Optical properties of thermally evaporated (As$_2$Se$_3$)$_{100-x}$Ag$_x$ thin films

V Ilcheva$^{a,b}$, P Petkov$^a$, V Boev$^b$, T Petkova$^{a*}$

$^a$Department of Physics, University of Chemical Technology and Metallurgy, 8 Kl. Ohridski Blvd, 1756 Sofia, Bulgaria
$^b$Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 10, 1113 Sofia, Bulgaria

Abstract

We obtained amorphous thin films by evaporation and condensation in three component systems based on As, Se and Ag. The aim was to investigate the influence of the third component on the thin film structure and optical properties. The refractive index and the film thickness were determined from the upper and lower envelopes of the optical transmission spectra, measured in the spectral range 400 – 2500 nm.

The absorption coefficient ($\alpha$) was determined after extrapolation the values of $n$ in the region of strong absorption (where $\alpha \geq 10^4$ cm$^{-1}$) and its spectral distribution was discussed. The dispersion of the refractive index was analyzed in terms of single-oscillator Wemple-DiDomenico model. The shift of the optical absorption edge was described using the non-direct transition model, proposed by Tauc. Optical band gap was calculated from the Tauc plot $\alpha h\nu=B(Eg_{Tauc} – h\nu)^2$ and the compositional dependence of the optical gap was discussed. In order to realize photoinduced changes in the films, they were illuminated by He-Ne laser and their transmission spectra were measured before and after illumination. The shift of the absorption edge of as – deposited and illuminated films was investigated and discussed as a function of the films composition.

Keywords: Chalcogenide thin films, optical properties, photoinduced changes;

* Corresponding author. Tel.: ++359 2 9792780; fax: ++ 359 2 722544.
E-mail address: vania_ilcheva@yahoo.com.
1. Introduction

Chalcogenide glasses based on sulfide, selenide and telluride alloys in binary or multi-component systems are very promising materials for various optical and photonic applications in the spectral range 0.6 to 15 μm. Up to now they have being studied mostly for applications as passive devices as lenses, windows, fibers but these glasses are also attractive for preparation of active devices such as laser fiber amplifiers and non-linear components [1].

The properties of the glassy binary chalcogenides are affected by the addition of third element. Experimental results reported by various workers have shown that the additives in various chalcogenide glasses change the optical properties [2].

In this paper the distribution of some optical parameters of thermally evaporated (As$_2$Se$_3$)$_{100-x}$Ag$_x$ layers as a function of their composition has been studied. The variation of the optical band gap has been discussed in terms of the local ordering modification due to Ag incorporation. The photoinduced changes in the three-component glassy system as a result of He-Ne laser illumination have been also studied and discussed.

2. Experimental

Three compositions of the glassy (As$_2$Se$_3$)$_{100-x}$Ag$_x$ alloys with $x = 0, 15$ and 20 mol. % Ag, synthesized by melt-quenching technique as described elsewhere [3], were used for thin film preparation by vacuum thermal evaporation (VTE).

The thermal evaporation process was carried out at a source-substrate distance of 0.12 m, a temperature of evaporation source of 700-800 K and a residual gas pressure of 1.33x10$^{-4}$ Pa. In order to avoid thickness non-uniformities, the substrates were rotated during the evaporation process. The thickness of prepared films varies from 627–1120 nm.

In order to minimize the gradient of Ag concentration through the film, the samples were thermally annealed in vacuum for 48 hour under the glass transition temperature of the glasses. The process of annealing leads to equalization of the silver concentration due to the thermally-induced dissolution and diffusion (TIDD) process, thoroughly described by T. Wagner at all [4].

Thin films of (As$_2$Se$_3$)$_{100-x}$Ag$_x$ chalcogenide glasses were illuminated using by He-Ne laser (632,8 nm) with intensity 1.2 mW/cm$^2$ at room temperature. The illumination was carried out through a diaphragm with an aperture of about 5 mm.

The optical transmission spectra of the thin films were recorded before and after illumination in the wavelength range of 400 to 2500 nm at room temperature using a double-beam computer-controlled Cary 5E UV–VIS–NIR spectrophotometer with an accuracy of ±0.5 nm. The optical constants were derived by Swanepoel method.

3. Results and discussion

3.1. Optical properties of as – deposited (As$_2$Se$_3$)$_{100-x}$Ag$_x$ films

The optical transmission spectra of the thin films were recorded in the wavelength range of 400 to 2500 nm. The films are transparent in the visible and near infrared spectral regions and the spectra show interference maxima and minima, approaching the transmission of the glass substrate (fig. 1).
The absorption edge is between 550 and 700 nm depending on the film composition. It gradually shifts to longer wavelengths when Ag is added into the As-Se amorphous matrix. The red shift of the absorption edge observed on the spectra after addition of silver is probably caused by formation of defect states, localized in the band gap.

