Optical properties of porous chalcogenide films for sensor application

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Abstract. The object of the present work is investigation of the optical properties of obliquely deposited thin films from As – S – Ge system. Aiming to obtain high porous coatings the deposition rate was varied in the range of 0.05-10 nm/s. The conditions for deposition of thin As – S - Ge films with columnar structure and high porosity were established. The role of the actual deposition conditions on the optical properties is examined. The optical constants (refractive index, $n$ and absorption coefficient, $\alpha$) and thickness, $d$ as well as the optical band gap, $E_g$, and slope parameter $B$ in dependence of the deposition angle and rate are determined from spectrophotometric measurements in the spectral range 400-2000 nm applying the Swanepoel’s envelope method and Tauc’s procedure. Increasing of the value of $n$ from 2.40 to 1.83 for thin film with composition As$_{10}$Ge$_{30}$S$_{60}$ with increasing deposition angle from 0˚ to 75˚ is observed. The possibility of using the thin films for optical sensing of SO$_2$ and H$_2$S was examined. Reversible changes of the refractive index, $\Delta n = 0.015$ were observed as a consequence of treatment virgin - exposure to H$_2$SO$_4$ vapors– annealing at 120 ºC.

1. Introduction

Fabrication of materials with high porosity is one approach for development of novel nanomaterials. The porous materials possess unique physical properties due to the extremely large surface-to-volume ratio and quantum confinement effects [1, 2]. Progress in synthesis, characterization and modelling of such materials would enable technological innovations in various applications ranging from microelectronics to optoelectronics and specifically biosensing [3].

Changes of the electrical and optical properties of porous materials due to filling of the pores with different gases make them attractive for application in gas sensing [4, 5]. The propylamine and nitrogen dioxide sensing properties of thin porous chalcogenide films from As$_{40}$S$_{60}$ and As-Ge-Te were investigated from Tsiulyanu et al. [6]. It was reported in [7] that thin films from As-S-Ge system could be applied as NH$_3$ gas sensors for concentrations higher than 250 ppm.

The object of investigation of the present work is the influence of the deposition conditions on the optical properties of chalcogenide films from As$_{40}$Ge$_{30}$S$_{60}$ system. The possibility for deposition of thin chalcogenide films with high porosity and their potential application as optical sensors of sulphur containing compounds such as SO$_2$ and H$_2$S was examined.

2. Experimental details

Bulk glasses from the system As - S - Ge were synthesized in a quartz ampoule from elements of 99.999 % purity by the method of melt quenching [8]. Thin films from previously synthesized bulk
glasses from As$_{40-x}$Ge$_x$S$_{60}$ system (for $x = 0, 10, 30, 35$) were deposited by thermal evaporation on rotated substrates or by the well known oblique deposition technique at angle of deposition 75°. The bulk materials were evaporated from a Ta boat (“Knudsen type”). The deposition rate was varied in the range of 0.05 - 1 nm/s. In the case of substrates continuously rotated during the evaporation process the substrate holder is a dome-shaped calotte that can be considered as a segment of a sphere. The evaporation sources are located close to (approximately at) the geometric centre of this sphere and the vapours of the evaporated compound fall normally on the substrates.

The composition of the thin films obtained was determined by a scanning electron microscope Jeol Superprobe 733 (Japan) with an X-ray microanalyser. The experiments were performed at an accelerating voltage of 20 kV, current of 1.4 nA and scanning time of 200 s for each spectrum. The transmittance (T) and reflectance (R) spectra of thin films were measured by UV-VIS-NIR spectrophotometer Carry 5E (Australia) in the region 400 - 2000 nm to an accuracy of ± 0.1 % and ± 0.5 %, respectively.

3. Results and discussion
Thin films from As$_{40-x}$Ge$_x$S$_{60}$ system for $x = 0, 10, 30, 35$ were thermally evaporated. The composition of the layer was controlled by X-ray microanalysis and was determined to be close to the expected one. The SEM cross-section images of thin films from As-Ge-S system are presented in figure 1.

