

# 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  $\text{Ge}_{30}\text{Se}_{70-x}\text{In}_x$  system were deposited by thermal co-evaporation of bulk glasses from Ge-Se system and  $\text{In}_2\text{Se}_3$ . 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,  $E_g^{\text{opt}}$ , were determined by spectral ellipsometric measurements. The thin film's structure was investigated by Raman spectroscopy.

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

**Keywords:** Chalcogenide, Transition temperature.

## 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<sup>1</sup>, phase storage<sup>2,3</sup> and high efficiency thermoelectric materials<sup>4</sup>.

The addition of a third element as an impurity in  $\text{GeSe}_2$  has a pronounced effect on the structure<sup>5,6</sup>. 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  $Z=2.67$ <sup>7</sup>, which are critical values in the Phillips<sup>8</sup> and Tanaka<sup>9</sup> 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<sup>7,10</sup>.

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<sup>10-13</sup>. 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<sup>14-16</sup>. The optical energy gap ( $E_g^{\text{opt}}$ ) for thin films from the  $\text{Ge}_x\text{Se}_{92-x}\text{In}_8$  system was investigated in<sup>16</sup>. 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<sup>17</sup> is a reason for the decomposition of the bulk material during the film deposition process<sup>18</sup>. 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<sup>18,19</sup>. 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<sup>20,21</sup>. 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  $\text{In}_2\text{Se}_3$  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.

## 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  $\text{In}_2\text{Se}_3$  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.

**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]
$\text{Ge}_{33}\text{Se}_{67}/\text{In}_2\text{Se}_3$ (10:1)	$\text{Ge}_{30.3}\text{S}_{65.7}\text{In}_{4.0}$	$\text{Ge}_{25.0}\text{Se}_{72.0}\text{In}_3$	$307.0 \pm 0.1$
$\text{Ge}_{35}\text{Se}_{65}/\text{In}_2\text{Se}_3$ (3:1)	$\text{Ge}_{30}\text{S}_{60}\text{In}_{10}$	$\text{Ge}_{27.5}\text{Se}_{63.6}\text{In}_{8.9}$	$277.0 \pm 0.1$
$\text{Ge}_{40}\text{Se}_{60}/\text{In}_2\text{Se}_3$ (2:1)	$\text{Ge}_{30}\text{S}_{55}\text{In}_{15}$	$\text{Ge}_{26.2}\text{Se}_{56.7}\text{In}_{17.1}$	$257.0 \pm 0.1$

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  $512 \times 512$  pixels.

The optical properties of the films deposited on silicon substrates were examined by UV-Visible phase modulated spectroscopic ellipsometric platform UVISSEL2 (HORIBA JobinYvon) in the spectral range of 190–2000 nm. The measurements were conducted in the range of 1.5–6 eV at  $70^\circ$  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  $50^\circ\text{C}$  below the expected glass-forming temperature<sup>12,13</sup> (see Table 1).

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

## 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  $\sim 2$  at.%. This deviation is comparable with the accuracy of the X-ray microanalysis (0.5–1.5 at.%)<sup>23</sup>. 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  $\text{Ge}_x\text{Se}_{100-x}$  system<sup>22</sup> shows that glasses with germanium content  $\leq 33$  at.% tend to phase separation of  $\text{GeSe}_2$  and Se while germanium rich glasses  $33 \leq \text{Ge} \leq 50$  at.% yield GeSe and  $\text{GeSe}_2$  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  $\Psi$  and  $\Delta$  as follows:  $I_s = \sin 2\Psi \sin \Delta$ ,  $I_c = \sin 2\Psi \cos \Delta$ . The validity of the model is determined by the calculation (Eq. (1)) of a common mean square error function ( $\chi^2$ ), which accounts for the discrepancies between the measured and simulated data for  $I_c$  and  $I_s$ <sup>24</sup>.

$$\chi^2 = \frac{1}{2N - P - 1} \sum_{i=1}^N \{ [I_{s\text{calc}}(hv) - I_{s\text{meas}}(hv)]^2 + [I_{c\text{calc}}(hv) - I_{c\text{meas}}(hv)]^2 \}$$

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,  $\epsilon_2$ , of the complex dielectric function was modeled by the Tauc-Lorentz dispersion model<sup>25</sup>, that considers a single transition.

