Photoinduced changes in As-Se-Ag amorphous films

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Abstract. Thin films from the As-Se-Ag system have been prepared on glass and silicon substrates by thermal vacuum evaporation from previously fabricated bulk glassy samples. The amorphous state of the samples has been proved by X-ray diffraction. Some optical properties of the amorphous As-Se-Ag thin films have been studied in relation to the Ag concentration in the sample. In order to investigate the photoinduced changes due to irradiation by with He-Ne laser light, transmission spectra of the thin films have been measured before and after irradiation. The optical characteristics as a function of the composition have been studied.

1. Introduction

The amorphous materials of the chalcogenides’ family are widely applicable in the field of semiconductor technologies. Their unique properties determine their potential application, such as optical storage media [1], memory devices [2], optical elements (lenses, waveguides, gratings, etc) [3], electrolytes for solid state batteries [4] and sensitive media in sensor systems for liquid [5] and gas analysis [6]. Moreover, these materials possess are transparent in the infra-red region of the spectrum beyond 12 μm, which make them suitable for producing filters, windows and fibers for the infrared range.

Numerous previous investigations have shown that interesting characteristics can be achieved by adding transition metals into the glass matrix. Silver containing glassy chalcogenides have been the object of scientific and practical interest due to the almost unlimited opportunity by composition variation to modify their behaviour. Petkova et al. [7] have studied the structure of (AsSe)80Ag20 glasses and reported that the incorporation of silver modifies the local ordering of the host matrix As-Se.

Accordingly, we decided to focus our research efforts on studying photoinduced changes in the three-component glassy (AsSe)1-xAg x system as a function of the silver content and time of irradiation by a He-Ne laser.

2. Experimental

Thin film samples were prepared by thermal evaporation on glass substrates from previously obtained bulk glassy samples with composition (AsSe)1-xAg x, where x = 0, 10, 15 and 20 at. %.
The thermal evaporation process was implemented under the following conditions: source-substrate distance - 0.12 m, temperature of the evaporation source - 700÷800 K and residual gas pressure of 1.33×10⁻⁴ Pa. In order to avoid thickness non-uniformity, the substrates were rotated during the evaporation process.

The amorphous character of the films obtained was proved by X-ray diffraction by using Philips Analyzer APD-15, Cu-Kα radiation.

Photodarkening kinetic was measured during irradiation of the amorphous films by a He-Ne laser (632.8 nm) with intensity 1.2 mW/cm² at room temperature. A Si-photodetector was used for real time registration of the transmitted light. The detector was connected to a computer for data collection and processing.

The optical transmission spectra of the thin films were measured in the visible and near IR region before and after irradiation by the He-Ne laser. The spectra were obtained using a double beam UV/VIS/NIR computer controlled spectrophotometer (Perkin Elmer, model Lambda–19) in the spectral region 400–2000 nm at room temperature. The accuracy of the measurement was ±1 nm.

The films thickness, as estimated from the optical transmission spectra by Swanepoel’s method [8], was about 700 nm.

3. Results and discussion

XRD patterns of the films with x=0 and 20 at. % are presented in figure 1. The absence of crystalline peaks proves the amorphous character of the films.

![Figure 1. X-Ray diffraction patterns of (AsSe)₁ₓAgₓ thin films with different Ag content.](image1.jpg)

Figure 2 shows the transmission spectra of the irradiated and fresh (not irradiated) (AsSe)₁ₓAgₓ films for x = 0, 10, 15, 20 at.%. There is a noticeable shift (Δλ) of the optical absorption edge to the longer wavelength after irradiation i.e. photodarkening. The maximum value of Δλ (9 nm) at transmission T = 20 % is achieved for the film without silver, while for the films with composition (AsSe)₇₅Ag₁₅ and (AsSe)₈₀Ag₂₀ it is about 4 nm. These results suggest that the photodarkening effect is most probably suppressed by the addition of silver.

The changes in the optical transmission T(t)/T(0) of the (AsSe)₁ₓAgₓ films for x = 0, 10, 15, 20 at.% films as functions of the exposure time are shown in figure 3. The photodarkening effect is found to decrease gradually as the silver content increases up to 15 %. Further increase of the amount of silver leads to saturation of the effect.

A decrease in photodarkening of metal containing As₂Se₃-Cu chalcogenides has been reported by Liu et al [10]. They have suggested that Cu atoms become an integral part of the structure and the
introduction of copper into the glassy matrix results in completion of all chemical bonds. The photodarkening effect is masked due to the production of metal-chalcogen bonding electronic states on top of the valence band \[10\]. The similarity in the electronic configuration of Cu and Ag presumes a similar influence of the silver additive on the effect of photodarkening. An increase of the coordination number of the chalcogen atoms is also responsible for the decrease of the photodarkening effect. Liu and Taylor \[10\] and Yan et al. \[11\] suggested that the coordination number of chalcogen atoms increases from two to four when the metal concentration is high enough. Ogusu et al. \[12\], however, concluded that this statement is incorrect. They assumed that Ag may be regarded as glass network modifiers.

From the structural model reported by Petkova et al, the average coordination of As atoms is 3.16 \(\pm\) 0.16, that of Se atoms is 2.65 \(\pm\) 0.16 and each Ag atoms has in average 2.76 \(\pm\) 0.3 neighbors. The average coordination number in amorphous \((\text{AsSe})_{80}\text{Ag}_{20}\) is 2.88 \(\pm\) 0.15. This value is higher than a characteristic parameter of the topological phase transition in chalcogenide glasses \(<N> = 2.67\) suggested by Tanaka \[13\] and, therefore, indicates the existence of a three-dimensional network structure.

One Ag atom is on the average surrounded by 4 Se and the Ag-Se distance is 2.66 \(\pm\) 0.03 Å. Although the latter value is quite close to that determined in \[7\] - 2.62 \(\pm\) 0.02 Å, the difference in the coordination numbers is significant. Besides a lower coordination number, these results suggest that the Ag-Se bonding has a strong covalent character. In this sense it can be stated that in the composition investigated Ag builds in the AsSe covalent matrix. The presence of the small Ag-Ag peak at about 2.98 \(\pm\) 0.04 Å is also remarkable. This value is not far from the nearest Ag-Ag distance in metallic Ag (2.89 Å). As the minimum Ag-Ag distance allowed in the RMC simulation was much lower (2.7 Å), the position of this peak is clearly determined by the experimental data. The increase in the average coordination number of the samples and the marks of Ag-Ag interaction in the \((\text{AsSe})_{80}\text{Ag}_{20}\) films are the most probable reasons for the saturation observed in the photodarkening kinetics.

![Figure 2](image-url)  
**Figure 2.** Transmission spectra of \((\text{AsSe})_{1-}\text{Ag}_{x}\) (\(x = 0, 10, 15, 20\) at.\%) films after 60 min exposure to He-Ne laser light with intensity 5 mW/cm².

![Figure 3](image-url)  
**Figure 3.** Kinetics of photodarkening of thin \((\text{AsSe})_{1-}\text{Ag}_{x}\) films.
4. Conclusion
The composition dependence of the transmission spectra and photodarkening characteristics in ternary (AsSe)$_{1-x}$Ag$_x$ glassy thin films have 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 the glassy matrix with respect to light exposure. A tendency of a decrease in the photodarkening effect is regularly observed in films with Ag content up to 15 mol. %. In the films with higher silver amount, the observed photoinduced effect is saturated, which probably is due to the appearance of Ag-Ag interactions.

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