10th International Conference on Solid State Chemistry, Pardubice, Czech Republic

Compositional dependence of the optical properties of vacuum evaporated thin GeSe$_2$-GeTe-PbTe films

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Abstract

Chalcogenide glasses from the GeSe$_2$-GeTe-PbTe system were synthesized by taking preliminary prepared GeSe$_2$, GeTe and PbTe in their molecular percentages and melting them in an evacuated quartz ampoule. Thin films were deposited on optical glass substrates BK-7 and Si-wafer substrates by thermal evaporation. Using X-ray microanalysis it was found that the film composition differs to a certain degree from the bulk composition. The changes in the optical properties of thin GeSe$_2$-GeTe-PbTe films were studied as a function of their composition, exposure to light and annealing. It is shown by XRD analysis that the thin films are amorphous up to layers with composition of Ge$_{27}$Se$_{51}$Te$_{14}$Pb$_8$. The optical constants (refractive index, $n$ and absorption coefficient, $\alpha$), the thickness, $d$ as well as the optical band gap, $E_g$, depending on the film composition were determined by spectrophotometric measurements in the region 450-2500 nm applying the Swanepoel’s envelop method and Tauc’s procedure. With the increase of the Te content in the layers, the absorption edge is shifted to the higher wavelengths, the refractive index increases from 2.54 for Ge$_{31}$Se$_{66}$Te$_3$ up to 3.37 for Ge$_{32}$Se$_{55}$Te$_{13}$ while the optical band gap decreases from 1.86 eV for to 1.30 eV for the same compositions. Similar dependence was observed with the increase of the PbTe content in the layers. After annealing of thin films, the values of $n$ decrease, the optical band gap increases and a shift of the absorption edge to the shorter wavelengths is observed.

Keywords: chalcogenides; thin films; structure; optical properties
1. Introduction

The chalcogenide glasses have a number of unique properties, such as wide range of transparency in the infrared region, photosensitivity, low phonon energy, high linear and non-linear refractive index, high excitation times and higher quantum efficiency of irradiation in comparison with the oxide glasses, which is due to the lower fundamental vibrational energy of the chemical bonds. Thin chalcogenide films already have found application in the field of optical technologies (optical fibre connections, optical switches, media for optical recording of information and optical sensors) [1-9]. That opens possibilities of creating complex optical systems, in which the light source, working elements, coupling elements and sensors are fabricated by similar materials, applying one and the same production process. Despite the successes achieved in that direction, the synthesis of new materials, suitable for such applications, as well as expanding the possibilities for implementation of the existing materials, is of special importance for material science and optical technologies.

Many papers have been published on the properties of Ge-containing glasses [10-12]. It is shown that GeSe₂ is good glass-forming material and it is used basically for preparation of multicomponent glasses applied for electrographic coatings, photoresists, ion selective electrodes [13]. The Ge-Se-Te [14, 15] and GeSe₂-PbTe [13] systems, as well as the chalcogenides GeTe [16] and PbTe [17, 18] were widely investigated during the last decade. The glass-forming region in the GeSe₂-GeTe-PbTe system and some physicochemical properties of glassy alloys were studied in [19]. Some papers were published on the optical properties of thin films from the GeSe₂-Sb₂Se₃-AgI (PbTe) systems [20, 21].

In the present work some new results from the photo- and thermo-induced changes in the optical properties and structure of thin films from the GeSe₂-GeTe-PbTe system depending on their composition after light illumination and annealing are presented.

2. Experimental

Bulk glasses from the Ge-Se-Te-Pb system with ten different compositions, situated into the glass forming region (Fig. 1) were synthesized by conventional melt quenching technique from GeSe₂, GeTe, and PbTe (preliminary prepared from elements Ge, Se, Te and Pb with high purity) in evacuated to a residual pressure of 1.10⁻⁵ Torr quartz ampoules. The samples were quenched in ice cold water at a cooling rate of 15°C.sec⁻¹. The glassy state was proven by XRD and electron microscopy analysis [19].

