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Spectroscopic studies of $(AsSe)_{100-x}Ag_x$ thin films

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ABSTRACT

Thin $(AsSe)_{100-x}Ag_x$ films have been grown onto quartz substrates by vacuum thermal evaporation or pulsed laser deposition from the corresponding bulk materials. The amorphous character of the coatings was confirmed by X-ray diffraction investigations. Their transmission was measured within the wavelength range 400–2500 nm and the obtained spectra were analyzed by the Swanepoel method to derive the optical band gap E_g and the refractive index n. We found that both parameters are strongly influenced by the addition of silver to the glassy matrix: E_g decreases while n increases with Ag content. These variations are discussed in terms of the changes in the atomic and electronic structure of the materials as a result of silver incorporation.

1. Introduction

Selenium is a promising material for a large number of applications in xerography, photocells, switching and memory devices. Nevertheless, in case of pure Se the carriers' life-time is short and sensitivity low. Se is often alloyed with Ge, Sb or As in order to achieve higher sensitivity and crystallization temperature as well as smaller aging effects [1–3]. As_2Se_3 and AsSe are predominantly covalent solids and they are among the most studied binary systems [4].

Silver-modified chalcogenide glasses exhibit a peculiar characteristic of mixed-ionic–electronic conductors, which provide dynamical ion movement by electron excitation. The preparation of thin films from these glasses with a good quality and desired composition can be a challenge in terms of their easy production and property reproducibility. The preparation techniques strongly influence the morphology and physico-chemical properties of prepared films. Mostly, authors report on the preparation of silver-containing thin films by photo doping [5], optically induced dissolution [6] or spin coating [7].

Availability of optical constants of chalcogenide materials (such as optical band gap, refractive index and extinction coefficient) is essential to evaluate their potential in optoelectronic applications [8]. Moreover, optical properties could also be closely related to material atomic structure, electronic band structure and electrical properties. An accurate measurement of optical constants can be easily performed on thin films. Optical properties of amorphous thin films can be determined by analysis of material transmission spectrum. This analysis pioneered by Manificer et al. [9] and extended by Swanepoel [10] has been successfully applied to different chalcogenide glasses, including As_2Se_3 [11]. Swanepoel's original work [10] was based on hypothesis of uniform film thickness. We note however that actual films usually exhibit a wedge-shaped profile, which may lead to errors in the analysis, if left unaccounted for. Later on, Swanepoel developed a method describing how to determine the optical properties of such non-ideal films [12], and since then the method was extended to most chalcogenide glasses [13]. The application of Swanepoel's methods is advantageous because they are non-destructive and yield the dispersion relation over a large range of wavelengths without any prior knowledge of the film thickness.

The aim of this work was the study of optical properties of thin As–Se–Ag amorphous films deposited by different methods and the evaluation of their dependence on composition, namely on silver amount added to the amorphous glassy matrix.

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2. Materials and methods

The $(AsSe)_{100-x}Ag_x$ glasses used in our experiments have been obtained by two subsequent monotemperature syntheses. The first step consisted of the preparation of binary AsSe glass under the following conditions: the respective amounts of arsenic and selenium with 5N purity (Alfa Aesar) were placed in quartz ampoules evacuated down to $\sim 10^{-3}$ Pa and heated in a rotary furnace. The temperature was maintained constant at the glass melting point while the melt was continuously stirred to ensure better homogenization. After preservation at 900 K for several hours the melt was quenched in a mixture of ice and water. For synthesis of $(AsSe)_{100-x}Ag_x$ glasses, the AsSe and commercial silver were mixed in required amounts followed by the same preparation procedure as described above.

Thin $(AsSe)_{100-x}Ag_x$ films were grown onto quartz substrates by vacuum thermal evaporation (VTE) and pulsed laser deposition (PLD) from the respective bulk glassy samples. The thermal evaporation process was conducted with a source-substrate distance of 0.12 m, a temperature of evaporation source of 700–800 K and a residual gas pressure of 1.33×10^{-4} Pa. In order to avoid thickness non-uniformities, the substrates were rotated during the evaporation process.

For PLD the synthesized bulk materials were prepared in form of targets of 13 mm diameter and 2 mm thickness by milling and pressing. The deposition process was carried out in a high vacuum chamber with a pulsed excimer KrF* laser source ($\lambda = 248$ nm, $\tau = 25$ ns). The experiments were performed at RT in vacuum at 10^{-4} Pa or in Ar at a dynamic pressure of 5 Pa. The quartz substrates were carefully cleaned with deionized water in a TRANSONIC T 310 ultrasonic bath. They were placed parallel with the target at a separation distance of 5 cm. For the deposition of each film we applied 3000 subsequent laser pulses at a repetition rate of 5 Hz. The laser beam was focused through an AR coated MgF_2 lens placed outside the chamber to get an incident fluence of 3.3 J/cm^2. Some test depositions were performed with doubled fluence of 6.6 J/cm^2. The beam was incident at 45° on target surface.

