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Temperature dependence of the optical properties of thin Ge-Se-In films

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ABSTRACT

This paper deals with the properties of the glasses and thin films from multi-component chalcogenide prepared by co-evaporation technique. The thin chalcogenide layers from the $Ge_{30}Se_{70-x}In_x$ system were deposited by thermal co-evaporation of bulk glasses from Ge-Se system and In_2Se_3. Using X-ray microanalysis it was found that the film compositions are close to the expected ones. The refractive index, *n*, and the optical band gap, E_g^{opt}, were determined by spectral ellipsometric measurements. The thin film's structure was investigated by Raman spectroscopy.

The temperature coefficients of the linear thermal expansion, α_l and the band gap, β_{Eg} were determined. Decrease of the values of α_l from $2.49 \times 10^{-4} K^{-1}$ to $4.55 \times 10^{-5} K^{-1}$ and β_{Eg} from -1.3×10^{-3} eV·K^{-1} to -0.7×10^{-3} eV·K^{-1} was observed when indium content in the thin films was increased from 0 to 17 at.%.

1. Introduction

The chalcogenide glasses from the Ge - Se - In system possess interesting structural, electrical and optical properties such as high ultrafast third-order optical nonlinearity, fast crystallization and activation energy for thermo-electrical conductivity that make them attractive as materials for ultrafast all optical switching, fiber amplifiers for optical telecommunication [1], phase storage [2,3] and high efficiency thermoelectric materials [4].

The addition of a third element as an impurity in $GeSe_2$ has a pronounced effect on the structure [5,6]. Thus, through the inclusion of a third element and variation of its concentration significant changes are possible to be achieved in the physical properties of the germanium containing chalcogenide glasses. The Ge-Se-In system forms glassy compositions over a range of average coordination number Z, including both Z = 2.40 and Z = 2.67 [7], which are critical values in the Phillips [8] and Tanaka [9] theories, respectively. Despite of the numerous works considering the structure of the glasses from Ge - S(Se) - In systems, the question for the coordination number of the indium atom remains still open. Structural investigation of the X-ray absorption fine structure (EXAFS) of the glasses from Ge - Se - In system suggests that the indium atoms are mainly 3-fold coordinated [7,10].

The large glass forming region of the Ge - Se - In system is a reason for the thermal and optical properties of these glasses to be varied in a wide range. The variation of the glass transition temperature, T_g, and mean atomic volume, V_m, for a composition with an average coordination number, Z have been reported [10–13]. The optical properties of thin films obtained by thermal evaporation of bulk glasses with germanium content between 5 and 28 at.% have been presented in [14–16]. The optical energy gap (E_g^{opt}) for thin films from the $Ge_xSe_{92-x}In_8$ system was investigated in [16]. The authors found that the optical band decreases with increasing the Ge content.

The difference in the bond energy of the various bonds in the multicomponent chalcogenide glasses [17] is a reason for the decomposition of the bulk material during the film deposition process [18]. Due to this phenomenon a significant deviation of the composition of the thin films from those of the bulk material is observed or a gradient of the elements distribution and optical properties in the depth of the coatings are found [18,19]. Recently, a possibility has been shown for the deposition of homogenous chalcogenide films with controllable composition by thermal co-evaporation of ternary indium containing chalcogenide films [20,21].

The present paper is focused on the optical and structural properties of thin films from the Ge - Se - In system obtained by co-evaporation of In_2Se_3 and bulk glasses from Ge - Se system. In point of view of their potential application the effect of temperature on the optical properties and thickness was analyzed.

2. Experimental details

Thin Ge - Se - In films were deposited on Si substrates, in vacuum of 10^{-3} Pa by thermal co-evaporation of previously weighed quantities of

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Table 1
Composition of bulk glasses and thin films determined by X-ray microanalysis.

Ratio of the deposition rates between the evaporated compounds	Expected composition	Thin film's composition	Annealing temperature [°C]
$Ge_{33}Se_{67}/In_2Se_3$ (10:1)	$Ge_{30,3}S_{65,7}In_{4.0}$	$Ge_{25.0}Se_{72.0}In_3$	307.0 ± 0.1
$Ge_{35}Se_{65}/In_2Se_3$ (3:1)	$Ge_{30}S_{60}In_{10}$	$Ge_{27.5}Se_{63.6}In_{8.9}$	277.0 ± 0.1
$Ge_{40}Se_{60}/In_2Se_3$ (2:1)	$Ge_{30}S_{55}In_{15}$	$Ge_{26.2}Se_{56.7}In_{17.1}$	257.0 ± 0.1

In_2Se_3 and bulk glasses from the Ge - Se system with different compositions aiming at keeping the germanium content in thin films constant. The ratio between the rates of deposition of each of the substances was controlled during the process of evaporation (see Table 1). The total deposition rate of both compounds was 2–3 Å/s. To obtain thin films with uniform composition, 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 close to (approximately at) the geometric centre of this sphere.

The composition of the thin films was determined by a scanning electron microscope (Joel JSM 5500 LV) with an X-ray microanalyser. Topology and adhesion of the surface were monitored by atomic force microscope Dimension Icon (Bruker) in Peak Force Quantitative Nanoscale Mechanical mode using SCANASYST-AIR tips (k = 0.4 N/m). The images were recorded at a scanning frequency of 0.5 Hz with a resolution of 512 × 512 pixels.