![Fig. 1. Bulk samples from the glass forming region (indicated by circles with numbers from 2-11) used in the study [19]](image-url)
Thin films (around 0.8 μm thick) were deposited by thermal evaporation from a Ta boat (“Knudsen type”) onto optical glass substrates BK-7, graphite and two-side polished Si wafers under vacuum of 6-8.10⁻⁶ Torr with deposition rate of 0.8-1.0 nm.s⁻¹. Their composition was determined by scanning electron microscopy with an X-ray microanalyser (Jeol Superprobe 733, Japan) at an electron accelerating voltage of 20 kV and a current of 1.4 nA.

Powder X-ray diffraction patterns were collected within the range from 5.3 to 80° 2θ with a constant step 0.02° 2θ on Bruker D8 Advance diffractometer with CuKα radiation and LynxEye detector. Phase identification was performed with the DiffracPlus EVA using ICDD-PDF2 Database.

The transmittance and reflectance spectra in spectral range 450-2500 nm of as-deposited, illuminated and annealed films were performed in an UV-VIS-NIR spectrophotometer (Cary 05E, USA).

In the case of semiconductors, the optical absorption coefficient, \( \alpha \), increases rapidly for photon energies higher than the energy of the optical bang gap, \( E_{\text{opt}}^{\text{eg}} \). At high values of the absorption coefficient, \( \alpha \), such as the condition \( \alpha d \geq I \) is realized, \( \alpha \) can be calculated from the equation:

\[
T = (1 - R)^2 e^{-\alpha d}
\]

(1)

where \( T \) is the transmittance, \( R \) is the reflectance and \( d \) is the film’s thickness. In the same spectral region the absorption coefficient can be described by the relation, suggested by Tauc [22]

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

(2)

where \( B \) is a substance parameter, \( h \) is Planck’s constant, \( \nu \) is the frequency and \( E_{\text{opt}}^{\text{eg}} \) is the optical band gap (Tauc’s gap).

The exposure time to saturation to a halogen lamp (60 mW.cm⁻²) (i.e. the time beyond which the absorption edge did not change) was experimentally established for each sample. Samples from all compositions were annealed for two hours in vacuum at temperature 25°C below \( T_g \) for each one.

3. Results and Discussion

3.1. X-ray microanalysis of thin Ge-Se-Te-Pb films

Data from the X-ray microanalysis of bulk samples and thin films deposited by thermal evaporation for three cross-sections (GeSe₂)₉₀₋ₓ(GeTe)ₓ(PbTe)₁₀, (GeSe₂)₇₀₋ₓ(GeTe)ₓ(PbTe)₃₀, and (GeSe₂)₉₂₋ₓ(GeTe)₈(PbTe)ₓ) from the GeSe₂-GeTe-PbTe system are shown in Table 1. It is clearly seen from the Table that according to the content of Pb in the thin films, they can be grouped into two groups; (i) thin films prepared from bulks with different compositions disposed on the line (GeSe₂)₉₀₋ₓ(GeTe)ₓ(PbTe)₁₀ without presence of Pb in the layers and (ii) thin films prepared from bulks with compositions disposed on lines (GeSe₂)₇₀₋ₓ(GeTe)ₓ(PbTe)₃₀ and (GeSe₂)₉₂₋ₓ(GeTe)₈(PbTe)ₓ) from which in the limits of the experimental error, the composition of the thin films are very close to the expected compositions of the bulks. The difference in values of each of elements presented in the glasses is due to the different rate of evaporation of fragments presented in the bulk samples. In the same time the accuracy of the method does not provide more accurate measurements which could explain the lower values of the Pb included in the films. After the end of evaporation process we usually found a residue from the bulk glass in the boat (50-
Table 1. Data for the composition of bulk glasses and thin GeSe$_2$-GeTe-PbTe films

