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Characterization of pulsed laser deposited chalcogenide thin layers

T. Petkova [a,*], C. Popov [b], T. Hineva [c], P. Petkov [c], G. Socol [d], E. Axente [d], C.N. Mihailescu [d], I.N. Mihailescu [d], J.P. Reithmaier [b]

[a] Institute of Electrochemistry and Energy Systems (IEES), Bulgarian Academy of Sciences, Sofia, Bulgaria
[b] Institute of Nanostructure Technologies and Analytics (INA), University of Kassel, Germany
[c] Laboratory of Thin Film Technology, Department of Physics, University of Chemical Technology and Metallurgy, Sofia, Bulgaria
[d] National Institute for Lasers, Plasma, and Radiation Physics, Bucharest-Magurele, Romania

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ABSTRACT

In this work we report on pulsed laser deposition (PLD) of chalcogenide thin films from the systems $(AsSe)_{100-x}AgI_x$ and $(AsSe)_{100-x}Ag_x$ for sensing applications. A KrF* excimer laser ($\lambda = 248$ nm; $\tau_{FWHM} = 25$ ns) was used to ablate the targets that had been prepared from the synthesised chalcogenide materials. The films were deposited in either vacuum (4×10^{-4} Pa) or argon (5 Pa) on silicon and glass substrates kept at room temperature. The basic properties of the films, including their morphology, topography, structure, and composition were characterised by complementary techniques. Investigations by X-ray diffraction (XRD) confirmed the amorphous nature of the films, as no strong diffraction reflections were found. The film composition was studied by energy dispersive X-ray (EDX) spectroscopy. The morphology of the films investigated by scanning electron microscopy (SEM), revealed a particulate-covered homogeneous surface, typical of PLD. Topographical analyses by atomic force microscopy (AFM) showed that the particulate size was slightly larger in Ar than in vacuum. The uniform surface areas were rather smooth, with root mean square (rms) roughness increasing up to several nanometers with the AgI or Ag doping. Based upon the results from the comprehensive investigation of the basic properties of the chalcogenide films prepared by PLD and their dependence on the process parameters, samples with appropriate sorption properties can be selected for possible applications in cantilever gas sensors.

1. Introduction

The chalcogenide glasses have recently focused significant scientific interest for the investigation of their basic properties and the possibility for applications in optics and optoelectronics, electrochemistry, sensor technique, etc. The main attention paid to these materials relies upon their large optical transmission range extending in the mid-infrared and covering usually the two atmospheric windows lying from 3 to 5 μm and from 8 to 12 μm. One can find in literature many reports on the implementation of thin chalcogenide layers in far infrared optics [1,2]. Chalcogenide glasses containing silver or silver salts are well known as super-ionic conducting glasses. Their conduction mechanism as well as their application in solid state electrochemical devices is currently subjects of extensive studies [3]. Till now only few papers have reported on chemical sensors based on chalcogenide glassy materials in the form of membranes [4] or thin films [5,6], but they revealed their potential for application in sensors. As major advantages of these amorphous inorganic materials we emphasize that they can be easily prepared in bulk or layered forms by various methods. They also possess high chemical stability and can easily change properties by small variations in composition due to their disordered amorphous structure. We mention that all these features are common requirements for materials applied in gas sensors.

Among the deposition methods used for fabrication of chalcogenide thin films, the vacuum thermal evaporation, DC/RF magnetron sputtering, and spin-coating technique stand presently for the most common choice [7,8]. However, the deposition of multi-component thin films with a desired degree of stoichiometry, acceptable homogeneity and good adhesion to the substrate still remains a difficult task. One of the most promising and prospective alternatives for preparation of such coatings is pulsed laser deposition (PLD). The proven advantages of PLD are among others: versatility, congruent transfer of target material to deposited films, ultimate purity of synthesised structures due to the use of light pulses for ablation, easy control of the entire process and possibility to deposit complex molecules and multistructures [9,10].

The main goals with the current work were the PLD synthesis of thin films from the system As–Se doped with AgI or Ag and the

* Corresponding author.
E-mail address: tpetkova@bas.bg (T. Petkova).

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comprehensive investigation of the dependence of film properties on process parameters in view of selecting chemical sensing samples for further study with respect to their sorption properties.

2. Experimental

The bulk materials with compositions $(AsSe)_{100-x}AgI_x$ and $(AsSe)_{100-x}Ag_x$ have been prepared by two-stage synthesis: (i) preparation of binary AsSe compound from elemental As and Se with 5N purity; (ii) synthesis of quasi binary alloys AsSe–AgI or AsSe–Ag from previously obtained AsSe and commercial AgI or Ag (Alfa Aesar). Similar preparation procedures were applied for both producing steps, namely the initial materials in respective amounts were placed in quartz ampoules evacuated down to $\sim 10^{-3}$ Pa, further subjected to regular increase of the temperature in a rotary furnace. The temperature was kept constant at the melting point of each component; the melt was continuously stirred for better homogenisation. The glasses were obtained by quenching in a mixture of ice and water [11].

