth. We used the Bruggeman model for determination of the porosity of the thin films. It was established that the porosity of the films increases with 25 % when the film's thickness decreases from 80 to 30 nm.

Keywords: optical properties, thin films, chalcogenide glass, refractive index.

INTRODUCTION

Chalcogenide glasses are characterized with high refractive index and wide region of transparency in the infrared. It is well known that the exposure to light of thin chacogenide films initiates changes in their refractive index and thickness [1]. Most applications of chalcogenide glasses and thin films are based on the photoinduced phenomena in these materials and on the respective changes in their optical properties [2 - 4].

Chalcogenide glasses and thin films from As - Ge - S system are of a great interest because of their large glass-formation region and high optical non-linearity [5-6]. The possibility of varying their refractive index in a wide range by changing their composition make them perspective candidates for fabrication of chalcogenide photonic crystals and Bragg gratings. Until now, most of the experiments on studying their optical properties were carried out on bulk samples and thin films with a thickness between 1 and 5 μm [7-8]. Furthermore, these materials can be deposited in very thin films (with a thickness smaller than 1 μm) in order to build photonic integrated circuits. The better knowledge of the optical constants (*n*, *k*) and thickness of thin chalcogenide films is of great importance for understanding the mechanism of the optical processes and will benefit their practical applications. For the design of multilayered systems it is very important to know the thickness dependence of the optical constants as well as to be able to accurately monitor the deposition process. It would open up the possibility of controllable tuning of the optical properties of thin chalcogenide films.

The main goal of the work is to study the optical properties of thin amorphous As - S - Ge films depending on their thickness and composition. We have also shown how the optical constants are influenced by the rate of thermal evaporation.

EXPERIMENTAL DETAILS

The synthesis of glasses from $As_{40-x}Ge_xS_{60}$ was accomplished in a silica ampoule at 970°C for 14 h [9]. Cooling was carried out in ice water. Thin films were deposited by thermal evaporation on graphite and optical glass substrates BK-7, with evaporation rate of about 0.5 nm/s in high vacuum better than 10^{-3}Pa. The process was interrupted when the target film thickness was achieved. The composition of the thin films obtained was determined in a scanning electron microscope with X-ray microanalyser Joel Superprobe 733 (Japan).

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Exposure to halogen lamp (20 mWcm^{-2}) was performed in air. The transmittance (T) and reflectance (R) were measured by a Cary 5E UV–VIS–NIR spectrophotometer (USA) in the range 350–2000 nm to an accuracy of ΔT = ±0,1% and ΔR = ±0,5%.

RESULTS AND DISCUSSION

The optical constants (refractive index, *n* and extinction coefficient, *k*) and thickness, *d*, of the thin $As_{40-x}Ge_xS_{60}$ films (for x = 10, 20, 30) were calculated using transmittance and reflectance measurements and applying the double methods developed by Theye and Abeles [10-12] for the films in the thickness range from 20-130 nm and through the conventional Swanepoel's method for thicker films [13].

The method of calculation of the optical constants of thin films in the thickness range of 20-130 nm is based on minimization of the discrepancy between theoretically calculated ($T(n(\lambda), k(\lambda), d)$ and $R(n(\lambda), k(\lambda), d)$) and experimentally measured values $T_{exp.}$ and $R_{exp.}$ of the transmittance and reflectance at normal incidence, until the difference becomes lower than the accuracy of the measurements, ΔT and ΔR [10, 11].

$$T(n(\lambda), k(\lambda), d) - T_{exp.} = \Delta T$$

$$R(n(\lambda), k(\lambda), d) - R_{exp.} = \Delta R \qquad (1)$$

Discontinuities appear in the solution for *n* and *k* due to the necessity of knowing the correct film thickness and loss of solutions in the interference extrema. The thickness *d* is not computed from the system (1), but is introduced as a parameter. For an initial approximation for the thickness we used the value, measured by a profilometer with an accuracy of ± 5 nm. Hence, varying the thickness slightly around the approximate one, we chose the value, yielding the smallest discontinuities in the solution for *n* and *k*. The accuracy in the determination of the refractive index, *n*, was better than ±0.005 and for the absorption coefficient, *k*, around the absorption edge it was about ±0.01 [14]. The accuracy of the methods in determining *d* is better than ±1 nm [14].

The results for films in thickness range of 20-130 nm were compared with the optical constants of thin films with thickness ~ 1.0 µm calculated by the Swanepeol's method [13] and the procedure presented in [14]. The dispersion of the refractive index for thin $As_{40-x}Ge_xS_{60}$ films for x= 10, 20, 30 is presented in Figs. 1 and 2.The dispersion curves of unexposed and exposed one-micron thick films with the same compositions are given with continuous or broken lines, respectively. It is seen that the refractive index of the unexposed film with composition $As_{20}Ge_{20}S_{60}$ and thickness 80 nm is the same as the one of the one-micron thick layer. In the case of $As_{10}Ge_{30}S_{60}$ it is observed reduction of the values of *n* of the unexposed film with thickness 52 nm in respect to the dispersion for the 1 µm one. Smaller photo-induced changes of the refractive index are observed for the 1 µm thick films from both compositions.