$$\begin{aligned} \epsilon_2 &= \frac{AE_0 r(E - E_g)^2}{(E^2 - E_0^w)^2 + r^2 E^2} \cdot \frac{1}{E}, E > E_g^{\text{opt}} \\ \epsilon_2 &= 0, E \leq E_g^{\text{opt}} \end{aligned} \quad (2)$$

The model includes the following parameters: band gap  $E_g$ , peak transition energy  $E_0$ ; broadening parameter  $\Gamma$  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  $\epsilon_2$ :

$$\epsilon_1 = \epsilon_\infty + \frac{2}{\pi} P \int_{E_g}^{\infty} \frac{\xi \epsilon_2(\xi)}{\xi^2 - E^2} d\xi \quad (3)$$

where  $\epsilon_\infty$  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  $\chi^2$  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 I have annealed the layers at temperatures  $50^\circ\text{C}$  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  $\lambda=1550$  nm for thin  $\text{Ge}_{30}\text{Se}_{70}$  and  $\text{Ge}_{26.2}\text{Se}_{56.7}\text{In}_{17.1}$  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  $\text{Ge}_{30}\text{Se}_{70}$  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  $\text{Ge}_{30}\text{Se}_{70}$  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  $\text{Ge}_{30}\text{Se}_{70}$  film can be related with the

temperature expansion of the layer during annealing and decrease of its density respectively. The calculated thickness after the annealing shows the effect of photo-induced contraction. It is known that the structural changes occur during the annealing of as deposited thin Ge-Se layers. The  $Ge_{30}Se_{70}$  film is composed by corner and edge shared  $GeSe_4$  tetrahedral units, which can be connected by Se - Se bridges providing some flexibility to the network <sup>26</sup>. The wrong Ge-Ge bonds also can be observed in thin films with that composition. They can interact with Se - Se bonds and to form new heteropolar Ge-Se bonds <sup>26</sup>.