<table>
<thead>
<tr>
<th>Bulk glasses (mol. %)</th>
<th>Bulk glasses (at. %)</th>
<th>Thin films (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(GeSe$<em>2$)$</em>{90}$(GeTe)$_{10}$</td>
<td>Ge$<em>{34}$Se$</em>{62}$Te$_4$</td>
<td>Ge$<em>{1}$Se$</em>{66}$Te$_4$</td>
</tr>
<tr>
<td>(GeSe$<em>2$)$</em>{81}$(GeTe)$<em>{9}$(PbTe)$</em>{10}$</td>
<td>Ge$<em>{32}$Se$</em>{57}$Te$_4$Pb$_4$</td>
<td>Ge$<em>{2}$Se$</em>{64}$Te$_4$</td>
</tr>
<tr>
<td>(GeSe$<em>2$)$</em>{68}$(GeTe)$<em>{22}$(PbTe)$</em>{10}$</td>
<td>Ge$<em>{34}$Se$</em>{50}$Te$_12$Pb$_4$</td>
<td>Ge$<em>{2}$Se$</em>{59}$Te$_8$</td>
</tr>
<tr>
<td>(GeSe$<em>2$)$</em>{54}$(GeTe)$<em>{36}$(PbTe)$</em>{10}$</td>
<td>Ge$<em>{35}$Se$</em>{43}$Te$_18$Pb$_4$</td>
<td>Ge$<em>{2}$Se$</em>{55}$Te$_13$</td>
</tr>
<tr>
<td>(GeSe$<em>2$)$</em>{72}$(GeTe)$<em>{8}$(PbTe)$</em>{20}$</td>
<td>Ge$<em>{29}$Se$</em>{53}$Te$_10$Pb$_8$</td>
<td>Ge$<em>{2}$Se$</em>{57}$Te$_15$Pb$_4$</td>
</tr>
<tr>
<td>(GeSe$<em>2$)$</em>{63}$(GeTe)$<em>{7}$(PbTe)$</em>{30}$</td>
<td>Ge$<em>{27}$Se$</em>{48}$Te$_14$Pb$_11$</td>
<td>Ge$<em>{2}$Se$</em>{51}$Te$_14$Pb$_8$</td>
</tr>
<tr>
<td>(GeSe$<em>2$)$</em>{53}$(GeTe)$<em>{17}$(PbTe)$</em>{30}$</td>
<td>Ge$<em>{28}$Se$</em>{42}$Te$<em>18$Pb$</em>{12}$</td>
<td>Ge$<em>{2}$Se$</em>{46}$Te$<em>{17}$Pb$</em>{15}$</td>
</tr>
<tr>
<td>(GeSe$<em>2$)$</em>{42}$(GeTe)$<em>{28}$(PbTe)$</em>{30}$</td>
<td>Ge$<em>{29}$Se$</em>{35}$Te$<em>24$Pb$</em>{12}$</td>
<td>Ge$<em>{2}$Se$</em>{30}$Te$<em>{28}$Pb$</em>{17}$</td>
</tr>
<tr>
<td>(GeSe$<em>2$)$</em>{54}$(GeTe)$<em>{6}$(PbTe)$</em>{40}$</td>
<td>Ge$<em>{24}$Se$</em>{42}$Te$<em>18$Pb$</em>{16}$</td>
<td>Ge$<em>{2}$Se$</em>{46}$Te$<em>{17}$Pb$</em>{15}$</td>
</tr>
<tr>
<td>(GeSe$<em>2$)$</em>{45}$(GeTe)$<em>{5}$(PbTe)$</em>{50}$</td>
<td>Ge$<em>{21}$Se$</em>{37}$Te$<em>22$Pb$</em>{20}$</td>
<td>Ge$<em>{2}$Se$</em>{38}$Te$<em>{25}$Pb$</em>{15}$</td>
</tr>
</tbody>
</table>

The XRD analysis of the composition of the residue from the material after deposition of thin films from one of the studied bulk compounds - (GeSe$_2$)$_{72}$(GeTe)$_{8}$(PbTe)$_{20}$ shows presence of various crystalline phases - PbSe, and small quantities of PbGe$_4$O$_9$, PbO, TeO$_3$. This could explain the lack of lead or the smaller Pb quantities found in the films from the studied system. Using the results from the X-ray analysis of the element content in thin GeSe$_2$-GeTe-PbTe we divided the system into two parts – first one is to study the optical properties of thin films from the system Ge$_{33}$Se$_{67-x}$Tex (0 ≤ x ≤ 13) and the second one is investigation of thin films from the GeSe$_2$-GeTe-PbTe system and studying the influence of PbTe content on their optical properties. In the text below we will discuss the properties of thin films according their composition determined by X-ray microanalysis.

