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Stress study of thin As-Se-Ag films obtained by vacuum thermal evaporation and pulsed laser deposition

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Thin $(As_2Se_3)_{100-x}Ag_x$ (x = 0 - 25 mol.%) films have been obtained on glassy and silicon substrates by vacuum thermal evaporation and pulsed laser deposition from the corresponding bulk materials. The stress of the layers deposited on silicon cantilevers was measured by a cantilever technique, which is commonly applied to solid inorganic thin films. The correlation between the stress and the composition as a function of the film preparation methods has been investigated and discussed. We showed that the addition of silver leads to changes in the glass properties, such as an increase of the density and compactness, related to the modification of the stress values.

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1. Introduction

Among the chalcogenides, arsenic selenides are amorphous semiconductors particularly exploited and studied because of their interesting properties, which open prospective opportunities of various applications in optics, electronics and optoelectronics (optical elements and memories, optical sensors, non-linear optical devices, holographic elements) [1], ecology (ionic and optical sensing, emission spectral analyzers) [2], materials engineering and science (switches, micromachining etc.) [3].

Silver containing chalcogenides showed a deviation in behavior due to modification in the local ordering of the host chalcogenide matrix after the silver incorporation observed in the bulk glasses as well as in the corresponding thin films. The presence of silver in the host glassy matrix induces new properties of glasses due to the modified structure. This prompted the scientific interest toward silver containing glasses in either bulk or thin film forms over last decades. The easy movable and small-sized Ag atoms are responsible for the high ionic conductivity and the fast optical response and optical sensitivity of the silver containing chalcogenides.

For most of applications, the mechanical behavior is an important characteristic of the material. The stress in thin films is in fact the sum of the thermal stress due to the different thermal expansion coefficients of the film and substrate, and the intrinsic stress induced in the film during the deposition process [4].

In the present work we comparatively investigated the effect of the silver content on the mechanical properties, and especially on the intrinsic stress of thin As-Se-Ag films prepared by vacuum thermal evaporation (VTE) and pulsed laser deposition (PLD) methods.

2. Experimental

Thin films were prepared by vacuum thermal evaporation (VTE) from previously synthesized bulk glasses with compositions $(As_2Se_3)_{100-x}Ag_x$, where x = 0, 5, 10, 15 and 25 mol. %. The evaporation process was carried out from a tantalum crucible in Leybold LB 370 vacuum set-up with a residual gas pressure of 1.33×10^{-4} Pa. A constant distance source – substrate of 0.12 m and temperatures of the evaporation source in the range of 700 - 800 K were used in all experiments. The substrates were rotated during the evaporation process to obtain uniform layers.

PLD was performed with a KrF* excimer laser source (λ = 248 nm, τ_{FWHM} =25 ns) operating at a repetition rate of 2 Hz. The incident laser fluence was 3.3 J/cm^2. The targets were prepared from the synthesized bulk materials after milling and pressing. The distance target – substrate was 3 cm. The working pressure was maintained at 4×10^{-4} Pa. 3000 pulses were applied for the deposition of each layer.

The film stress was evaluated by the bending method using silicon micro-machined cantilevers (Fig. 1), on which the chalcogenide films under investigation were deposited.

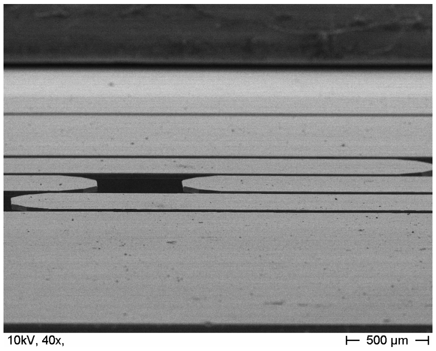


Fig. 1. SEM micrograph of the cantilever array used for determination of the stress (in this case coated with PLD ($As_2Se_3)_{85}Ag_{15}$.

The cantilever substrates consisted of seven grids with a thickness of 45 µm, a width between 0.7 and 2.0 mm and a length between 2.0 and 8.0 mm. During depositions, the substrates were kept at room temperature. This configuration allows an accurate stress measurement in a wide range. The deflection of the cantilever grids was determined from the curvature of the substrate measured by the depth of the focus of an optical microscope. The films were kept in dark under dry atmosphere for 3 months and measured again to study the relaxation of the film stress [5].