![Figure 1. Cross-section images obtained by SEM of thin As$_{40-x}$Ge$_x$S$_{60}$ films deposited at different rates: As$_{40}$S$_{60}$ (0.4 nm/s) (a); As$_{40}$S$_{60}$ (0.1 nm/s) (b); As$_{40}$S$_{60}$ (0.06 nm/s) (c); As$_{30}$Ge$_{10}$S$_{60}$ (0.4 nm/s) (d); As$_{10}$Ge$_{30}$S$_{60}$ (0.1 nm/s) (e) and As$_{10}$Ge$_{30}$S$_{60}$ (0.06 nm/s) (e) at 75° angle of incidence of the vapours. (The marker corresponds to 1 μm.)](image)

The germanium containing layers clearly demonstrate columnar structure even at deposition rate of 0.4 nm/s while for thin As$_{40}$S$_{60}$ films columns were observed at 0.1 nm/s. At very low deposition rates (0.06 nm/s) of the thin As$_{40}$S$_{60}$ film no columns were formed (figure 1c).

The refractive index, $n$ and thickness, $d$ of the thin film were calculated from transmission spectra using Swanepoel’s method [9]. The program used to calculate $n$ will determine it to an accuracy of ± 0.5 % for an error in the transmittance of ± 0.1 % [10]. In figure 2 a comparison is given of the dispersions of the refractive index of thin films deposited normally or obliquely at 75° angle of
incidence of the vapors. Due to their microstructure the obliquely deposited films demonstrated lower refractive index for all compositions. The most drastically decreased values of $n$ were found for the thin film with composition $\text{As}_{10}\text{Ge}_{30}\text{S}_{60}$. The results for $n$ are summarized in table 1.

![Dispersion of the refractive index of thin As$_{40-x}$Ge$_x$S$_{60}$ films for $x = 0$ (a); 10 (b); 30 (c); 35(d); evaporated on rotated substrates ($0^\circ$) and oblique deposition ($75^\circ$).](image)

Table 1. Calculated values for the optical parameters (refractive index, $n$, optical band gap, $E_g$ and structural parameter, $B$), thickness, $d$, average coordination number, $Z$ and porosity, $\phi$ of thin As-Ge-S films.

| Composition | $Z$ | Conditions of deposition | $d, m$ | $n$ (at $\lambda = 1550$ nm) | $E_g$ [eV] | $B$ [cm$^{-1/2}$ eV$^{-1/2}$] | $\phi$ |
|-------------|-----|--------------------------|--------|-----------------------------|-----------|-----------------------------|-------|
| $\text{As}_2\text{S}_3$ | 2.40 | normal deposition | 1.23 | 2.29 | 2.35 | 770 | 0.001 |
| | | oblique deposition at $75^\circ$ | 0.81 | 2.23 | 2.33 | 738 | |
| $\text{As}_{30}\text{Ge}_{10}\text{S}_{60}$ | 2.50 | normal deposition | 1.08 | 2.31 | 2.32 | 745 | |
| | | oblique deposition at $75^\circ$ | 0.76 | 2.10 | 2.48 | 644 | 0.036 |
| $\text{As}_{10}\text{Ge}_{30}\text{S}_{60}$ | 2.70 | normal deposition | 0.87 | 2.28 | 2.15 | 591 | 0.277 |
| | | oblique deposition at $75^\circ$ | 1.3 | 1.78 | 2.63 | 378 | |
| $\text{As}_{5}\text{Ge}_{35}\text{S}_{60}$ | 2.75 | normal deposition | 0.88 | 2.42 | 2.05 | 568 | 0.035 |
| | | oblique deposition at $75^\circ$ | 1.41 | 2.35 | 2.00 | 501 | |

The reflectance and transmittance spectra were used for calculation of the linear absorption coefficient, $\alpha$ and optical band gap, $E_g$ through the equations:
\[
T = (1 - R)^2 \exp(-\alpha d)
\]

where \( T \) is transmittance, \( R \) is reflectance and \( d \) is thin film’s thickness. Analysis of the strong absorption region \( (10^4 \leq \alpha \leq 10^5 \text{ cm}^{-1}) \) was carried out using the following well-known quadratic equation, often called Tauc’s law [11]:

\[
(\alpha h\nu)^{1/2} = B(h\nu - E_{g}^{\text{opt}})
\]

where \( B \) is a substance parameter, which depends on the electronic transition probability, \((h\nu)\) is the photon energy and \( E_{g}^{\text{opt}} \) is the so-called Tauc’s gap. The comparison for the refractive indices, \( n \) for wavelength \( \lambda = 1550 \text{ nm}, \) optical band gap and slope parameter \( B \) for thin film prepared on rotated substrates and obliquely deposited films at angle 75° is given in table 1. Significant variation of the band gap when changing the angle of incidence of the vapours is observed for thin As\(_{10}\)Ge\(_{30}\)S\(_{60}\) layer. The lower values of \( B \) for the thin films with columnar structure are due to larger structural disorder.