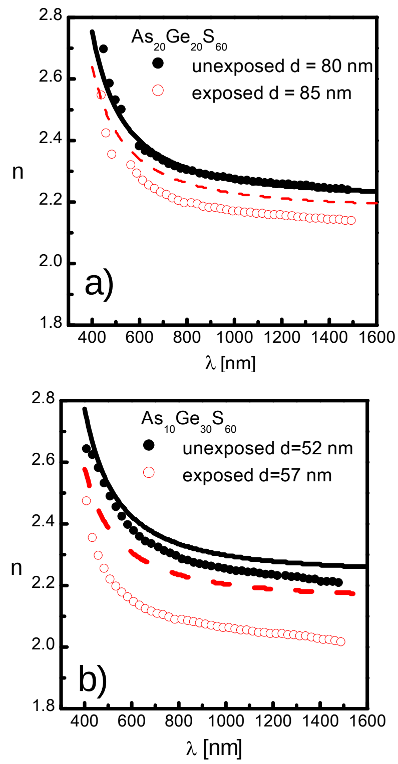

Fig. 1. Comparison of the dispersion of the refractive indices of thin As-Ge-S films for *d*< 0.1µm (symbols) and *d*~ 1.0 µm (lines).

The photo-induced changes for thin $As_{30}Ge_{10}S_{60}$ are negligible and are not presented in Fig. 1. Obtained changes for the refractive index after illumination was $\Delta n = 0.01$.

One possible reason for negligible changes in $As_{30}Ge_{30}S_{60}$ film is that in some ternary Ge-As-S(Se) materials, photo-darkening and photo-bleaching might be compensated by an appropriate choice of composition leading to photo-stability effect [15]. Such hypothesis could be interesting for the concept of intrinsically photo-stable amorphous chalcogenides. Therefore attention of this work is thus focused on $As_{30}Ge_{10}S_{60}$ thin films optical properties and their stability/changes induced by light exposure.

Furthermore, we investigated the dependence of the refractive index of thin $As_{30}Ge_{10}S_{60}$ films on the film's thickness. Fig. 2 illustrates the influence of the thickness of the above thin films on the dispersion of *n*. We have compared five layers of different thickness (29, 59, 89, 107 and 135 nm). The refractive index of the film 89 nm thick matches those of 107 and 135 nm while films with thicknesses 29 and 59 demonstrate lower values for *n*.

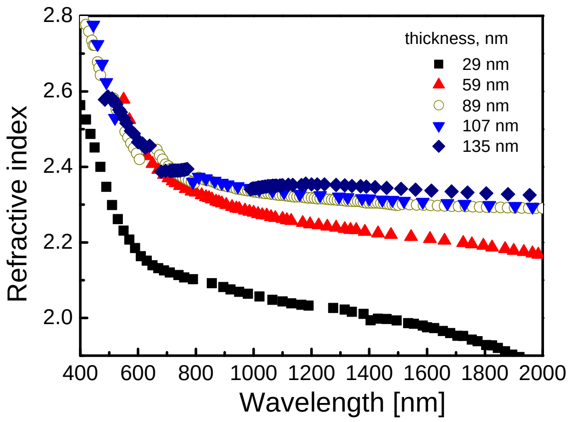

Fig. 2. Dispersion of the refractive index of thin $As_{30}Ge_{10}S_{60}$ films with different thicknesses.

The calculated value of k was used to determine the optical band gap. The extinction coefficient is related to the absorption coefficient by the following relationship:

$$\alpha = 4\pi k / \lambda \qquad (2)$$

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 [16]:

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

where B is a substance parameter, which depends on the electronic transition probability, (hν) is the photon energy and E_g^{opt} is the so-called *Tauc's* gap. The variation of E_g^{opt} when varying the thickness of the films is shown in Fig. 3a. It is seen that the value of E_g^{opt} decreases below some value of the film's thickness.The thickness dependence of the substance parameter, B is given in Fig 3b. It is seen that B decreases with decreasing of the thickness, which is indication for increasing of the structural disorder of the thin films.

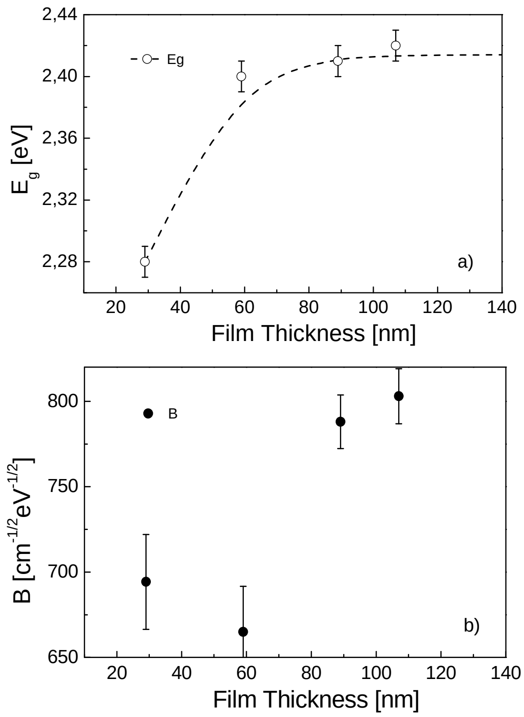

Fig. 3. Optical band gap, E_g (a) and structural parameter, B (b) for thin $As_{30}Ge_{10}S_{60}$ films with different thicknesses.