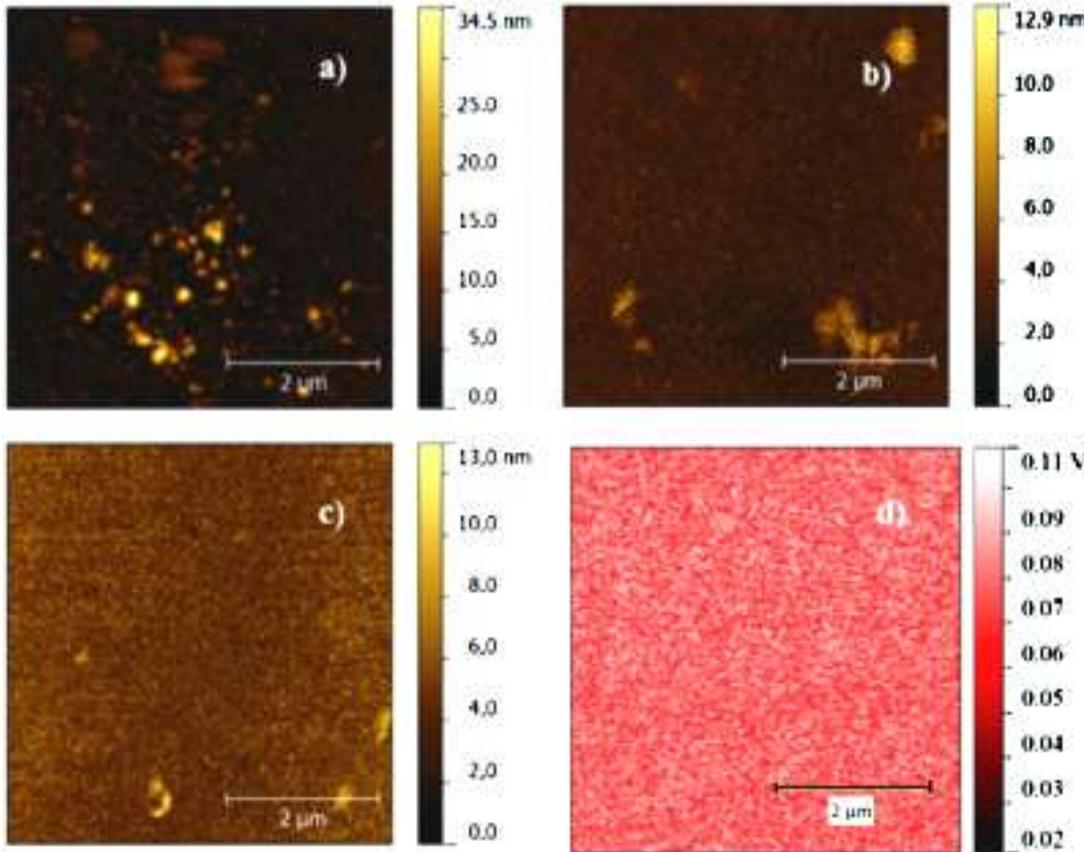


Fig. 1. AFM topological images of the thin films with composition  $Ge_{25.0}Se_{72.0}In_{3}$  (a);  $Ge_{27.5}Se_{63.6}In_{8.9}$  (b) and  $Ge_{26.2}Se_{56.7}In_{17.1}$  (c). The map of adhesion for thin  $Ge_{27.5}Se_{63.6}In_{8.9}$  layer corresponding to the topological map (d).

Table 2: Surface roughness (RMS) and grains diameter determined by AFM. The relative errors in RMS and grains diameter do not exceed  $\pm 5\%$ .

Thin film composition	RMS [nm]	Typical grains diameter [nm]
$Ge_{25.0}Se_{72.0}In_{3}$	3.15	45–50
$Ge_{27.5}Se_{63.6}In_{8.9}$	1.01	20–30
$Ge_{26.2}Se_{56.7}In_{17.1}$	1.17	25–30

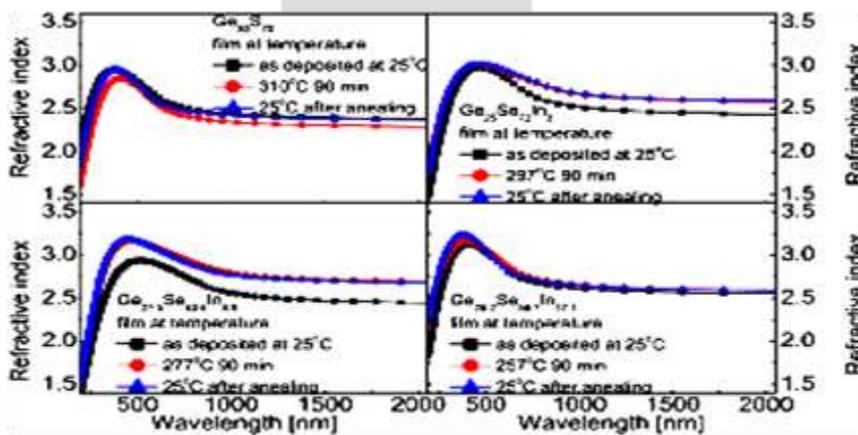


Fig. 2. The dispersion of the refractive index of the as-deposited thin Ge - Se - In films (at 25 °C), heated up to the annealing temperature (temperature is given in the figure for each composition) and at 25 °C after annealing. The error bars are within the symbols sizes.

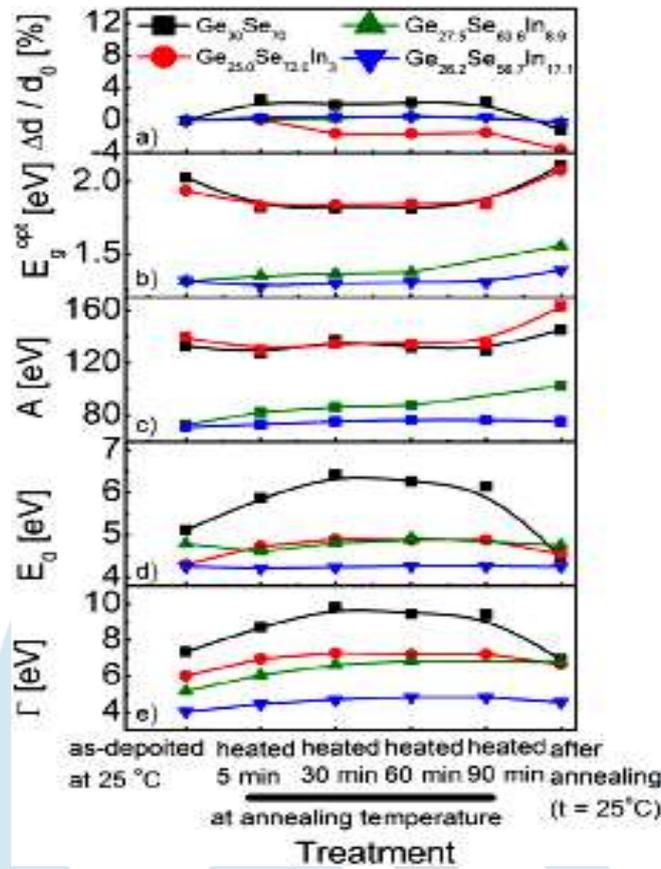


Fig. 3. Relative changes of the film thickness, optical band gap and parameters in the Tauc-Lorenz formula (Eq. (2)) during and after the annealing procedure of thin Ge-Se-In films (lines are only drawn as guide to the eye). The error bars are within the symbols sizes