![Fig. 1. Transmission spectra of the (As₂Se₃)₁₋ₓAgₓ thin films](image)

The optical constants and the thickness of the thin films were calculated from the transmission spectra using the method suggested by Swanepoel [5] for the case of uniform thin layers, which is based on the upper and lower envelopes of the transmission spectrum at normal incidence.

Fig. 2 shows the spectral dependence of the refractive index $n$ of (As₂Se₃)₁₋ₓAgₓ films. The overall tendency is the increase of $n$ with silver content in the films, which is probably related to an increase in the number of heteropolar bonds. These bonds replace part of the homopolar bonds, presented in the structural units leading to an increase in the effective polarisability [6].

![Fig. 2. Spectral distribution of the refractive index of (As₂Se₃)₁₋ₓAgₓ films](image)

The dispersion of the refractive index has been analyzed in terms of the Wemple–Di Domenico model [7,8], which is based on the single-oscillator formula.

\[
(\text{As}_2\text{Se}_3)_{1-x}\text{Ag}_x, \quad n(\lambda) = 2.53 + 142578/\lambda^2, \\
(\text{As}_2\text{Se}_3)_{1-x}\text{Ag}_x, \quad n(\lambda) = 2.63 + 169998/\lambda^2, \\
(\text{As}_2\text{Se}_3)_{1-x}\text{Ag}_x, \quad n(\lambda) = 2.67 + 199486/\lambda^2.
\]
\[ n^2 (h \nu) - 1 = \frac{E_d E_0}{E_0^2 - (h \nu)^2} \]  

(1)

By plotting \((n^2 - 1)^{-1}\) versus \((h \nu)^2\) and fitting a straight line, the single-oscillator energy \((E_0)\) and the dispersion energy \((E_d)\) can be determined from the slope, \((E_0 E_d)^{-1}\) and the intercept, \(E_0/E_d\) on the vertical axis, respectively. The values of the dispersion parameters \(E_d\) and \(E_0\) are presented in Table 1. The proportion between \(E_0\) and \(E_{g_{opt}}\) will be discussed later, taking into account the relation \(E_0 = 2E_{g_{opt}}\), found by Tanaka [9].

The absorption coefficient \(\alpha\) for all investigated films was determined in the region of strong absorption \((\alpha \geq 10^4 \ cm^{-1})\), which involves optical transitions between the valence and conduction bands [6]. For that purpose, the obtained values of \(n\) were extrapolated in the high absorption region and \(\alpha\) was estimated using an equation given in Ref. 4.

The spectral dependences of the absorption coefficient \(\alpha\) of films with different Ag content are plotted in Fig.3. It is obvious that the introduction of silver leads to increase of the absorption coefficient.

![Fig. 3. Spectral distribution of absorption coefficient in (As₂Se₃)₁₋ₓAgₓ films](image)

As we mentioned above, the high absorption region \((\alpha \geq 10^4 \ cm^{-1})\) corresponds to transitions between extended states in both valence and conduction bands where the Tauc law [10] is valid. Thus, above exponential tail, the absorption coefficient of amorphous semiconductors can be described by the relation \(\alpha h \nu = B(h \nu - E_g)^m\), where \(h \nu\) is the photon energy; \(E_g\) - the optical band gap; \(B\) - constant that depends on the transition probability; \(m\) - index, depending on the nature of electronic transitions. For amorphous materials non-direct optical transitions \((m = 2)\) are observed.

<table>
<thead>
<tr>
<th>Glass composition</th>
<th>(E_d) (eV)</th>
<th>(E_0) (eV)</th>
<th>(E_{g_{opt}}) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As₂Se₃</td>
<td>20.934</td>
<td>3.82</td>
<td>1.79</td>
</tr>
<tr>
<td>(As₂Se₃)₈₅Ag₁₅</td>
<td>21.618</td>
<td>3.59</td>
<td>1.74</td>
</tr>
<tr>
<td>(As₂Se₃)₈₀Ag₂₀</td>
<td>21.354</td>
<td>3.42</td>
<td>1.72</td>
</tr>
</tbody>
</table>
Optical band gap $E_g^{\text{opt}}$ was determined from intercept on the energy axis of linear fit of high absorbing region ($\alpha \geq 10^4 \text{ cm}^{-1}$) in plot $(\alpha h \nu)^{1/2}$ versus $h \nu$ (where $\alpha$ is absorption coefficient and $h \nu$ is energy of incident photons) known as Tauc extrapolation [10].

The derived from the Tauc plots optical band gaps of the films are presented in table 1. The dependence between $(\alpha h \nu)^{1/2}$ vs. $h \nu$ corresponds to a straight line giving a proof that non-direct transitions are responsible for the optical absorption in the high-energy spectral region [6]. The obtained values of $E_g^{\text{opt}}$ for initial As$_2$Se$_3$ chalcogenide matrix are in a good agreement with the results, published earlier [11].