The PLD targets were next prepared from the synthesised glasses by milling, pressing and sintering. The deposition of thin $(AsSe)_{100-x}AgI_x$ and $(AsSe)_{100-x}Ag_x$ films was conducted by ablation of the targets from the respective bulk materials with a KrF* excimer laser source ($\lambda = 248$ nm, $\tau_{FWHM} = 25$ ns). The incidence fluence was set at 6.6 J/cm^2, for deposition of each film we applied 3000 laser pulses. The films were deposited in either vacuum (4×10^{-4} Pa) or argon at a dynamic pressure of 5 Pa on silicon or glass substrates, kept at room temperature and placed parallel 5 cm from the target.

After deposition, the films were characterised with respect to their structure, composition, morphology, growth rate and topography in order to investigate the influence of the process parameters and glass composition on their behaviours. The structure was studied by X-ray diffraction (XRD) with a *DRON UM1* diffractometer using Cu K_α excitation radiation. We worked in a θ–2θ configuration within the range 20–65° and with a step of 0.05° and acquisition time 2 s. Energy dispersive X-ray (EDX) analysis of the film composition was achieved with a scanning electron microscope (SEM, *JEOL JSM-840A*) equipped with a Link Analytical Spectrometer (*AN10000*) (operated at an accelerating voltage of 20 kV). As a rule, the analysis was carried out at four points for each sample. The oxygen content inside films was monitored by wavelength dispersive spectroscopy (WDS) using an accelerated voltage of 10 kV, a beam current of 300 nA, LDE W-Si multilayer pseudo crystal and ZrO_2 as the standard. Scanning electron microscopy (SEM) investigations was done with a *Hitachi S4000* apparatus in order to study the film morphology. From SEM cross-section (XSEM) micrographs we evaluated the film thickness. The surface topography of the films was studied by atomic force microscopy (AFM, *NanoScope II*) in a tapping mode. The obtained images were analysed with the *Gwyddion* software.

3. Results and discussion

The amorphous nature of the $(AsSe)_{100-x}AgI_x$ and $(AsSe)_{100-x}Ag_x$ films has been evidenced by XRD studies. The diffraction patterns of the films from both series were very similar with broad halo and without sharp peaks belonging to crystalline phases of any component of the film composition (Fig. 1). The films prepared in Ar showed a higher halo background as compared to films deposited in vacuum. This feature is related to the role of the Ar ions as additional transporters of the molecules. As known, the presence of a low-pressure ambient gas results in plasma confinement leading to the deposition of thicker films [9,10].

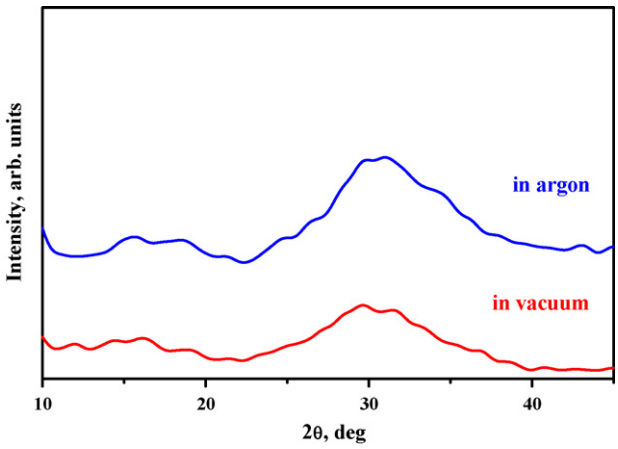

Fig. 1. Typical X-ray patterns of As–Se–AgI films prepared by PLD.

The compositions of some of the films deposited in vacuum were measured by EDX and are presented in Table 1. The results exhibit some peculiarities, namely: (i) in some cases deviations from the unity ratio As–Se were found; (ii) loss of dopant (Ag or AgI) 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 AgI or Ag in the film composition is most probably caused by the difference in the enthalpy of deposition of the evaporated fragments. The dissociation of the target material during the laser ablation generates fragments (As–Se, silver, iodine, etc.) with various mass and velocity, which are 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. No oxygen was detected in the films by WDS within the accuracy of the method (±1%).