During the same VTE and PLD runs, $(As_2Se_3)_{100-x}Ag_x$ thin films were deposited also onto BK7 glass substrates and single side polished Si wafers in order to monitor their thickness and morphology. The thickness was determined by cross-section scanning electron microscopy (SEM), while for selected samples interferometry was applied to verify the results. The compositions of some of the films were measured by EDX as already discussed in [6].

3. Results

The film stress (σ) was determined *ex situ* by the deflection of the cantilever grids, and calculated with Stoney´s equation [7]:

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

where d is the film thickness, R the radius of the curvature of the substrate, E, ν and D the Young`s modulus, Poisson`s ratio and thickness of the substrate, respectively

In our case, the thickness of the films (up to 0.85 µm) was much smaller than that of the substrate (45 µm), which allowed applying the approximated Stoney's equation for the stress determination:

$$\sigma = \frac{E}{3(1-\nu)}\frac{hD^2}{(L^2+h^2)d},$$

where L is the length of the cantilever and h - the maximum deflection of the cantilever tip.

The results for the stress in $(As_2Se_3)_{100-x}Ag_x$ thin films prepared by VTE and PLD as a function of composition are presented in Fig. 2.

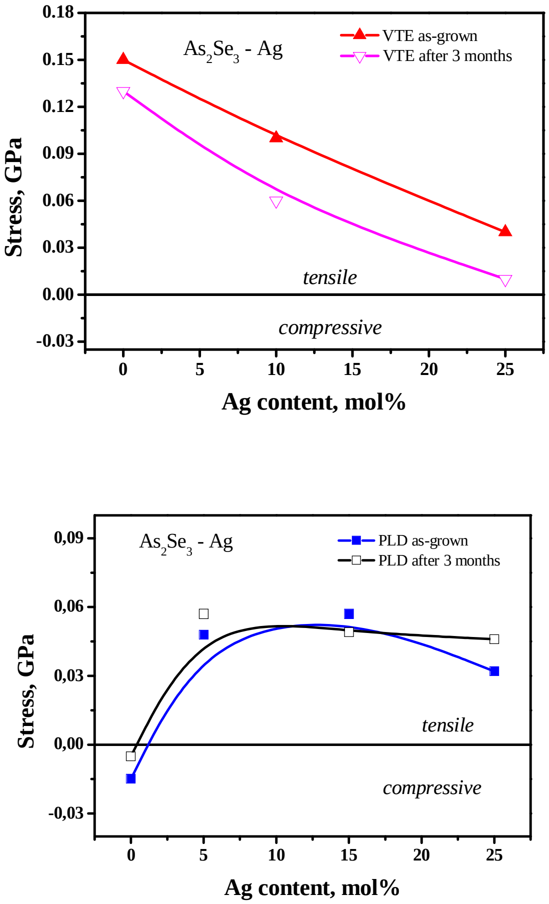


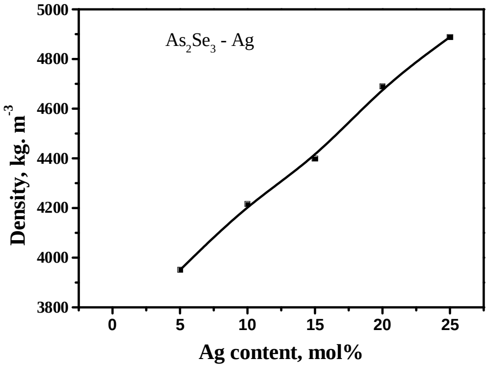
Fig. 2. Intrinsic stress of VTE (left) and PLD(right) As_2Se_3–Ag layers.

Several trends are observed in the compositional dependence of the stress. All as-deposited VTE films exhibit a tensile stress which decreases with the increase of the silver content. After 3 months the stress decreased but the tendency connected with the Ag concentration remains unchanged.

The as-grown PLD films are also under tensile stress, with the exception of the undoped As_2Se_3 layers, which showed a slight compressive stress. The intrinsic stress of the as-grown PLD films is lower than that of the VTE layers, and it remains almost unchanged (within the measurement errors) with the conservation time.