The decrease of the band gap with addition of silver is related to the structural transformation in the material as a result of silver incorporation. According [12] the basic structural units in As-Se glasses are AsSe$_3$ pyramids. The addition of Ag in to As-Se matrix leads to decrease of the AsSe$_3$ pyramids, which are replaced by Ag$_3$AsSe$_3$ structural units [13]. The appearance of new structural units causes an increase of disorder and number of defects in the material structure.

The decrease in the optical band gap could be discussed in the frame of Mott and Davis model [14], finding out a relation between the degree of disorder and defects in amorphous structure and the width of the localized states near the mobility edges. As a result of insufficient number of atoms, unsaturated bonds together with some saturated bonds (like dative bonds) are produced. These unsaturated bonds cause the formation of some defects in the material, responsible for the presence of localized states in the band gap of the amorphous solids. As we mentioned above, the introduction of silver results to an increase of the number of defects, due to formation of structural units with greater and/or smaller coordination than the regular structural units, which leads to increase in the density of the localized states and consequently decrease in the optical band gap of the material. We can conclude from the results listed in Table 1, that the values of the gaps $E_0$ and $E_g^{\text{opt}}$ satisfy the already introduced relationship $E_0 = 2E_g^{\text{opt}}$.

3.2. Photoinduced changes in the films after He-Ne laser illumination

![Graph showing transmission spectra of the (As$_2$Se$_3$)$_{1-x}$Ag$_x$ thin films](image-url)
The transmission spectra of \((\text{As}_2\text{Se}_3)_{1-x}\text{Ag}_x\) thin films before and after illumination are shown in Fig. 4. Transmission spectra, recorded after illumination of the films show a significant shift (\(\Delta\lambda\)) of the optical absorption edge to longer wavelength (dashed lines in Fig. 4), i.e. photodarkening.

According [15], photoinduced effects are strongly related to the source of the light exposure, the intensity of the illumination light and the illumination time. The effect is very sensitive to the film composition and deposition technique.

The maximum of the photodarkening effect in \((\text{As}_2\text{Se}_3)_{100-x}\text{Ag}_x\) is observed in the film without silver (\(x = 0\)). The photodarkening effect is found to decrease gradually as silver content increases up to 15 %, i.e. the effect is most probably suppressed by the addition of silver into chalcogenide matrix (fig. 5).

Fig. 5 shows the dependence of the absorption edge shift, defined as transmission \(T=20\%\) \((\Delta\lambda = \lambda_{\text{exposed}} - \lambda_{\text{unexposed}})\) on the Ag content in \((\text{AsSe})_{100-x}\text{Ag}_x\). The results are in good agreement with our previous investigation of the \((\text{As}_2\text{Se}_3)_{100-x}\text{Ag}_x\) system [16], where the photodarkening effect in the As-Se-Ag system is masked due to the production of metal-chalcogen electronic bonding states on top of the valence band [16].

4. Conclusion

\((\text{As}_2\text{Se}_3)_{100-x}\text{Ag}_x\) amorphous thin films with three different compositions have been successfully deposited by vacuum thermal evaporation and their optical properties have been determined from the transmission spectra, measured at normal incidence.
The refractive index calculations, carried out by the modified Swanepoel method show tendency of increase of n with silver content over the entire studied spectral range, which is probably related to an increase in the effective polarisability after structural transformations in the films.

Optical band gap $E_{\text{g opt}}$, determined by Tauc extrapolation is found to decrease after silver addition. The decrease is probably due to the formation of defects in the amorphous structure, giving rise to the localized states density increase and consequently decreasing of optical band gap of the material.

The dispersion of the refractive index has been analyzed in terms of the Wemple–Di Domenico model in order to determine the values of the dispersion parameters - single-oscillator energy $E_0$ and dispersion energy $E_d$. The values of $E_0$ and $E_{\text{g opt}}$ satisfy the Tanaka relationship $E_0 = 2E_{\text{g opt}}$ value typical to the amorphous materials.

The compositional dependence of the photodarkening in ternary (As$_2$Se$_3$)$_{1-x}$Ag$_x$ glassy thin films has been studied in relation to the Ag concentration. It has been observed that the addition of silver decreases the photodarkening effect and contributes to the stabilization of glassy matrix with respect to the light exposure.

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References

[1] Krkal M, Wagner T, Vlcek Mil, Vlcek Mir and Frumar M. Optical properties and structure of amorphous films Ag$_x$(As$_{0.33}$S$_{0.67-y}$Se$_y$)$_{100-x}$. J. Non-Cryst Solids 2006; 352:2662-66.