3.2. Optical properties of thin Ge-Se-Te films

As it was mentioned above first we will study the optical properties of thin films from the system Ge-Se-Te and their changes after exposure to light and annealing. More precisely said this system could be presented as system Ge$_{33}$Se$_{67-x}$Tex. On Fig. 2, using the results from the XRD analysis, the diffractograms of two of the compositions from this system - Ge$_{31}$Se$_{66}$Te$_3$ and Ge$_{32}$Se$_{65}$Te$_{13}$ deposited from bulks from

![Fig. 2](image-url)
the cross-section \((\text{GeSe}_2)_{90-x}(\text{GeTe})_x(\text{PbTe})_{10}\) are presented. It is seen that the films are amorphous (the other two films from this system are amorphous, too). The substitution of Se by Te seems to lead to small traces of the crystalline phase of PbSe included in the amorphous GeSe$_2$ matrix in thin Ge$_{32}$Se$_{55}$Te$_{13}$ films.

Fig. 3a shows the optical transmittance spectra of thin Ge-Se-Te films. The plots show fringes due to the interference at various wavelengths. The maxima and minima of these fringes are used to calculate the optical constants characterizing the thin films from the above system. They shift towards higher wavelengths with the increase of tellurium content in the layers. This may be due to the influence of the absorption coefficient \(\alpha\) and scattering of light by charged defects [23].

The refractive index, \(n\) and the thickness, \(d\) of the thin GeSe$_2$-GeTe-PbTe films were calculated from the interference extrema in the transmittance spectra using Swanepoel’s method [24, 25]. The program used to calculate \(n\) determines it to an accuracy of ± 0.5 % for an error in the transmittance of ±0.1 % [25]. The spectral dependence of the refractive index, \(n(\lambda)\) of as-deposited Ge-Se-Te films is plotted in Fig. 3b. The decrease in the value of the refractive index with the wavelength (Fig. 3b) shows the normal dispersion behavior of the amorphous material. In previous work [20] we found a value for \(n = 2.38\) at \(\lambda = 1550\) nm for as-deposited GeSe$_2$ thin film. The addition of 3 at.% of tellurium in GeSe$_2$ leads to an increase in \(n\) with 0.08 in GeSe$_2$ films. For the films with higher content of tellurium was found that \(n\)

![Fig. 3. a) spectral dependence of the transmission coefficient (films thickness ~ 800 nm); b) refractive index dispersion \(n(\lambda)\) and c) Tauc’s plot \((\alpha h\nu)^{1/2}\) vs. photon energy of as-deposited thin films with different composition from Ge-Se-Te system](image)

increases and for composition Ge$_{32}$Se$_{55}$Te$_{13}$ its value reaches a value of 3.27. The difference in the increasing step of the refractive index probably is due the presence of phase separation in the films prepared by evaporation of bulk glasses containing Pb in them.
Fig. 3c shows the variation of \((a h \nu)^{1/2}\) as a function of photon energy, \(h \nu\), for Ge\(_{33}\)Se\(_{67-x}\)Te\(_x\) thin films. The character of plots indicates the allowed indirect transitions are responsible for the absorption of Ge-Se-Te films for all compositions. The values of the optical band gap, \(E_{\text{g}}^{\text{opt}}\), are obtained by extrapolating the linear region of the plots. The optical band gap of virgin Ge\(_{33}\)Se\(_{67}\) thin films was found to be 2.42 eV. It is clear from Fig. 3c that the optical band gap decreases with increasing Te content in virgin films assuming values from 1.81 eV for Ge\(_{31}\)Se\(_{60}\)Te\(_3\) to 1.30 eV for Ge\(_{32}\)Se\(_{55}\)Te\(_{13}\). Dependence like this is demonstrated in [26] for the influence of tellurium on the optical gap in thin films from the system Ge\(_{10}\)Se\(_{90-x}\)Te\(_x\). The decrease of the optical band gap with Te content could be explained with the character of the chemical order of amorphous chalcogenide glasses. According to the model described by Kastner et al. [27] the main contribution for states near the valence band in chalcogenide glasses comes from the lone-pair \(p\)-orbitals of chalcogen atoms. It is well known that the electronegativities of Ge, Se and Te are 2.01, 2.55 and 2.1, respectively, i.e. the tellurium is less electronegative than selenium, so the substitution of Te for Se may raise the energy of some lone-pair states and hence broaden the valence band [26].

