Mechanical behaviour of thin As-S-AgI films for sensor applications

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Abstract. The mechanical behaviour of chalcogenide thin films is of great importance for a variety of applications. The requirements for homogeneity, uniformity, surface smoothness, excellent adhesive strength and minimal residual stress are decisive for the technological performance of thin films in the field of optical and sensor devices. Thin films from the system have been prepared by vacuum thermal evaporation from the corresponding bulk glasses. The film structure and surface morphology have been studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The investigated chalcogenide films are amorphous as revealed by XRD, featureless and with smooth surfaces viewed from the AFM pictures. The stress measurements of the thin films deposited on silicon cantilevers have been carried out by cantilever bending technique. The results obtained have been discussed with respect to the film composition and structure. The change of the stress from tensile to compressive registered in the films with AgI content higher than 15 mol. % could be explained with structural transformations.

1. Introduction

The interest in semiconductor glasses including also chalcogenide glasses (mainly in the form of thin films) in the last decades has been caused by the fact that they can find different technological applications and can be prepared easily by compositional variation determining the material properties. In general, thin chalcogenide glassy films gain scientific interest for optical applications because of their infrared transmission ability and light–induced effects leading to non-linear changes in optical constants, such as photodarkening, photobleaching, photopolymerization, photocristallization, photodecomposition, which have already found applications in diffraction gratings, planar channel waveguides, holography, photoresists, optical memories, etc. [1–6].

Recently, the advantages of applying chalcogenide glasses in chemical or gas sensors operating at room temperatures, such as compactness, sensitivity, low-cost and low-power consumption have been widely investigated [7–9].

The mechanical behaviour of chalcogenide thin films is of great importance for variety of applications. The requirements for homogeneity, uniformity, surface smoothness, excellent adhesive strength and minimal residual stress are decisive for the technological performance of thin films in the
field of optical and sensor devices. The film stress appears during the deposition process as a result of different thermal expansion coefficients of the film and the substrate, intrinsic residual thermal strains and structural rigidity. High stress values can cause a number of negative consequences, e.g., bending of the film-substrate structure, peeling and cracking of the coatings, etc.

2. Experimental
The bulk samples of \((\text{As}_2\text{S}_3)_{(100-x)} (\text{AgI})_x\) system \((0 \leq x \leq 30)\) were prepared by standard melt-quenching technique from \(\text{As}_2\text{S}_3\), previously synthesized by us, and commercial \(\text{AgI}\) (Alfa Aesar, Johnson Matthey). The initial substances with a total weight of 5 g were sealed in evacuated quartz ampoules \((10^{-3} \text{ Pa})\). The glassy state and homogeneity of the synthesized samples was determined by electron microscopy and X-ray analysis [10].

Thin films were deposited from the corresponding bulk glasses by thermal vacuum evaporation in a standard high-vacuum installation “Hochvacuum” B 30.2. The process conditions were as follows: \(1.33 \times 10^{-3} \text{ Pa}\) residual pressure in the chamber; 0.12 m source-substrate distance; evaporation temperature ranging within 1200–1300 K depending on the glass composition. The evaporation time was determined from the desired thickness of the films. An inductively heated covered ribbon tantalum evaporator was used. The substrates were rotated during the deposition which allows the preparation of homogeneous films and avoids thickness non-uniformity.

The glassy nature of the samples was verified by X-ray diffraction analysis. The XRD spectra were recorded by means of a Philips APD15 X-ray diffractometer. The diffraction data were collected at the constant rate of 0.2 /min over an angle range of \(2\theta = 20 – 70 \degree\) using CuK\(\alpha\) radiation \((\lambda=1.54178 \text{ Å})\). All X-ray investigations were performed at ambient temperature.

The morphology and thickness of the films were investigated by scanning electron microscopy (SEM, Hitachi S-4000), while their topography was observed by atomic force microscopy (AFM, CP–II) in tapping mode.

The film stress was evaluated by the bending method using silicon micro-machined cantilevers, on which the chalcogenide films under investigation were deposited. These cantilever substrates consist of seven beams with thickness of 35 \(\mu\text{m}\), width between 0.7 and 2.0 mm and length between 2.0 and 8.0 mm; this configuration allows accurate stress measurements in a wide range. The deflection of the cantilever beams, from which the curvature of the substrate was determined, was measured by the depth of the focus of an optical microscope.

3. Results and discussion
X-ray results show spectra without peaks in the diffractograms (figure 1). Very similar broad halos corroborate that samples are typical glasses.