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 \( n_{\text{eff}} \) in the non-absorbing region follows the equation:

\[
1 - \phi = \frac{\left( \frac{n_{\text{eff}}^2}{n_{c}^2} - \frac{n_{d}^2}{n_{c}^2} \right)^{1/3}}{\left( \frac{n_{\text{eff}}^2}{n_{c}^2} \right)^{1/3} \left( 1 - \frac{n_{d}^2}{n_{c}^2} \right)^{1/3}}
\]

where \( n_{c} \) and \( n_{p} \) are the refractive indices of the continuous media and pores, respectively, while \( \phi \) 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. The results for porosity calculated applying equation 3 are presented in table 1. We found that the values for \( \phi \) varied in the range of 0.002 to 0.277. The maximal value for \( \phi \) was obtained for the thin film with composition As\(_{10}\)Ge\(_{30}\)S\(_{60}\) where the average coordination number is \( Z = 2.7 \). We suggest that the observed behaviour of the porous parameter, \( \phi \) for thin As - Ge - S films can be related to the structure of the thin films. According to [12] the free volume and atomic compactness of the glasses from nonstoichiometric section As\(_2\)S\(_3\)-Ge\(_2\)S\(_3\) reach maximal values at coordination numbers around 2.7.

Furthermore we probed the possibility of potential application of the obliquely deposited coatings for optical sensing of different gasses. The idea for application of porous materials as optical sensors is based on the changes of the effective refractive index due to filling of the pores with gas. We performed initial sensing experiments by exposing the thin films to the vapours of sulphur acid (H\(_2\)SO\(_4\)). The results from the testing of thin films with composition As\(_{40}\)S\(_{60}\) and As\(_{30}\)Ge\(_{10}\)S\(_{60}\) are presented in figure 3. Notable changes of the refractive index are observed for unexposed coatings, while the exposed ones remain unaffected by the gas exposure. Increase of the values of \( n \) was observed after exposure of thin film to the vapours of the acid. It is well known that the population of the As-As bonds is higher in as-deposited thin films [13]. These bonds interact with S-S bonds during the illumination and forming As-S bonds. We can expect that the vapours of H\(_2\)SO\(_4\) consist of H\(_2\)S and SO\(_2\) molecules and these sulphur containing species interact with As-As.

The variation of the refractive index with different treatments is shown in figure 3d. It was observed that after 20 min of gas exposure the refractive index changed with 0.015. This change is
reversed after 3 min. annealing at 120 °C. We can suggest that the sulphur containing species in the H₂SO₄ vapours create weak bonds that are broken after short annealing.

Figure 3. Refractive index of thin films with composition As₄₀S₆₀ unexposed (a); As₄₀S₆₀ exposed (b) As₃₀Ge₁₀S₆₀ unexposed (c) before and after treatment with sulphur acid vapours and periodic changes of the value of \( n \) for thin As₄₀S₆₀ layer in consequences of treatment virgin (V) -exposure to vapours for 20 minutes and annealing (A) (d)

In figure 3d 3 cycles of interaction with vapours and subsequent annealing for thin As₂S₃ film are demonstrated. This result demonstrates the possibility for application of thin As-Ge-S layers as optical sensors. For a complete understanding of this effect additional information for the binding energy of different kind of bonds and structural units and surface of thin films is required.

4. Conclusions
The conditions for preparation of thin As-Ge-S films with columnar structure were investigated. The SEM images showed that columnar structure is observed at deposition rates in the range of 0.1 – 0.4 nm/s. The refractive index of the films is varied in very wide range from 1.78 to 2.42 at \( \lambda = 1550 \) nm depending on layers’ composition and their microstructure. It was found that maximal porosity possess the thin films with composition As₁₀Ge₃₀S₆₀ and average coordination number \( Z = 2.7 \). The possibility was demonstrated for the application of thin As-Ge-S films in optical sensing of sulphur compounds. The large variation in \( n \) and sensitivity to gasses provide an opportunity for the films from the studied system to be applied in multi-layered structures where the response to small changes in the optical parameters of thin films is greater.
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