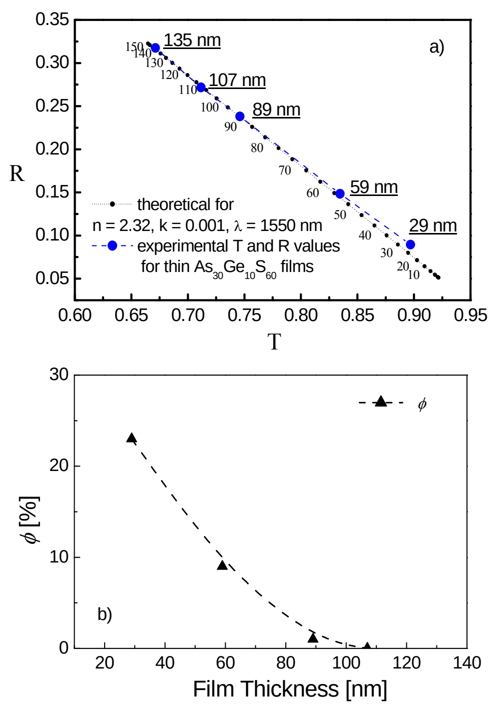

Fig. 4. Theoretical R-T dependence for thin $As_{30}Ge_{10}S_{60}$ films and experimental data for thin $As_{30}Ge_{10}S_{60}$ films (a). The parameters of the theoretical line are given in the graphs. Porosity ϕ *vs.* film thickness (b).

Theoretical T-R dependence for thin films with refractive index n = 2.32, k = 0.001 and d = 20 - 160 nm at λ = 1550 nm and experimental results for thin $As_{30}Ge_{10}S_{60}$ films are shown in Fig. 4. It is seen that thin films with thickness larger than 90 nm follow the theoretical line while at smaller thicknesses a deviation of the experimental results is observed. The above results are in agreement with previous reports, which claim the existence of a critical value for d, above which optical constants are thickness independent [12, 17].

We used the effective medium theory for determination of the porosity of the thin films. According to the Bruggeman model, a porous semiconductor material can be considered as a mixture of two phases and its effective refractive index n_{eff} in the non-absorbing region follows the equation:

$$1-\phi=\frac{\left(\frac{n_{eff}^2}{n_c^2}-\frac{n_d^2}{n_c^2}\right)}{\left[\left(\frac{n_{eff}^2}{n_c^2}\right)^{1/3}\left(1-\frac{n_d^2}{n_c^2}\right)\right]} \quad (4)$$

where n_c and n_d are the refractive indices of the continuous media and pores, respectively, while ϕ is the porosity. We have considered as continuous media the thin films deposited at normal incidence and duly used the data obtained for their refractive index. We found that the values for ϕ varied in the range of 0.2 % to 23 % for thin films with thicknesses 88 and 29 nm. The increasing in the porosity of the thin layers with d <80 nm is a probable cause for the increasing of the photo-induced changes in the refractive index. The increase of the porosity probably results in increased flexibility of the glass network, and also enables oxygen from the air to penetrate into the volume of the thin layer. According to [18], the oxidation process leads to a substantial increase of the effect of photobleaching (increase in the width of the band gap) and therefore a reduction in the refractive index.

CONCLUSIONS

In the present work the influence of the thickness on the optical constants of thin As-Ge-S films and their photo-induced changes were investigated. It was established that the refractive index and optical band gap decrease for the film thickness smaller than 80 nm. The photo-induced changes of the refractive index and optical band gap increase when film's thickness decrease. Through applying the model for the effective media proposed by Bruggeman we found that the values for porosity ϕ varied in the range of 0.2 % to 23 % for the thin films in the thicknesses range 88 -29 nm. The increase of porosity probably results in enhanced flexibility of the glass network and oxidation processes into the volume of the thin layer.

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ЗАВИСИМОСТ НА ОПТИЧНИТЕ СВОЙСТВА НА АМОРФНИ As-Ge-S ТЪНКИ ФИЛМИ ОТ ДЕБЕЛИНАТА

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(Резюме)

В тази статия са представени резултати от изследване на оптичните свойства на тънки As - S - Ge филми и зависимостта им от състава и дебелината на филмите. Оптичните константи (показател на пречупване, *n* и показател на поглъщане, k) са определени от спектрите на пропускане, T и отражение, R. Резултатите за показателя на пречупване показаха, че оптичните константи на As - S - Ge филми за стойности на d> 80 nm не зависят от дебелината на филма. За тънки филми с d< 80 nm стойността на показателя на пречупване е силно повлияна от подложката и зависи от условията на отлагане на тънкия слой. Моделът на Bruggeman е използван за определяне на порьозността на тънки слоеве. Установено е, че порьозността на филмите нараства с 25%, когато дебелината на слоевете намалява.