Journal of Physics: Conference Series **113** (2008) 012023 doi:10.1088/1742-6596/113/1/012023

Influence of the preparation method on the As-Se-AgI thin films behaviour

T Hineva [1, 5], T Petkova [2], P Petkov [1], V Mikli [3], G Socol [4], C N Mihailescu [4] and I N Mihailescu [4]

[1] Laboratory of Thin Films Technology, Department of Physics, University of Chemical Technology and Metallurgy, 8 Kl. Ohridsky Blvd, 1756 Sofia, Bulgaria
[2] Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 10, 1113 Sofia, Bulgaria
[3] Center for Materials Research, Talin Technical University, 5 Ehitagate, 19086 Talin, Estonia
[4] National Institute for Laser, Plasma and Radiation Physics, 409 Atomistilor Street, PO-Box MG-36, RO-77125 Bucharest-Magurele, Romania

E-mail: thineva@mail.bg

Abstract. Bulk glasses of the $(As_2Se_3)_{1-x}(AgI)_x$ and $(AsSe)_{1-x}(AgI)_x$ systems, where x = 5, 10, 15 up to 35 mol.% have been prepared by the melt-quenched technique. The thin films have been deposited by means of vacuum thermal evaporation (VTE) and pulsed laser deposition (PLD). The XRD investigation reveals a generally amorphous structure; small peaks are only observed in the samples with the highest AgI. The film compositions have been determined by EDS (energy dispersive X-ray microanalysis). WDS (wavelength dispersive spectroscopy) studies have shown that the films do not contain oxygen within the accuracy of the method (1 %). The films are dense with smooth surface as revealed by using scanning electron microscopy (SEM) and atomic force microscopy (AFM).

1. Introduction

Amorphous chalcogenides are advanced low-phonon-energy materials transparent in the infrared region of the spectrum with unique optical properties (high linear and non-linear index of refraction, photoinduced changes of the index of refraction, photoinduced shift of the absorption edge). The optical behavior of these materials defines their application in optics, electronics and optoelectronics (optical elements and memories, optical sensors, non-linear optical devices, holographic elements), in ecology (ionic and optical sensing, emission spectral analyzers etc.), in materials engineering and science (switches, micromachining etc.) [1].

The preparation techniques of thin chalcogenide films can strongly influence the structure, the surface and the physico-chemical properties of the films prepared (see [2] and papers cited there). The differences in the thin films prepared can limit or, alternatively, support their possible applicability. The aim of the present paper is to present the influence of the film deposition technique on both the

[5] To whom any correspondence should be addressed.

morphology and the composition of thin amorphous As-Se-AgI films prepared by two different methods: vacuum thermal evaporation (VTE), and pulsed laser deposition (PLD).

2. Experimental details

$(As_2Se_3)_{1-x}(AgI)_x$ and $(AsSe)_{1-x}(AgI)_x$ bulk samples were prepared by the melt-quenching technique. The homogeneity and composition of the bulk samples prepared were verified by electron microscopy carried out by a X-ray microanalytical system Philips SEM 505 EDA 9100/MicrospecWDX2A.

The thermal evaporation was performed in a Leybold LB 370 vacuum installation with a residual gas pressure of 1.33×10^{-4} Pa using a suitable tantalum crucible. The experiments were carried out with a constant geometry of the experimental setup and evaporation temperatures in the range 850-1000 K monitored by a Ni-Ni/Cr thermocouple.

The PLD system was evacuated to a residual pressure of less than 10^{-4} Pa prior to the laser deposition. The depositions were performed using a KrF excimer laser source (λ = 248 nm, $\tau_{FWHM} \geq 7.4$ ns) operating at a repetition rate of 2 Hz. The incident laser fluence was 3.3 J/cm^2.

Films with compositions: $(As_2Se_3)_{1-x}(AgI)_x$ and $(AsSe)_{1-x}(AgI)_x$ (x = 0-35 mol%) were deposited onto BK7 glass substrates and single side polished Si wafers. To avoid non-uniformity in the thickness of the films the substrates were rotated during the deposition. The thickness of the layers studied ranged from 300 nm up to 1050 nm as measured by interference microscopy.

The EDX analyses of the films were carried out on a JEOL JSM-840A scanning electron microscope (SEM) equipped with a Link Analytical AN10000 spectrometer by EDS (energy dispersive X-ray microanalysis). Accelerating voltage of 20 kV was used. Typically four points were taken for each sample. The oxygen content in the films was studied by WDS (wavelength dispersive spectroscopy) using accelerating voltage 10 kV, beam current 300 nA, LDE (W-Si multilayer pseudo crystal) crystal and ZrO_2 as the standard. The surface morphology and topography of the films were investigated by SEM (Hitachi S4000 and JEOL JSM- 840A) and atomic force microscopy (AFM) using a Stand-alone SMENA head from NT-MDT in tapping mode.

3. Results and discussion

Generally, chalcogenide materials are more volatile in comparison with metals and oxides [1], especially when they contain iodine. The EDAX results of the bulk samples compositions show very close values to those calculated preliminary (see table 1).

Table 1. EDX results for bulk samples AsSe series.