The other group of experiments, made by us, was related to studying of the irreversible changes of the optical properties in the thin films from the system Ge\(_{33}\)Se\(_{67-x}\)Te\(_x\). The investigation was performed on films, deposited in one vacuum cycle on two BK-7 substrates. After the measurement of \(T_{\text{ad}}R\) of as-deposited thin films and calculation of the optical constants \(n, k\) and the film thicknesses \(d\), one of the films was at first illuminated and then annealed and the other one – annealed and then exposed. As it was mentioned above, the illumination was performed using halogen lamp for time, at which the optical constants stop to change, while the annealing was made in vacuum at temperature 25 °C lower than the \(T_g\) of each composition of bulk samples. The results for the changes in the refractive index, optical band gap and films' thickness after exposure to light or annealing are presented in Table 2. It is seen that both the illumination and the annealing lead to decrease of the refractive index (\(\Delta n = 0.03-0.08\) for the exposed films and \(\Delta n = 0.08-0.10\) for annealed ones) and increase of the optical band gap with 0.03-0.05 eV and 0.11-0.15 eV for

<table>
<thead>
<tr>
<th>Composition</th>
<th>Refractive index at 1550 nm</th>
<th>Optical band gap (eV)</th>
<th>Film thickness (nm)</th>
<th>(\Delta \lambda) (nm)</th>
<th>Annealed films</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge(<em>{31})Se(</em>{66})Te(_3)</td>
<td>2.54</td>
<td>2.49</td>
<td>2.46</td>
<td>1.81</td>
<td>1.86</td>
</tr>
<tr>
<td>Ge(<em>{32})Se(</em>{64})Te(_4)</td>
<td>2.80</td>
<td>2.72</td>
<td>2.70</td>
<td>1.55</td>
<td>1.58</td>
</tr>
<tr>
<td>Ge(<em>{33})Se(</em>{59})Te(_8)</td>
<td>2.78</td>
<td>2.75</td>
<td>2.70</td>
<td>1.45</td>
<td>1.49</td>
</tr>
<tr>
<td>Ge(<em>{32})Se(</em>{55})Te(_{13})</td>
<td>3.37</td>
<td>3.34</td>
<td>3.27</td>
<td>1.30</td>
<td>1.33</td>
</tr>
</tbody>
</table>

the exposed and annealed films, respectively as well as the film thickness for all compositions from the studied system. As an illustration the changes of transmittance, \(n\) and \(E_{\text{g}}^{\text{opt}}\) for as-deposited, exposed and annealed Ge\(_{32}\)Se\(_{55}\)Te\(_{13}\) films are presented on Fig. 4. It is seen that after exposure to light the optical transmittance edge of Ge\(_{32}\)Se\(_{55}\)Te\(_{13}\) film shifts to shorter wavelength. This photo-induced effect is so-
Fig. 4. a) spectral dependence of the transmission coefficient; b) refractive index dispersion $n(\lambda)$ and c) Tauc’s plot $(\alpha h \nu)^{1/2}$ vs. photon energy of as-deposited, exposed and annealed thin Ge$_{32}$Se$_{55}$Te$_{13}$ films.

called photobleaching [29] (Fig. 4a). As it is shown on Fig. 4a, after thermal annealing the transmission edge is shifted again to shorter wavelength in the annealed state. These shifts are irreversible and they are valid for all compositions from the Ge-Se-Te system. The magnitude of the shift $\Delta \lambda$ increases with the increase of the intensity of illumination and the illumination time. The effect of photobleaching ($\Delta \lambda = 70$ nm at $T = 20 \%$) is hardly expressed for the composition Ge$_{32}$Se$_{55}$Te$_{13}$ (Table 2). The occurrence of photobleaching in a-Ge-Se-Te films is due to photo-induced structural changes. The calculated values for $n$ and $E_{opt}^g$ demonstrated that the effect of annealing is stronger than that of exposure to light of films from the Ge$_{33}$Se$_{67-x}$Te$_x$ system (Figs. 4b and 4c). No change of the optical constants values was observed after illumination of the annealed films, which shows that no reversible changes appear in these films. For comparison we will mention that for thin GeSe$_2$ films [20] we have found that the effect of photo- and thermo-induced changes in the refractive index was expressed as a decrease in $n$ with 0.05 and 0.11, respectively and an increase in the $E_{opt}^g$ value with 0.11 and 0.18 eV, respectively.
3.3. Optical properties of thin Ge-Se-Te-Pb films