The optical properties of the films deposited on silicon substrates were examined by UV–Visible phase modulated spectroscopic ellipsometric platform UVISEL2 (HORIBA JobinYvon) in the spectral range of 190–2000 nm. The measurements were conducted in the range of 1.5–6 eV at 70° incident angle. The annealing of the films is performed in argon atmosphere in the temperature cell of the ellipsometric platform. The thin films were annealed at a temperature 50 °C below the expected glass-forming temperature [12,13] (see Table 1).

Raman scattering measurements were carried out using a confocal Raman microscope Labram HR (Horiba JobinYvon), objective 20× or 50 × LWD, excitation line 785 nm, laser power on the sample 200 W/mm^2, exposition 5 s and accumulation 10×.

3. Results and discussion

The results for the composition of thin Ge - Se- In films obtained by thermal co-evaporation are presented in Table 1. It is seen that the deviation of the indium content from the expected concentration is ~2 at.%. This deviation is comparable with the accuracy of the X-ray microanalysis (0.5–1.5 at.%) [23]. The results showed that the germanium content in the layers is lower in respect to the expected one. The lack of germanium can be explained on the basis of the phase separation observed in the glasses from Ge - Se system. The phase diagram of the Ge_xSe_{100-x} system [22] shows that glasses with germanium content ≤33 at.% tend to phase separation of $GeSe_2$ and Se while germanium rich glasses 33 ≤ Ge ≤ 50 at.% yield GeSe and $GeSe_2$ phases.

The optical constants of the thin films were determined by spectroscopic ellipsometric measurements in the spectral range 190–2000 nm. In our calculations the samples were modeled as isotropic layers with rough surfaces on absorbing substrates. The ellipsometric ratio $\rho = \tan\Psi\exp(i\Delta)$ is determined from the quantities I_s and I_c, which are related to ψ and Δ as follows: $I_s = \sin2\Psi\sin\Delta$, $I_c = \sin2\Psi\cos\Delta$. The validity of the model is determined by the calculation (Eq. (1)) of a common mean square error function (χ^2), which accounts for the discrepancies between the measured and simulated data for I_c and I_s [24].

$$\chi^2 = \frac{1}{2N-P-1}\sum_{i=1}^{N}\{[Is_{calc}(h\nu) - Is_{meas}(h\nu)]^2 + [Ic_{calc}(h\nu) - Ic_{meas}(h\nu)]^2\} \quad (1)$$

where N and P are the total number of data points and the number of fitted parameters, respectively.

To obtain the best fit of the experimental data, the dispersion of the imaginary part, ε_2, of the complex dielectric function was modeled by the Tauc-Lorentz dispersion model [25], that considers a single transition.

$$\varepsilon_2 = \frac{AE_0\Gamma(E-E_g)^2}{(E^2-E_0^2)^2+\Gamma^2E^2}\cdot\frac{1}{E}, \quad E > E_g{}^{opt},$$
$$\varepsilon_2 = 0, \quad E \le E_g{}^{opt} \quad (2)$$

The model includes the following parameters: band gap E_g, peak transition energy E_0; broadening parameter Γ linked to the FWHM of the absorption peak, the factor A related to the strength of the absorption peak.

The real part of the dielectric function is obtained by the Kramers-Kronig integration of ε_2:

$$\varepsilon_1 = \varepsilon_\infty + \frac{2}{\pi}P\int_{E_g}^{\infty}\frac{\xi\varepsilon_2(\xi)}{\xi^2-E^2}d\xi \quad (3)$$

where ε_∞ is the high frequency dielectric constant. The addition of a thick top layer, taking into account surface roughness and/or oxidation leads to an improvement of the coincidence - the value determined for χ^2 is 0.49. With the increase of the indium in the thin films, the thickness of the rough overlayer is slightly decreased. The data from the AFM (Fig. 1) shows that the topology of all samples is „grains-like “with size of the grains in the range 20–50 nm. The surface roughness determined as Root Mean Squared (*RMS*) decreased with increasing the In content in the thin layers (see Table 2). The AFM analysis of the film adhesion shows that it is homogeneous for all parts of the film's surface, which implies homogeneous chemical composition and structure in the scale tens nm (Fig. 1d).

In order to determine the influence of the temperature on the optical parameters, we need to take into account the presence of the effect of thermo-bleaching which is observed for the thin layers from the ternary germanium containing chalcogenide glasses. That is why we have annealed the layers at temperatures 50 °C below the T_g and followed the changes of the experimental parameters. The results for the dispersion of the refractive index, n of the as-deposited, heated to the annealing temperature samples and samples after the first round of annealing are shown in Fig. 2. It is seen that the increasing of indium content in the as-deposited thin layers results into an increase of the values of n (from 2.39 to 2.56 at telecommunication wavelength λ = 1550 nm for thin $Ge_{30}Se_{70}$ and $Ge_{26.2}Se_{56.7}In_{17.1}$ films, respectively) in the entire investigated spectral range.

The heating of the samples up to the annealing temperature specific for each composition of the samples leads to changes of n due to volume changes and rearrangement of the bonds in the glassy network. When the samples were heated up to the annealing temperature the refractive index of thin $Ge_{30}Se_{70}$ film decreased while that of the indium containing layers increased. The variation of the thickness and dispersion parameters included in Eq. (2) of thin Ge - Se-In films at different moments during first annealing procedure is presented in Fig. 3. As it can be seen, the thickness of the $Ge_{30}Se_{70}$ film increases at higher temperature. The calculated values of the thickness of the sample cooled down to room temperature showed that effect of volume contraction ($\Delta d/d_0 = -1.2\%$) is obtained as result of the annealing. Thus, the decrease of the refractive index of the thin $Ge_{30}Se_{70}$ film can be