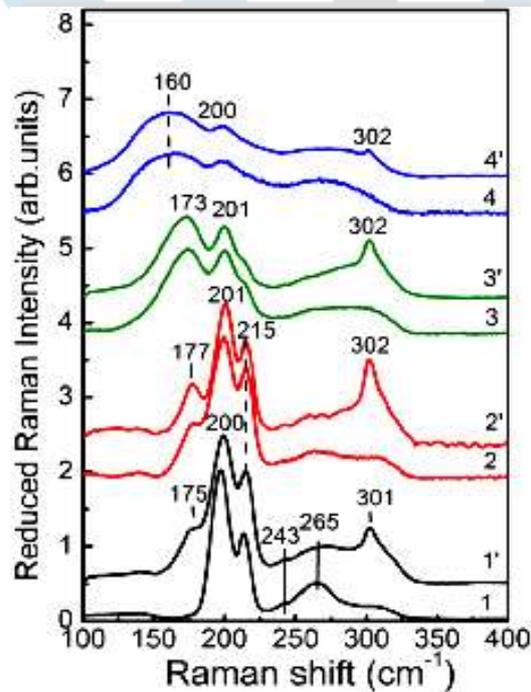


Fig. 4. Raman spectra of the as-deposited thin Ge-Se-In films:  $Ge_{30}Se_{70}$  (1);  $Ge_{25.0}Se_{72.0}In_3$  (2);  $Ge_{27.5}Se_{63.6}In_{8.9}$  (3);  $Ge_{26.2}Se_{56.7}In_{17.1}$  (4). The numbers with prime show the Raman spectra of the same films after annealing.

According to [11], the formation of  $In_2Se_3$  clusters in the Ge-Se-In glasses in the series  $Ge_xSe_{94-x}In_6$  and  $Ge_ySe_{88-y}In_6$  for indium content 6–12 at.% is a reason for the modification of the molecular mobility of the structure. The confirmed presence of  $In_2Se_3$

structural units in glasses with composition  $\text{Ge}_5\text{Se}_{80}\text{In}_{15}$  makes them inhomogeneous at microscopic level<sup>7</sup>. The values of the optical band gap,  $E_g^{\text{opt}}$  for as deposited films extracted from the parameters in Eq. (2) are shown in Fig. 3. It is seen that the increase of indium in the thin films results in a decrease of the  $E_g^{\text{opt}}$  values from 1.93 eV for the thin  $\text{Ge}_{25.0}\text{Se}_{72.0}\text{In}_3$  film to 1.29 eV for the  $\text{Ge}_{26.2}\text{Se}_{56.7}\text{In}_{17.1}$  layer. Due to the increase of the optical band gap the effect of thermo-bleaching were observed for all investigated thin films after annealing.

In the Raman spectra of the  $\text{Ge}_{30}\text{Se}_{70}$  films two strong scattering bands at 198 and 214  $\text{cm}^{-1}$ , and a complex broad band centered at 265  $\text{cm}^{-1}$  with two shoulders at 243 and 305  $\text{cm}^{-1}$  are observed (Fig. 4). According to<sup>27</sup> the 202 and 218  $\text{cm}^{-1}$  Raman modes are related with the Ge–Se stretching vibrations in the corner- and edgesharing tetrahedra, respectively<sup>28</sup>. The Ge–Ge stretching vibrations of the ethane-like units  $\text{Se}_3\text{Ge} - \text{GeSe}_3$  are active at  $\sim 180 \text{ cm}^{-1}$ . The stretching vibrations of Se–Se bond in the helical Se and  $\text{Se}_8$  rings are Raman active at 265 and 271  $\text{cm}^{-1}$ , respectively. The band at  $\sim 300 \text{ cm}^{-1}$  originates from the IR active asymmetric Ge–Se stretching vibration modes.