	As, [at%]	Se, [at%]	Ag, [at%]	I, [at%]
AsSe	50.44	49.56		
$(AsSe)_{95}(AgI)_5$	46.69	47.01	3.36	2.94
$(AsSe)_{85}(AgI)_{15}$	41.85	41.86	8.25	8.05
$(AsSe)_{75}(AgI)_{25}$	36.34	36.57	13.75	13.34
$(AsSe)_{70}(AgI)_{30}$	34.02	34.81	15.70	15.47
$(AsSe)_{65}(AgI)_{35}$	32.26	32.29	18.22	17.24

The results from the XRD investigation reveal the non-crystalline nature of the films as seen in figure 1. The broad halo and lack of sharp peaks in the diffractograms support the assumption for the amorphous character of the coatings. The WDS studies showed that the films do not contain oxygen within the accuracy of the method (1 %).

The mechanisms of VTE and PLD deposition are different [1, 4]. Very often the films prepared by PLD exhibit new properties, different from those of films deposited by other classical methods [1]. The optical band gaps E_g of PLD films of the As_2Se_3 series are smaller than those of VTE films [3]. During different experiments it was found that the PLD films exhibit much better adhesion to the substrate.

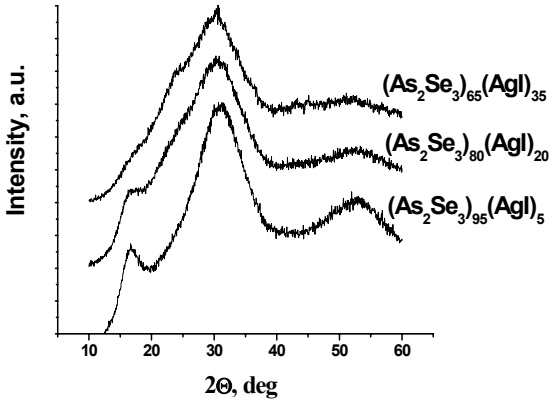

Figure 1. Typical XRD curve of VTE films with composition $(As_2Se_3)_{95}(AgI)_5$, $(As_2Se_3)_{80}(AgI)_{20}$, $(As_2Se_3)_{65}(AgI)_{35}$.

Table 2. EDX results for $(As_2Se_3)_{1-x}(AgI)_x$ films and $(AsSe)_{1-x}(AgI)_x$ films.

	As, [at.%]	Se, [at.%]	Ag, [at.%]	I, [at.%]
PLD films				
$(As_2Se_3)_{90}(AgI)_{10}$	37.32	58.70	2.51	1.47
$(As_2Se_3)_{80}(AgI)_{20}$	36.27	55.34	5.72	2.68
$(As_2Se_3)_{65}(AgI)_{35}$	29.87	45.96	14.69	9.48
VTE films				
$(As_2Se_3)_{95}(AgI)_5$	38.94	59.36	0.80	0.90
$(As_2Se_3)_{85}(AgI)_{15}$	38.27	56.56	1.80	3.13
$(As_2Se_3)_{65}(AgI)_{35}$	35.16	45.38	7.95	11.52
$(AsSe)_{85}(AgI)_{15}$	46.28	45.62	0.156 [a]	8.10
$(AsSe)_{75}(AgI)_{25}$	45.24	42.33	0.48	11.96
$(AsSe)_{65}(AgI)_{35}$	46.86	37.40	2.01	13.74

[a] Ag was under the detection limit - large normalization was used.

The EDAX results of the films presented in table 2 can be discussed with respect to the preparation mechanism:

a) Similarity between VTE and PLD films:

- The higher the AgI content in the source target material, the bigger the difference between the elemental composition of the film obtained and the initial composition of the bulk samples,
- The AgI molar percentage in the film is smaller compared to that in the bulk samples.

The AgI deficit in the films composition is most probably due to the characteristics of the evaporation and deposition processes. The enthalpy of AgI evaporation exceeds that of As-Se and the probability of re-evaporation of AgI from the substrate is larger; As-Se and Se molecules and atoms stick easier to the substrate [5].On the other hand, a number of publications have reported electron-induced chemical modification [6, 7] of photo-sensitive films under the action of electron beams. During the EDAX study, the highly mobile Ag^+ ions are able to migrate toward or away from the irradiated region. This motion depends on the film structure and on the incident radiation energy. For instance, Romero [6] has observed migration of silver away from the irradiated regions during transmission electron microscope (TEM) study of the Ag/a-GeSe bilayer. In what concerns As-Se-AgI glasses, we believe that the structure is rather loose due to the iodine property to break the glass network. We, therefore, could expect higher mobility of the Ag^+ ions and very low Ag content in the $(AsSe)_{1-x}(AgI)_x$ VTE films, respectively.

b) Distinctions between VTE films and PLD films:

- In VTE films the iodine percentage is higher than that of silver. Conversely, the Ag content is higher compared to the iodine concentration in the PLD films.

The above can be explained by taking into account the energy of vaporization and the kinetic characteristics of the two techniques. The high energy of the ion plasma formed during the PLD facilitates the evaporation of silver.