4. Discussion

Generally, the structure of the silver containing chalcogenide thin films is similar to that of the corresponding bulk glasses [8]. The structure of the initial binary As_2Se_3 glass consists of $AsSe_{3/2}$ pyramidal units which we suppose are the major building units also for the VTE and PLD films [9]. The mechanical stability, and in particular the intrinsic stress of the films, are strongly related to the material density, compactness and structural rigidity, as it has been already proved by the mechanical stress study of other chalcogenides [5].The data on the density and compactness collected from the physico-chemical study of bulk As-Se-Ag glasses [9] are presented in Figs.3 and 4.



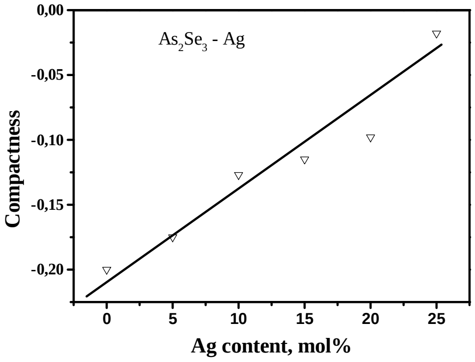


Fig. 3. Bulk density as a function of the silver contentFig. 4. Bulk compactness as a function of the silver content.

The density of the glasses increases with the silver content in the glass composition. The relation is conditioned by the introduction of silver atoms into the As_2Se_3 chalcogenide network, which results in a closer and denser packing of the new structural units in the complex glass. The density is related to the compactness of the material and, therefore, an analogous compositional trend in the density and the compactness is observed. The compactness increases with silver content and approaches zero value as seen from Fig. 4, i.e. the experimental values tend to the theoretical ones leading to a maximum compact structure of the glass.

These regular changes of the properties of the bulk materials are expected to define a regular alternation of the stress of the thin films prepared by VTE and PLD. The experimental results (Fig. 2) however, show differences in the compositional dependency of the stress for the films deposited by the two methods, reflecting the peculiarities of the process conditions. PLD films are better ordered and denser due to the higher energy of deposition supported by the piston action of the laser plasma [10]. Contrarily, VTE layers have a more defected structure, as already reported in our earlier studies [11]. The as-grown As_2Se_3 PLD films exhibit low compressive stress, which turns into tensile with the addition of only 5 mol.% Ag. The incorporation of silver atoms distorts the dense packing of the As_2Se_3 matrix, leading to the generation of microvoids. The further increase of the Ag content up to 25 mol.% does not influence significantly on the tensile stress which fluctuates between 35 and 55 (± 5) MPa.

The glassy matrix of the as-grown As_2Se_3 VTE films is characterized by low compactness and contains a considerable free volume, due to the presence of microvoids “frozen” in the structure during deposition. This free volume stays at origin of the higher tensile stress on the order of (150 ± 10) MPa for these films. The evaporation process conditions explain the presence of fragments of As_2Se_3 and Ag_2Se in the vapour phase. Moreover, due to relatively low temperature of evaporation, the Ag_2Se units could be destroyed and free silver atoms can also appear in the vapour phase. These silver atoms start to occupy the microvoids in the matrix, which results in reorganization of the structural units and densification. As a consequence, the tensile stress decreases almost proportional with the silver content, dropping down to (45 ± 5) MPa for 25 mol.% Ag. It should be mentioned that, the values found for the $(As_2Se_3)_{75}Ag_{25}$ thin films deposited by both methods are very close, irrespective of the compositional tendency of the intrinsic stress. It suggests that this composition, which is at the border of the glass-forming region [9], has a compact and stable structure.

The stress relaxation with time observed after 3 months is well expressed for the VTE films (Fig. 2). The reduction of the stress by 15 – 35 MPa is connected to the structural relaxation of poorer VTE films. In the case of PLD films, such a relaxation is not observed, which could be related to their ordered and compact structure after deposition.

5. Conclusions

The different deposition conditions and mechanisms of VTE and PLD determine the variations in the structure of As-Se-Ag films and the differences in the intrinsic stress and its compositional dependency. The additions of Ag atoms in VTE films decrease the stress due to their incorporation in the existing microvoids, leading to the formation of more compact structure. For PLD films, the stress changes from slightly compressive to tensile when silver is added, and maintains constant values over the whole concentration region. The stress relaxation with time shows also different behaviors following the tendency observed for the as-deposited films. Within 3 months, a reduction of the stress is obvious for VTE films due to structural relaxation, while the stress of PLD films remains almost unchanged.

Acknowledgements

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