The Raman spectra show that the addition of 3 at.% indium results in significant changes of the most intensive scattering band (Fig. 4). The intensity of the band at  $\sim 200 \text{ cm}^{-1}$  relative to that of the band at  $\sim 214 \text{ cm}^{-1}$  decreases. A broad band in the frequency range of 230–325  $\text{cm}^{-1}$  is observed due to decrease of the intensity of the band centered at  $\sim 265 \text{ cm}^{-1}$ . New band  $\sim 178 \text{ cm}^{-1}$  is appeared in Raman spectrum of as-deposited layer. The further increase of the indium content in the thin films shifts the maxima of this band to the lower frequencies - 173 and 163  $\text{cm}^{-1}$  for the thin films with composition  $\text{Ge}_{27.5}\text{Se}_{63.6}\text{In}_{8.9}$  and  $\text{Ge}_{26.2}\text{Se}_{56.7}\text{In}_{17.1}$ , respectively. According to<sup>29,30</sup> the Raman spectra of the polycrystalline layered  $\gamma\text{-In}_2\text{Se}_3$  at room temperature demonstrate strong scattering band at 183  $\text{cm}^{-1}$  and some bands with lower intensity at 125, 150 and 202  $\text{cm}^{-1}$ . In the Raman spectrum of the  $\alpha$ -phase of  $\text{In}_2\text{Se}_3$  high-intensity bands at 174 and 202  $\text{cm}^{-1}$ , low intensity bands at 236, and 253  $\text{cm}^{-1}$  and a strong shoulder at 142  $\text{cm}^{-1}$  are observed. In [6] a band at 154  $\text{cm}^{-1}$  is detected in the Raman spectra of  $\text{GeSe}_2\text{-In}_2\text{Se}_3\text{-CsI}$  glasses. The authors attributed this band to the symmetric stretching vibration mode of the  $\text{InSe}_4^-$  tetrahedral units. According to results from EXAFS measurements on glasses from the Ge - Se - In system, the indium atoms are mainly 3-fold coordinated forming neutral  $\text{InSe}_3$  triangles<sup>7,10</sup>. The authors have not found indications for the presence of In–In and In–Ge bonds, which suggests that no ethane-like  $\text{Se}_3\text{In} - \text{InSe}_3$  and  $\text{Se}_3\text{Ge} - \text{InSe}_3$  units are present in the glassy network of Ge - Se - In glasses or their population is below the measurement sensitivity. As reported in<sup>31</sup> for the  $\text{InS}_4^-$  tetrahedral and neutral  $\text{InS}_{3/2}$  planar triangle units in the structure of the  $\text{GeS}_2\text{-InS}_3$  glass, we suppose that the scattering frequencies of the neutral  $\text{InSe}_3$  triangles are higher than those of  $\text{InSe}_4^-$  tetrahedral units and probably the shift of the band from 179  $\text{cm}^{-1}$  to 163  $\text{cm}^{-1}$  is due to the increase of populations of  $\text{InSe}_4^-$  units in respect to the neutral  $\text{InSe}_3$  triangles. The increase of the population of  $\text{InSe}_4^-$  units could be due to the formation of  $\text{In}_2\text{Se}_3$  clusters, which can be observed in glasses with indium content higher than 6 at.%<sup>11</sup>.

Looking for a correlation between the structure and optical properties of the thin films the dispersion of the refractive index has been analyzed on the basis of the Wemple-Di-Domenico (WDD) model<sup>32,33</sup>. According to the model, the refractive index of solid materials in a transparent region is described with the single-oscillator formula:

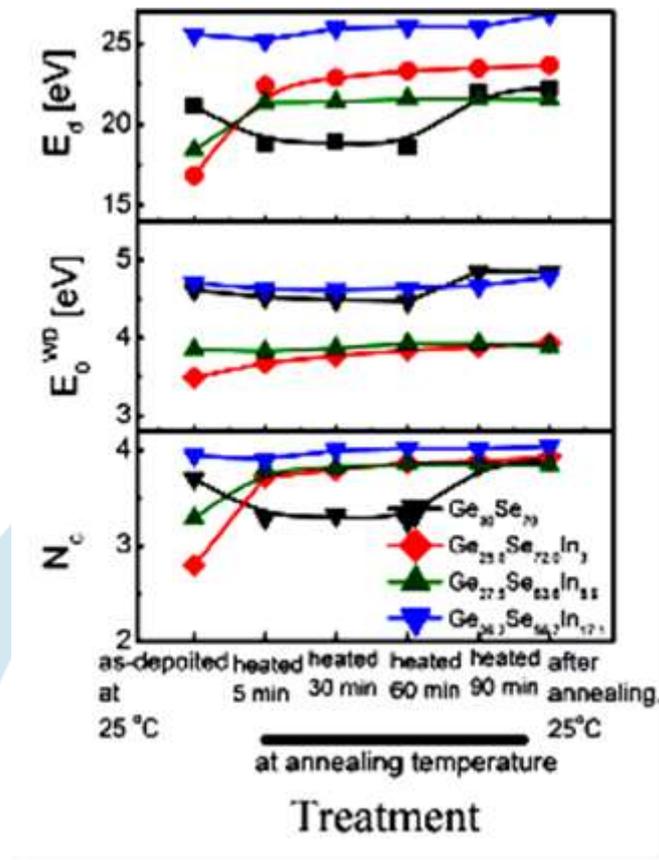
$$n^2 = 1 + \frac{E_d E_0^{WD}}{E_0^{WD2} - (hv)^2} \quad (4)$$

where  $(hv)$  is the photon energy,  $E_0$  WD is the oscillator energy and  $E_d$  is the oscillator strength or dispersive energy. The dispersive energy is related to other physical parameters of material through the empirical formula:

$$E_d = \beta N_c Z_a N_e \quad (5)$$

where  $N_c$  is the effective coordination number of the cation nearestneighbour,  $Z_a$  is the formal chemical valence of the selenium anion ( $Z_a=2$ ),  $N_e$  is the effective number of the valence electrons per anion, and  $\beta$  is a two-valued constant with either an ionic or a covalent value ( $\beta=0.26 \pm 0.03 \text{ eV}$  and  $\beta=0.37 \pm 0.04 \text{ eV}$ , respectively). Plotting  $(n^2-1)^{-1}$  against  $(hv)^2$  in the spectral range where absorption of the thin films is zero, allows one to determine the oscillator parameters ( $E_0$  and  $E_d$ ) by transformation of equation to the linear form. The values of the correlation coefficient of the linear fit were better than 0.995.

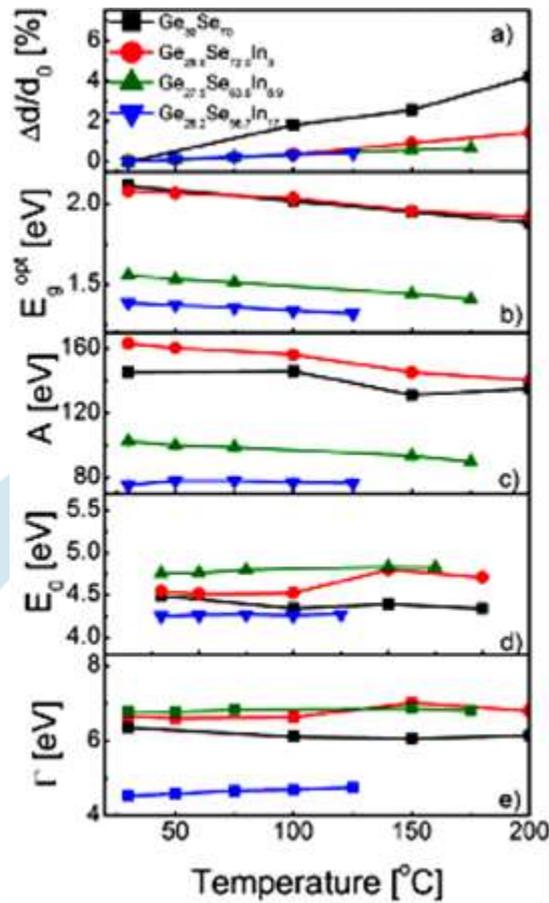
The calculated values for  $N_c$ ,  $E_0$  and  $E_d$  and their evolution during the annealing of the samples are presented in Fig. 5. The obtained value for  $N_c$  of the as-deposited  $\text{Ge}_{30}\text{Se}_{70}$  film was 3.28. It is well known that Ge atoms are mostly 4-fold coordinated in  $\text{GeSe}_4$  tetrahedral units<sup>27</sup> and 3 coordinated in ethane-like units  $\text{Se}_3\text{Ge}-\text{GeSe}_3$ . It is seen that as a result of the annealing of the thin  $\text{Ge}_{30}\text{Se}_{70}$  film the value of  $N_c$  increases to 3. This result is in agreement with the literature data that the homopolar Se–Se bonds interact with Ge–Ge bonds in ethane-like units during annealing. As a result, the population of the 4-fold coordinated Se Ge atoms in the  $\text{GeSe}_4$  tetrahedral units increases.