![Figure 1. X-ray diffraction patterns for some glass compositions of the \((\text{As}_2\text{S}_3)_{(100-x)} (\text{AgI})_x\) system.](image)

Typical SEM images of \((\text{As}_2\text{S}_3)_{(100-x)} (\text{AgI})_x\) thin films are presented in figure 2. The top-view SEM picture (figure 2a) reveals uniform, homogeneous, featureless and smooth surface of an amorphous phase. Neither defects (liquation separation) nor traces of initial nucleation are visible on the film surface. The cross–section view (figure 2b) shows that the film possesses also an internal amorphous
compact structure. The lack of features and voids in depth of the film and also at the substrate/film interface is indicative of coatings with good quality and adhesion.

Figure 2. SEM images of (As$_2$S$_3$)$_{85}$(AgI)$_{15}$ thin film (a) top-view image and (b) cross-section.

The surface images of the films investigated obtained by AFM were similar and the (As$_2$S$_3$)$_{85}$(AgI)$_{15}$ sample is given as an example in figure 3. The data determined for the mean height and rms roughness of all films under study are listed in table 1.

Table 1. Composition, thickness, rms roughness and height of (As$_2$S$_3$)$_{100-x}$(AgI)$_x$ thin films.

| Compound            | Thickness [nm] | Rms roughness [nm] | Max. height [nm] |
|---------------------|----------------|--------------------|------------------|
| As$_2$S$_3$        | 1700           | 5.05               | 25.82            |
| (As$_2$S$_3$)$_{95}$(AgI)$_5$ | 2600           | 1.51               | 5.58             |
| (As$_2$S$_3$)$_{90}$(AgI)$_{10}$ | 1850           | 0.23               | 1.47             |
| (As$_2$S$_3$)$_{85}$(AgI)$_{15}$ | 1760           | 0.29               | 1.27             |
| (As$_2$S$_3$)$_{80}$(AgI)$_{20}$ | 1470           | 6.66               | 22.11            |
| (As$_2$S$_3$)$_{75}$(AgI)$_{25}$ | 1350           | 4.60               | 16.47            |
| (As$_2$S$_3$)$_{70}$(AgI)$_{30}$ | 1400           | 5.34               | 60.16            |

The results from the topographic analyses are in good agreement with the information obtained by the SEM investigation and confirm that the vacuum thermal evaporated thin films possess relatively uniform surfaces with a high degree of smoothness.

The film stress ($\sigma$) was measured by the bending cantilever method and was calculated by the Stoney’s equation:

$$\sigma = \frac{E}{6(1-\nu)} \frac{D^2}{Rd},$$

where $d$ is the film thickness, $R$ is the radius of the curvature of the substrate, $E$ and $\nu$ are the Young’s modulus and Poisson’s ratio of the substrate, respectively, and $D$ - the substrate thickness.

The variation of the stress with the film composition is presented in figure 4. The magnitude and the sign of the stress depend on the composition and structure of the film as well as on their mechanical and thermomechanical properties.

Figure 3. AFM 3D image of (As$_2$S$_3$)$_{85}$(AgI)$_{15}$ thin film.
The results from the stress measurements show alteration in the sign and magnitude with the AgI content and with the time. The higher tensile stress of the samples with 5% AgI can be related to the initial incorporation of atoms with larger atomic radius into the As$_2$S$_3$ pyramidal structure.

As the AgI amount increases, the Ag atoms occupy the microvoids and, thus, the glass density increases, too, and the structure stabilizes. This densification and stabilization of the structure leads to a reduction of the tensile stress and a change in the sign of the mechanical stress to compressive in the samples with 25 and 30% of AgI.

![Figure 4. Compositional dependence of the initial stress and stress after 3 months for (As$_2$S$_3$)$_{100-x}$(AgI)$_x$ films.](image)

4. Conclusion
Thin amorphous films from the (As$_2$S$_3$)$_{100-x}$(AgI)$_x$ system were prepared by thermal vacuum evaporation from synthesized bulk glasses. The glassy state of the samples was established by X-ray diffraction. The coatings possess smooth, featureless and uniform surfaces as revealed by morphological and topological studies. The compositional dependence of the mechanical stress and its variation with time were determined. The highest tensile stress is observed in (As$_2$S$_3$)$_{95}$(AgI)$_5$ and further incorporation of AgI leads to stabilization of the structure, decrease of the tensile stress and change in the sign of the stress to compressive in the samples with 25 and 30% of AgI. In accordance to the results obtained for the homogeneity, uniformity, surface smoothness, adhesive strength and residual stress, we assumed that the chalcogenide thin films described possess qualities for technological performance in the field of optical and sensor devices.

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