In the second part of our investigation we will determine the optical constants of thin films from the GeSe$_2$-GeTe-PbTe system for which no data was found in the literature. Thin films with the following composition Ge$_{29}$Se$_{57}$Te$_{10}$Pb$_4$, Ge$_{27}$Se$_{51}$Te$_{14}$Pb$_8$, Ge$_{25}$Se$_{43}$Te$_{19}$Pb$_{15}$, Ge$_{25}$Se$_{30}$Te$_{28}$Pb$_{17}$, Ge$_{22}$Se$_{46}$Te$_{17}$Pb$_{15}$ and Ge$_{22}$Se$_{38}$Te$_{25}$Pb$_{15}$ (Table 1) were deposited from bulk samples from cross-sections (GeSe$_2$)$_{70-x}$(GeTe)$_x$(PbTe)$_{30}$ and (GeSe$_2$)$_{92-x}$(GeTe)$_x$(PbTe)$_x$. According to the XRD analysis the first two films are amorphous. For the films containing 15 at. % Pb a crystalline phase of PbSe with predominant (h00) orientation was recognized, which is characteristic for thin films from these materials. In the layers with composition Ge$_{25}$Se$_{30}$Te$_{28}$Pb$_{17}$ the crystalline phase Pb$_2$SeTe was observed. It seems that as a result of the heating during the evaporation process of the bulk samples from the Ge-Se-Te-Pb system a part of the selenium would displace the tellurium in PbTe, giving rise thus to the formation of a new compound, i.e. crystalline PbSe or Pb$_2$SeTe built in the amorphous Ge-Se-Te phase. Diffractograms of some of the studied thin films are shown on Fig. 5 as illustration of the results from XRD analysis.

![Diffractograms of thin films with composition: a)Ge$_{27}$Se$_{51}$Te$_{14}$Pb$_8$; b) Ge$_{25}$Se$_{30}$Te$_{28}$Pb$_{17}$](image)

Fig 5. Diffractograms of thin films with composition: a)Ge$_{27}$Se$_{51}$Te$_{14}$Pb$_8$; b) Ge$_{25}$Se$_{30}$Te$_{28}$Pb$_{17}$.

The refractive index dispersion $n(\lambda)$ (a) and Tauc’s plot $(a\lambda^2)^{1/2}$ vs. photon energy (b) of as-deposited thin films with different composition from the (GeSe$_2$)$_{92-x}$(GeTe)$_x$(PbTe)$_x$ system are plotted on Fig. 6. The values of the refractive index at 1550 nm as well as of the optical band gap are summarized in Table 3. From the spectral dependence of the transmission coefficient was seen that the maxima and minima of fringes on the plots shift towards higher wavelengths with the increase of tellurium and lead content in the layers (Fig. 6a) and that the contribution of Pb is bigger in comparison with the effect of Te (Fig. 3a). It was found (Fig. 6b) that the refractive index for the as-deposited thin films increases with the increase of the Te and Pb content in the films and highest values were obtained for the composition Ge$_{22}$Se$_{46}$Te$_{17}$Pb$_{15}$ ($n = 3.74$) deposited from bulk samples from cross-sections (GeSe$_2$)$_{92-x}$(GeTe)$_x$(PbTe)$_x$. As the refractive index reflects the average mass of atoms making up the films, it increases when the content of Pb increases (Pb is the heaviest atom in the compound) [30]. In our previous paper [19] we have shown that the compactness of chalcogenide glasses increases with the increase of the PbTe content in glasses due to their structure densification. The glass structure becomes more dense because of including of Te and Pb atoms in the glassy network of glasses. As an addition crystalline PbSe and PbTe clusters exist in the films, i.e. there is a separation. In the same time the optical band gap decreases from 1.81 eV for the composition Ge$_{31}$Se$_{66}$Te$_3$ up to 1.14 eV Ge$_{22}$Se$_{46}$Te$_{17}$Pb$_{15}$ (Fig. 6c). The observed decrease
is bigger then the decrease due only to influence of Te content in the layers ($E_g^{\text{opt}} = 1.30 \text{ eV}$ for Ge$_{32}$Se$_{55}$Te$_{13}$). In chalcogenide glasses containing a high concentration of chalcogen elements the lone-