**Fig. 5.** Dispersive energy,  $E_d$ , oscillator energy,  $E_0$  WD and effective coordination number of the cation nearest-neighbour,  $N_c$  during and after the annealing procedure of thin Ge-Se-In films (lines are only drawn as guide to the eye). The error bars are within the symbols sizes.

It is seen that the increase of the indium content in the films results to increasing of the values of  $N_c$  while those of  $E_0$  decrease. For the Ge-Se-In system the values of  $N_c$  are determined from the coordination of the Ge and In atoms in the glassy network of the thin films. Indium atoms are mainly 3-fold coordinated<sup>7</sup> or in the case of the phase separation for indium content higher than 6 at.%, In forms 4-fold coordinated charged  $\text{InSe}_4^-$  tetrahedral units<sup>29,30</sup>.

The addition of 3 at.% indium to the system Ge-Se significantly reduces the calculated values of  $N_c$  for the as-deposited layer. It can be suggested from the Raman spectrum that at this concentration the indium atoms break the Se-Se chains and/or interact with the bridging selenium atoms between germanium and as a result the population of the corner shared  $\text{GeSe}_4$  tetrahedral units decreases<sup>34</sup>. The calculated values for  $N_c$  were 3.70 and 3.94 for thin layers with composition  $\text{Ge}_{27.5}\text{Se}_{63.6}\text{In}_{8.9}$  and  $\text{Ge}_{26.2}\text{Se}_{56.7}\text{In}_{17.1}$ , respectively. The increase of the  $N_c$  values for the thin films with a higher indium content can be due to the formation of  $\text{In}_2\text{Se}_3$  clusters<sup>11</sup>.



**Fig. 6. Relative changes of the film thickness, optical band gap and parameters in the Tauc-Lorentz formula (Eq. (2)) at different temperatures for the annealed thin Ge - Se - In films (lines are only drawn as guide to the eye). The error bars are within the symbols sizes.**

After the annealing of the as-deposited films eliminated the effect of irreversible structural changes, we heated thin layers and determined the temperature dependence of the band gap and linear coefficient of thermal expansion in the temperature range of 25–200 °C. Fig. 6 demonstrates the variation of the thickness and dispersion parameters included in the Tauc-Lorentz formula as a function of the temperature for annealed Ge Se-In films. As the temperature of the layers increases, a linear increase of the film's thickness and decrease of the optical band gap are observed. The most significant expansion was observed for the  $\text{Ge}_{30}\text{Se}_{70}$  layer. If one defines a linear coefficient of thermal expansion according to:

$$\alpha_l = \frac{1}{d_0} \frac{\Delta d}{\Delta T} \quad (6)$$

where  $d_0$  is the initial thickness of the films at room temperature 25 °C, the calculations show that the addition of indium in the binary germanium glass significantly reduces the thermal expansion of the material from  $(2.49 \pm 0.01) \times 10^{-4} \text{ K}^{-1}$  to  $(4.55 \pm 0.08) \times 10^{-5} \text{ K}^{-1}$  for thin films of  $\text{Ge}_{30}\text{Se}_{70}$  and  $\text{Ge}_{26.2}\text{Se}_{56.7}\text{In}_{17.1}$ , respectively. The calculated value for the linear coefficient of thermal expansion,  $\alpha_l$  for thin  $\text{Ge}_{30}\text{Se}_{70}$  film is close to those for the melts from  $\text{Ge}_x\text{Se}_{100-x}$  system for  $4 \leq x \leq 16.5$  ( $0.6-3.2 \times 10^{-4} \text{ K}^{-1}$ ) and one order of the magnitude higher than the values for  $\alpha$  ( $=3.0-4.8 \times 10^{-5} \text{ K}^{-1}$ ) of the same bulk glasses<sup>35</sup>. Therefore higher value of  $\alpha_l$  of the thin  $\text{Ge}_{30}\text{Se}_{70}$  layer can be explained on the base of the film is less relaxed and thus structurally closer to the undercooled liquid than the bulk glass of the same chemical composition<sup>36</sup>.