The top-view SEM pictures of films from both systems revealed the uniform and homogeneous character of their surfaces (Fig. 2). Neither defects (liquation) nor traces of initial nucleation were visible, while the presence only of some submicron-sized particulates is noticed. The existence of particulates of various shapes and dimensions is a well-known phenomenon in PLD and various efficient techniques have been developed in view of their control and elimination [12,13]. We note however that for the envisaged application of the As–Se–Ag(AgI) films as sensitive layers in gas chemical sensors the presence of the particulates could be advantageous, since they increase the effective active surface for interaction with gaseous analytes. We determined the thickness of the films from cross-section SEM micrographs. It was in all cases within the range (450–900) nm (Table 1), corresponding to growth rates of (0.15–0.30) nm/pulse. The growth rate was (1.2–1.6) times

Table 1
Deposition ambient, composition and thickness of As–Se–Ag(AgI) films synthesised by PLD

Sample	Target composition	Film composition (±2 mol.%)	Ambient	Thickness (nm)
B2-4	$As_{45}Se_{45}(AgI)_{10}$	$As_{42}Se_{48}Ag_6I_4$	Vacuum	
B2-5			Argon	850
B7-4	$As_{35}Se_{35}(AgI)_{30}$	$As_{38}Se_{46}Ag_4I_{12}$	Vacuum	550
B7-5			Argon	900
C1-2	$As_{45}Se_{45}Ag_{10}$	$As_{41}Se_{51}Ag_8$	Vacuum	750
C1-3			Argon	900
C3-4	$As_{40}Se_{40}Ag_{20}$	$As_{37}Se_{52}Ag_{11}$	Vacuum	450
C3-3			Argon	650

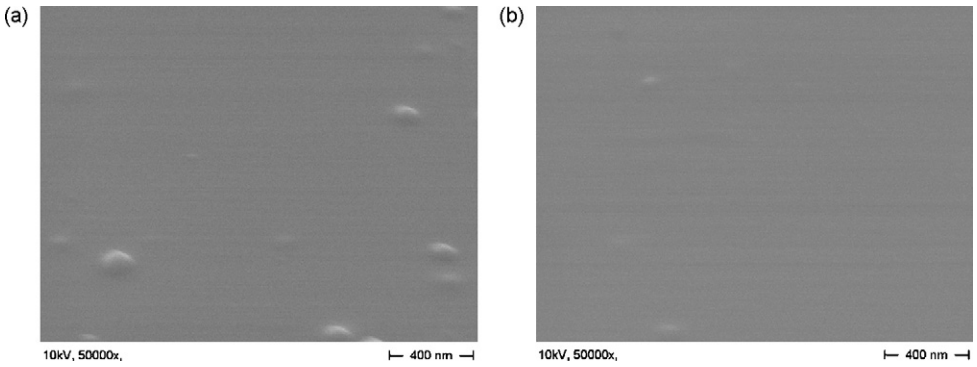

Fig. 2. Typical top-view SEM micrographs of PLD As–Se–Ag(AgI) films: (a) sample B2-4 and (b) sample C3-4 (see Table 1).

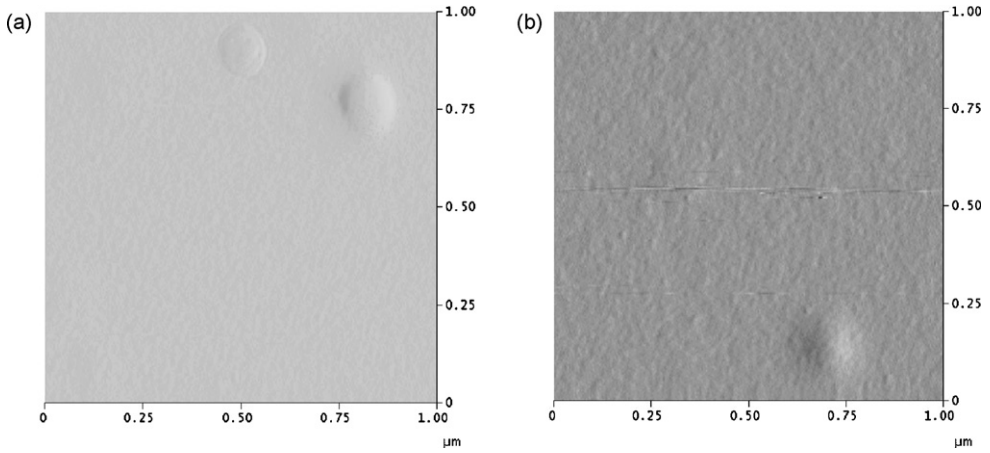

Fig. 3. AFM images of PLD As–Se–Ag(AgI) films: (a) sample B7-4 and (b) sample C2-2 (see Table 1).

higher for the films synthesised in Ar ambient in comparison with those grown in vacuum. This increase is a consequence of plasma confinement (as discussed above) which was clearly visible from the change of plasma expansion from "plumes" in vacuum to a "cigar-like" shape in Ar [14].