Table 3. Data for the optical constants of thin GeSe$_2$ – GeTe – PbTe films

<table>
<thead>
<tr>
<th>Composition</th>
<th>Refractive index at 1550 nm</th>
<th>Optical band gap (eV)</th>
<th>Film thickness (nm)</th>
<th>$\Delta \lambda$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge$<em>{32}$Se$</em>{64}$Te$_4$</td>
<td>2.80</td>
<td>2.72</td>
<td>2.70</td>
<td>1.55</td>
</tr>
<tr>
<td>Ge$<em>{30}$Se$</em>{55}$Te$_{14}$Pb$_4$</td>
<td>3.03</td>
<td>2.95</td>
<td>2.90</td>
<td>1.54</td>
</tr>
<tr>
<td>Ge$<em>{29}$Se$</em>{57}$Te$_{10}$Pb$_4$</td>
<td>3.08</td>
<td>3.04</td>
<td>2.94</td>
<td>1.43</td>
</tr>
<tr>
<td>Ge$<em>{32}$Se$</em>{55}$Te$_{14}$Pb$_4$</td>
<td>3.66</td>
<td>3.62</td>
<td>3.82</td>
<td>1.20</td>
</tr>
<tr>
<td>Ge$<em>{30}$Se$</em>{57}$Te$_{10}$Pb$_4$</td>
<td>3.74</td>
<td>3.69</td>
<td>3.97</td>
<td>1.25</td>
</tr>
<tr>
<td>Ge$<em>{29}$Se$</em>{57}$Te$_{10}$Pb$_4$</td>
<td>3.30</td>
<td>3.24</td>
<td>3.83</td>
<td>1.14</td>
</tr>
</tbody>
</table>
pair forms the top of the valence band and the antibonding band forms the bottom of conduction band [31]. The optical band gap corresponds closely to the energy difference between the top of the valence band and the bottom of the conducting band. The results from studying changes in the optical constants in Ge-Se-Pb films [30] demonstrate that the width of the tails of localized states in the energy gap increases when the Pb content in the films increases. It is known that the width of the tails of localized states is connected with disorder in the films, which increase with the increase of Pb content in Ge-Se-Te films. The increase of disorder is responsible for the decrease of the optical band gap.

The results from studying changes in the refractive index, optical band gap and films’ thickness after exposure to light or annealing as well as the shift of the absorption edge after annealing are presented in Fig. 7 and Table 3. It is found that the shift of the absorption edge after exposure to light is negligible as well as the changes in the optical band gap. After annealing the value of the shift decreases with the increase of Pb content and these values are smaller than the values obtained from changing the concentration only of Te. From plots of the refractive index dispersion it could be concluded that the state of the layers after annealing is the end one and in the system only irreversible changes are possible. Since in the as-deposited films are presented Ge-Se, Ge-Te, Se-Te, Ge-Pb, Pb-Se and Pb-Te bonds the illumination or annealing of thin films cause a reduction in the number of some of them which could explain the changes in their optical properties.

**Fig. 7.** a) spectral dependence of the transmission coefficient; b) and c) refractive index dispersion $n(\lambda)$ and c) Tauc’s plot $(a\nu)_{1/2}$ vs. photon energy of as-deposited, exposed and annealed thin Ge$_{24}$Se$_{43}$Te$_{18}$Pb$_{15}$ films.
4. Conclusions

The conditions for deposition of thin films from the new chalcogenide GeSe₂-GeTe-PbTe system were established and it was shown that the composition of most of the coatings was close to the expected one, except the films on the cross-section with 10 mol.% PbTe. The surface microstructure of the layers is smooth and most of them are amorphous. Crystalline inclusions of nano-sized PbSe and Pb₂SeTe particles were observed on the films with high Pb content.

With the increase of PbTe (or Te) content in the layers, the absorption edge is shifted to the longer wavelengths, the refractive index values increase while the optical band gap decreases. After exposure to light and after annealing of the films, the refractive index decreases, while the optical band gap and the films thickness increase. The annealing effect is stronger than the illumination one for the films from the GeSe₂-GeTe-PbTe system.

Acknowledgments

This work was financially supported by the Ministry of Education, Youth and Science, Bulgaria (National Science Fund – contract DO02-123/15.12.2008).

References