The optical band gap of the annealed thin Ge-Se-In films demonstrated linear dependence on the temperature (Fig. 6b). Similar linear dependence of  $E_g^{\text{opt}}$  was observed for  $\text{GeSe}_2$  films for temperature higher than  $-100 \text{ °C}$ <sup>37</sup>. The temperature coefficient of the optical band gap of thin Ge-Se-In films is calculated by following formula:

$$\beta_{Eg} = \frac{\Delta E_g}{\Delta T} \quad (7)$$

where  $E_{g0}$  is the calculated value of the optical band gap at room temperature (25 °C),  $\Delta E_g^{\text{opt}}$  is the difference between the values for  $E_g^{\text{opt}}$  at a certain temperature and  $E_{g0}$ . The addition of the indium in the thin films results in a decrease of  $\beta_{Eg}$  in the temperature interval 25–100 °C from  $-1.3 \pm 0.1 \times 10^{-3} \text{ eV} \cdot \text{K}^{-1}$  for thin  $\text{Ge}_{30}\text{Se}_{70}$  film to  $(-1.0 \pm 0.1) \times 10^{-3} \text{ eV} \cdot \text{K}^{-1}$  and  $(-0.7 \pm 0.1) \times 10^{-3} \text{ eV} \cdot \text{K}^{-1}$  for thin films with compositions  $\text{Ge}_{27.5}\text{Se}_{63.6}\text{In}_{8.9}$  and  $\text{Ge}_{26.2}\text{Se}_{56.7}\text{In}_{17.1}$ , respectively. For comparison, the literature data for the temperature coefficient of the optical band gap of  $\text{As}_2\text{Se}_3$  glasses reports  $-0.7 \times 10^{-3} \text{ eV} \cdot \text{K}^{-1}$ <sup>38</sup>. Using the published data in<sup>37</sup> for the optical band gap at different temperatures for  $\text{GeSe}_2$  layer we calculated value for  $\beta_{Eg}$  as that for thin  $\text{Ge}_{30}\text{Se}_{70}$  film in present work  $-1.3 \times 10^{-3} \text{ eV} \cdot \text{K}^{-1}$ .

The strength of the absorption peak - parameter A (Fig. 6c) decreases for all the investigated compositions when the temperature of the samples increases. The maximum of the absorption band  $E_0$  change its position with temperature for thin  $\text{Ge}_{30}\text{Se}_{70}$  and  $\text{Ge}_{25.0}\text{Se}_{72.0}\text{In}_3$  film while it becomes constant for indium rich  $\text{Ge}_{27.5}\text{Se}_{63.6}\text{In}_{8.9}$  and  $\text{Ge}_{26.2}\text{Se}_{56.7}\text{In}_{17.1}$  layer.

## Conclusions

The possibility to deposit thin films from the ternary Ge - Se - In system by co-evaporation of Ge - Se and  $\text{In}_2\text{Se}_3$  has been examined. The optical and structural properties of the thin films have been investigated by spectroscopic ellipsometry and Raman spectroscopy. It is found that the refractive index increases from 2.39 to 2.56, while the optical gap decreases from 2.03 to 1.29 eV for thin films with composition  $\text{Ge}_{30}\text{S}_{70}$  and  $\text{Ge}_{26.2}\text{Se}_{56.7}\text{In}_{17.1}$ , respectively. The annealing of the as-deposited layers leads to an increase of the optical band gap of the thin films. The temperature coefficients of the linear thermal expansion and the band gap were determined by the second round heating of the thin films. It was found that the values of  $\alpha_l$  decrease from  $(2.49 \pm 0.01) \times 10^{-4} \text{ K}^{-1}$  to  $(4.55 \pm 0.08) \times 10^{-5} \text{ K}^{-1}$  and those of  $\beta E_g$  from  $(-1.3 \pm 0.1) \times 10^{-3} \text{ eV} \cdot \text{K}^{-1}$  to  $(-0.7 \pm 0.1) \times 10^{-3} \text{ eV} \cdot \text{K}^{-1}$  when indium content in the thin films increases from 0 to 17 at.%. The high optical powers propagating in the optical fibers cause the increase of their temperature and the fiber's geometric and optical parameters are changed, respectively. This is a reason for the deterioration of the optical signals propagating therein. The results for  $\alpha_l$  and  $\beta E_g$  show that the inclusion of indium leads to improvement the stability of the geometry and optical properties of waveguide structures from germanium selenide in case of temperature variations. On the other hand, the combination of the materials with high and low values of the temperature coefficient of the linear expansion can find application for the optical fiber interferometric temperature sensors<sup>39</sup>.

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