Compositional dependence of the optical properties of silver containing As$_2$Se$_3$ thin films

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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 extrapolating the values of $n$ in the region of strong absorption (where $\alpha \geq 10^4$ cm$^{-1}$); its spectral distribution is discussed. The dispersion of the refractive index was analyzed in terms of the single-oscillator Wemple-DiDomenico model. The shift of the optical absorption edge was described using the non-direct transition model proposed by Tauc. The optical band gap was calculated from the Tauc plot $\alpha h\nu = B(Eg^{opt} - h\nu)^2$; the compositional dependence of the optical gap is also discussed.

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 $\mu$m. Up to now, they have been studied mostly for applications as passive devices, such as lenses, windows, fibers; however, these glasses are also attractive for preparation of active devices, such as laser fiber amplifiers and non-linear components [1].

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

In this paper, we present studies of the distribution of the optical parameters of VTE-layers as a function of the composition. The variation of the optical band-gap is discussed in terms of the local ordering modification due to Ag incorporation.

2. Experimental
Three compositions of the glassy (As$_2$Se$_3$)$_x$Ag$_{1-x}$ alloys with $x = 0, 15$ and 20 mol. % Ag, synthesized by melt-quenching 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, evaporation source temperature of 700-800 K and a residual gas pressure of $1.33 \times 10^{-4}$ Pa. In order to avoid thickness non-uniformities, the substrates were rotated during the evaporation process. The thickness of prepared films varied from 627–1120 nm. The optical transmission spectra of the thin films were recorded 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 applying the Swanepoel method.

3. Results and discussion

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, with the spectra exhibiting interference maxima and minima and approaching the transmission of the glass substrate (figure 1).

The absorption edge is between 550 and 700 nm depending on the film composition. It gradually shifts to the longer wavelengths when Ag is added into the As-Se amorphous matrix. The red shift of the absorption edge observed in the spectra after addition of silver is probably caused by formation of defect states localized in the band gap.

The optical constants and the thickness of the thin films were calculated from the transmission spectra using the method suggested by Swanepoel [4] for the case of uniform thin layers, which is based on the upper and lower envelopes of the transmission spectrum at normal incidence.

Figure 1. Transmission spectra of the (As$_2$Se$_3$)$_{1-x}$Ag$_x$ thin films.

Figure 2 shows the spectral dependence of the refractive index $n$ of (As$_2$Se$_3$)$_{1-x}$Ag$_x$ films. The overall tendency is an increase in $n$ with the 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, present in the structural units, leading to an increase in the effective polarizability [5].

Figure 2. Spectral distribution of the refractive index of (As$_2$Se$_3$)$_{1-x}$Ag$_x$ films.

Figure 3. Spectral distribution of the absorption coefficient in (As$_2$Se$_3$)$_{1-x}$Ag$_x$ films.
The dispersion of the refractive index was analyzed in terms of the Wemple–Di Domenico model [6,7], which is based on the single-oscillator formula $n^2(\hbar \nu) - 1 = \frac{E_d E_0}{E_d^2 - (\hbar \nu)^2}$. By plotting $(n^2 - 1)^{-1}$ versus $(\hbar \nu)^2$ and fitting a straight line, the single-oscillator energy ($E_0$) and the dispersion energy ($E_d$) can be determined from the slope, $(E_d E_0)^{-1}$, and the intercept, $E_d/E_0$, 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 $E_{gopt}$ will be discussed later, taking into account the relation $E_0 = 2E_{gopt}$, found by Tanaka [8].

The absorption coefficient $\alpha$ for all films investigated was determined in the region of strong absorption ($\alpha \geq 10^4$ cm$^{-1}$), which involves optical transitions between the valence and conduction bands [5]. For this purpose, the values of $n$ obtained were extrapolated in the strong-absorption region and $\alpha$ was estimated using the equation given in [4].

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

As we mentioned above, the strong-absorption region ($\alpha \geq 10^4$ cm$^{-1}$) corresponds to transitions between extended states in both valence and conduction bands where Tauc law [9] is valid. Thus, above the exponential tail, the absorption coefficient of amorphous semiconductors can be described by the relation $\alpha h \nu = B(\hbar \nu - E_g)^m$, where $h \nu$ is the photon energy; $E_g$, the optical band gap; $B$, a constant that depends on the transition probability; $m$, an index depending on the nature of electronic transitions. For amorphous materials, non-direct optical transitions ($m = 2$) are observed.

The optical band gap $E_{gopt}$ was determined from the intercept on the energy axis of the linear fit in the strong-absorption region ($\alpha \geq 10^4$ cm$^{-1}$) of the plot $(\alpha h \nu)^{1/2}$ versus $h \nu$ (where $\alpha$ is the absorption coefficient and $h \nu$ is the incident photons energy), known as Tauc extrapolation [9].

The optical band gaps of the films derived from the Tauc plots are presented in table 1. The dependence $(\alpha h \nu)^{1/2}$ 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 [5]. The values obtained of $E_{gopt}$ for the initial As$_2$Se$_3$ chalcogenide matrix are in good agreement with the results published earlier [10].

| Glass composition       | $E_d$, eV | $E_0$, eV | $E_{gopt}$, eV |
|-------------------------|-----------|-----------|----------------|
| As$_2$Se$_3$            | 20,934    | 3,82      | 1,79           |
| (As$_2$Se$_3$)$_{85}$Ag$_{15}$ | 21,618    | 3,59      | 1,74           |
| (As$_2$Se$_3$)$_{80}$Ag$_{20}$ | 21,354    | 3,42      | 1,72           |

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 to [11], the basic structural units in As-Se glasses are AsSe$_3$ pyramids. The addition of Ag in to As-Se matrix leads to a decrease in the AsSe$_3$ pyramids, which are replaced by Ag$_3$AsSe$_3$ structural units. The appearance of new structural units causes an increase of the disorder and the number of defects in the material structure.

The decrease in the optical band gap can be discussed in the framework of Mott and Davis model [12] relating the degree of disorder and defects in an amorphous structure to 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 (such as 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 in 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 an increase in the density of the localized states and, consequently, a 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 $E_{g^{opt}}$ satisfy the already introduced relationship $E_0 = 2E_{g^{opt}}$.

Conclusions

$(\text{As}_2\text{Se}_3)_{100-x}\text{Ag}_x$ amorphous thin films with three different compositions were successfully deposited by vacuum thermal evaporation; their optical properties were determined from the transmission spectra measured at normal incidence.

The refractive index calculations, carried out by the modified Swanepoel method, show the tendency of an increase in $n$ with the silver content over the entire spectral range studied, which is probably related to an increase in the effective polarizability after structural transformations in the films.

The optical band gap $E_{g^{opt}}$, 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 an increase in the localized states density and, consequently, a decrease in the optical band gap of the material.

The dispersion of the refractive index was 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 $E_{g^{opt}}$ satisfy the Tanaka relationship $E_0 = 2E_{g^{opt}}$, as is typical for amorphous materials.

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