The AFM examination confirmed the results concerning the film topography obtained from the SEM study. The $(AsSe)_{100-x}AgI_x$ and $(AsSe)_{100-x}Ag_x$ films exhibited uniform and smooth surfaces with some particulates, as discussed above (Fig. 3). The roughness of the films was next determined by analysis of the AFM images in areas free of particulates. Fig. 4 shows the influence of the dopant (AgI or Ag) concentration upon the rms roughness. The latter increases rather linearly with the dopant concentration, a trend better visible in the case of AgI. Generally, the roughness of the films grown in vacuum was close for both types of dopants, while PLD in Ar resulted in slightly rougher coatings when doping with Ag than

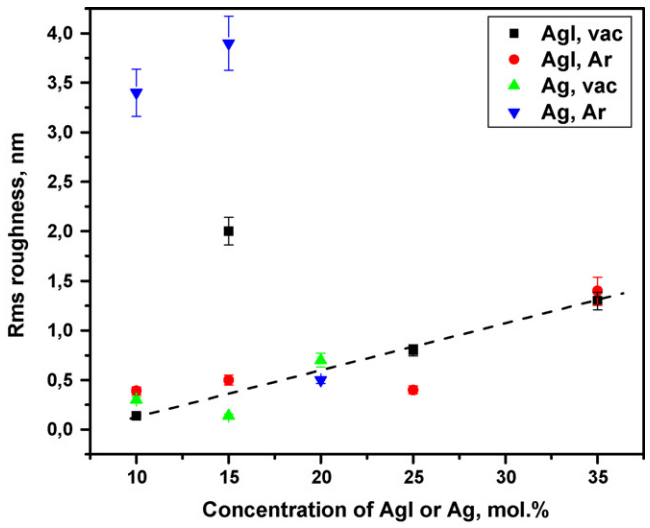

Fig. 4. Influence of the dopant concentration on the rms roughness of PLD As–Se–Ag(AgI) films. The line is given as an eye guide.

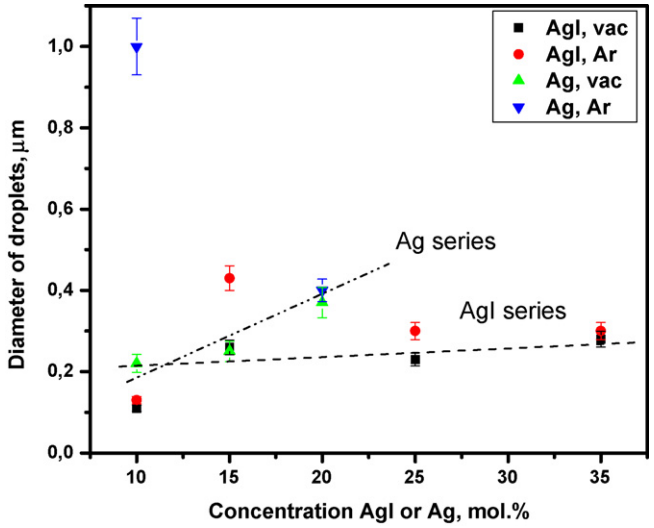

Fig. 5. Influence of the dopant concentration on the droplet size on PLD As–Se–Ag(AgI) films The lines for two series are drawn as eye guides.

with AgI. The distribution of the particulate size was also studied. It was found that the deposition of films with higher Ag concentration leads to the formation of larger particulates, while the variation of AgI content has only a marginal influence on the particulate size (Fig. 5). The observed slight increase of the particulate diameter for films deposited in Ar vs. those synthesised in vacuum could be the result of collisions between ablated substance and the Ar molecules [15,16]. These collisions may significantly slow-down the small particulates. As an effect, part of them will be eliminated due to gravitation, while some others will cluster in larger particulates by coalescence [9,15,16].

4. Conclusions

Thin $(AsSe)_{100-x}AgI_x$ and $(AsSe)_{100-x}Ag_x$ films were prepared by pulsed laser deposition from the respective bulk glasses. The amorphous nature of the target materials was preserved in the deposited films. Their compositions show losses of silver and iodine in comparison with the target materials, which are higher at higher dopant concentrations. In same cases a deviation of the As–Se ratio from unity was also found, which was stronger for a larger doping with Ag or AgI. The PLD films exhibited homogeneous surfaces covered with some particulates. The roughness of the particulate-free areas was in the order of few nanometers. The observed topography could be beneficial for application of the obtained As–Se–AgI(Ag) coatings as sensitive layers in chemical cantilever-based sensors, because of the increased active surface for interaction with gaseous analytes.

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