The SEM studies of the freshly prepared VTE and PLD films revealed a smooth and homogeneous surface typical for an amorphous phase, which is spongier in the VTE films, as seen in figures 2 and 3.

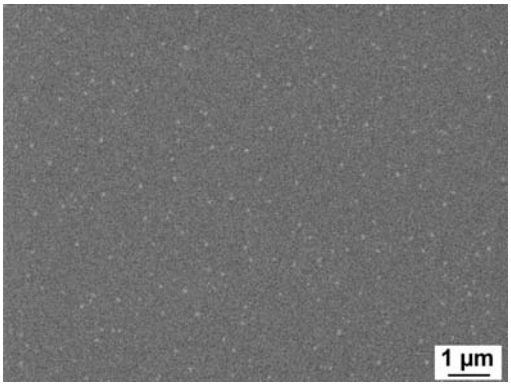

Figure 2. SEM patterns of the VTE $(AsSe)_{85}(AgI)_{15}$ film.

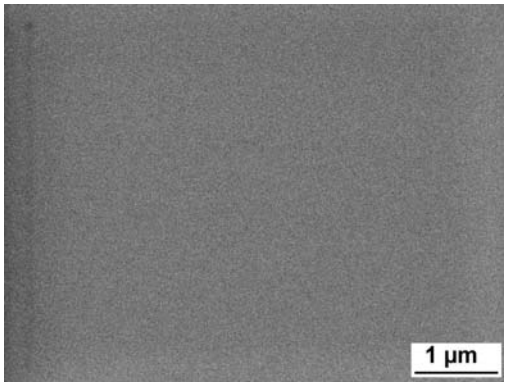

Figure 3. SEM pattern of the PLD $(As_2Se_3)_{90}(AgI)_{10}$ film.

The roughness distribution on the film surface was extrapolated from the AFM histograms. The average values of the roughness in the VTE film is about 5 nm at 530 nm layer thickness that was derived from the sample area of 2x2 μm. The average roughness of the PLD films is lower compared to the VTE films as seen from the three-dimensional pictures (figures 4 and 5).

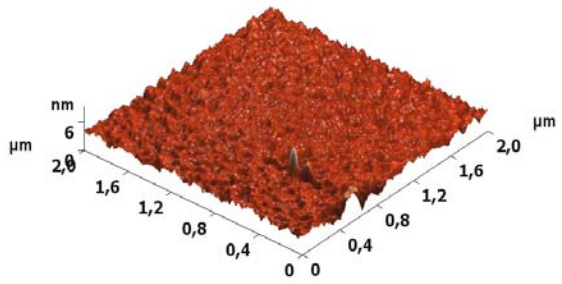

Figure 4. 2X2 3D image of the VTE $(As_2Se_3)_{85}(AgI)_{15}$ film, 530 nm thickness.

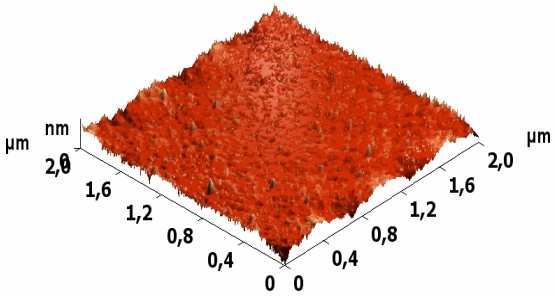

Figure 5. 2X2 3D image of the PLD $(As_2Se_3)_{90}(AgI)_{10}$ film, 650 nm thickness.

4. Conclusion

Films prepared by the two methods do not show substantial differences in what concerns their roughness and smoothness. Using PLD one can obtain more uniform and thicker films with better adhesion and composition closer to the composition of the respective bulk glass than is the case with the VTE films. The Ag content is found to be higher compared to the iodine content in the PLD films while in the VTE films the iodine content exceeds the amount of Ag.

Acknowledgment

This research was supported by the Ministry of Education and Science of Republic of Bulgaria under contract VUF 05 /2005 and by NATO contract CBP.EAP.CLG.982793.

References

[1] Frumar M, Frumarova B, Nemec P, Wagner T, Jedelsky J and Hrdlicka M 2006 *J. Non-Cryst. Solids* **352** 544–61
[2] Krbal M, Wagner T, Kohoutek T, Nemec P, Orava J and Frumar M 2007 *J. Phys. and Chem. of Solids* **68** 953–7
[3] Hineva T, Petkova T, Popov C, Petkov P, Reithmaier J P, Fuhrmann-Lieker T, Axente E, Sima F, Mihailescu C N, Socol G and Mihailescu I N 2007 *J. Optoelectron. Adv. Mater.* **9** 326-9
[4] Nemec P and Frumar M 2003 *J. Optoelectron. Adv. Mater.* **5** 1047-58
[5] Gmelin L 1981 *Gmelin Handbuch* vol A3 (Verlag Chemie GmbH)
[6] Romero J S, Fitzgerald A G and Rose M J 2004 *Appl. Surf. Sci.* **234** 369-73
[7] Yoshida N, Itoh M and Tanaka K 1996 *J. Non-Cryst. Solids* **198-200** 749-52