X-ray diffraction (XRD) investigations of thin coatings were performed with a Philips Analyzer APD-15 with CuK_α radiation in the 2θ range from 10° to 60°. The thickness of the films was measured with a white light interferometer Zygo NewView 5000 with vertical resolution up to 0.1 nm, 5× Michelson and 50× Mirau objectives, X–Y motor desk for stitching and extended vertical scan length up to 20 mm.

The optical transmission spectra of the thin films were recorded in the wavelength range of 400–2500 nm at room temperature using a double-beam computer-controlled Cary 5E UV–vis–NIR spectrophotometer with an accuracy of ±0.5 nm. The experimental data were processed by a computer program based upon the Swanepoel method.

3. Results and discussion

The $(AsSe)_{100-x}Ag_x$ films grown by both methods are amorphous as evidenced by XRD study. The absence of sharp peaks in diffractogramms, verifying the amorphous structure, and the observed broad halo are characteristic for the films prepared by VTE as well as by PLD (Fig. 1).

The thickness of films varies depending on composition, namely on silver content, deposition technique and applied conditions (Fig. 2). The PLD films prepared in low pressure argon are thicker than those deposited in vacuum under identical conditions. This is due to confinement of plasma by the ambient gas [14,15], a well known phenomenon confirmed by us in case of AsSe–AgI thin films deposition [16]. The thickness decrease with the percentage of Ag,

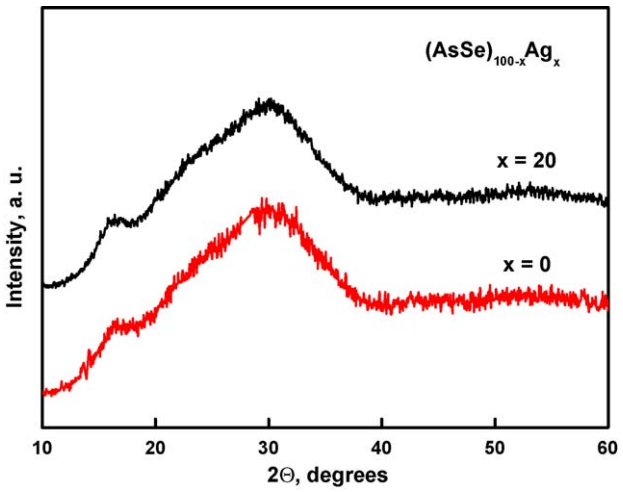

Fig. 1. Typical X-ray diffraction patterns of AsSe and AsSe–Ag films.

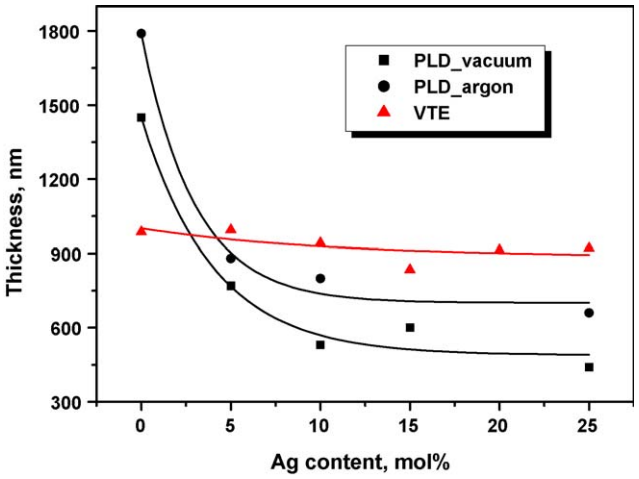

Fig. 2. The thickness of $(AsSe)_{100-x}Ag_x$ films prepared by PLD and VTE as a function of the Ag content.

clearly visible in case of PLD films, could be attributed to higher reflectivity of respective samples. Indeed, due to higher reflectivity, the laser beam energy transfer to target is worsening and the flux of ablated substance is decreasing. Conversely, in case of VTE deposited films the silver content has a marginal influence on thickness only.

The compositions of some of the films were measured by EDX [16]. The results exhibited some characteristic peculiarities, namely: (i) in some cases deviations from the unity ratio As/Se were found. This deviation increased significantly when changing the incident fluence from 3.3 to 6.6 J/cm^2. [17] This is why the most of the results reported in this paper referred to structures deposited at 3.3 J/cm^2. (ii) Some loss of Ag is observed and the higher the dopant concentration in the target materials, the bigger the differences in the film composition, including also the As/Se ratio, compared with the bulk samples. The deficiency of Ag in the film composition is most probably caused by the difference in the enthalpy of deposition of the evaporated fragments transported to the substrate. The enthalpy of deposition is different for various fragments and the quantity of each fragment deposited onto the substrate depends on it.

The transmission spectra recorded within the spectral range 400–2500 nm show interference maxima and minima at higher wavelengths approaching the transmission of substrate. A red shift