Amorphous SnSe$_2$ films

F. SAVA[*], A. LÖRINCZI, M. POPESCU, G. SOCOL[a], E. AXENTE[a], I. N. MIHAILESCU[a], M. NISTOR[a]

National Institute R&D of Materials Physics, 77125 Bucharest-Magurele, 105 bis, Atomistilor str., P. O. Box. MG. 7, Romania
[a]National Institute of Lasers, Plasma and Radiation Physics, 77125-Bucharest-Magurele, P. O. Box MG. 6, Romania

Amorphous SnSe$_2$ films were prepared by pulsed laser deposition (PLD) and pulsed electron deposition (PED) from solid polycrystalline targets. The atomic scale structure has been revealed by X-ray diffraction. Hardness properties and electrical properties were measured. The peculiarities of the structures of the films prepared by PLD and PED methods were investigated discussed.

1. Introduction

The amorphous materials are important both from fundamental and application points of view [1, 2]. The theory of the condensed matter in the disordered state is not fully developed, while many applications are found in electronics and optoelectronics [3, 4] for various non-crystalline materials. The chalcogenide materials, and especially the amorphous or glassy chalcogenides, are materials sensitive to light and other radiations [5-24]. They have been suggested for applications as sensors and optical memories [25-35]. The system Sn-Se is poorly studied and its interest consists in the special properties related to the presence of a metal (Sn) and a chalcogen (Se), with different valences and ionicities that govern the structure and the properties, as e.g. the gas sensing properties.

Mooser and Pearson [36] predicted that SnSe$_2$ would exhibit semiconductor behavior. SnSe is a semiconductor with the melting point of 860 ^{o}C and has an energy gap of ~ 1 eV. Thin films of tin-selenium have been reported to have numerous applications in photovoltaic systems and as memory switching devices [37]. The structure of SnSe$_2$, as well as that of SnS$_2$ belongs to the hexagonal CdI$_2$ type (C6). The characteristic layer-type growth allows for the preparation of excellent single-crystal samples with suitable geometry for optical measurements.

Domingo et al. [38] have studied the fundamental optical absorption in SnS$_2$ and SnSe$_2$. Direct transitions band gaps of 1.62 and 2.88 eV were found for SnSe$_2$ and SnS$_2$, respectively. For SnSe$_2$ crystals a conductivity of 3.6 Ω^{-1} cm^{-1}, electron concentration of 10^{18} cm^{-1} and a mobility of 27 cm^2/V.s were determined.

Bindu and Nair [39] prepared the first tin selenium films by heating Se-Sn layers. By controlling the individual film thicknesses and the conditions of heating, SnSe$_2$ or composite films of SnSe$_2$ + SnSe were formed. The photoconductivity of these films fulfils the basic requirements for their integration into photovoltaic structures.

Bhat and Gireesan [40] prepared amorphous thin SnSe$_2$ films by evaporation. The influence of heat treatment upon crystallization was investigated. Recently [41] SnSe$_2$ films were prepared by annealing a hydrazinium-based precursor of the metal chalcogenide deposited on a substrate. A thin film field effect transistor was produced using the tin-selenium (SnSe$_2$) as channel layer. Sharma et al. [42] prepared SnSe films by thermal evaporation of the material in the presence of a carrier gas, and characterized the obtained SnSe nanocrystalline thin films.

In this paper we present our results concerning the preparation of amorphous SnSe$_2$ thin films, by pulsed laser deposition and pulsed electron deposition. Data on structure and properties of these films are reported.

2. Experimental

2.1 Bulk SnSe$_2$ compound

The targets for PLD and PED deposition of thin films were prepared by mixing the corresponding Sn and Se pure elements (5n) in a quartz ampoule. The ampoule was heated at the melting point of SnSe$_2$ (657 ^{o}C) [43]. The temperature of synthesis was increased over a period of 8 h to 730 ^{o}C. Thereafter, the temperature was held constant for more than 20 h. Periodic shaking and rocking of the ampoule was made in order to get a homogeneous composition. Finally, the ampoule was cooled to room temperature in a mixture of ice and water. The ingot (19 mm in diameter and 40 mm in length), exhibits grey color, and a characteristic crystalline morphology, with the radial extension of the crystallites and a specific internal core of diameter of ~5 mm, as seen in the optical microscope.

The bulk density, measured by Archimedes's method is 5.05 g/cm^3, very near to that already reported (5.0 g/cm^3) in the literature [44].

The crystalline ingot, having low mechanical resistance, has been cut in several disc-shaped pieces of

thickness 2 mm using the wire method. The discs were polished before investigation.

The structure of the $SnSe_2$ samples was analyzed by X-ray diffraction. A TUR M-62 diffractometer provided with a copper target tube was used.

Fig. 1 shows the X-ray diffraction pattern recorded on polished discs. The identification of the crystalline phases in the ingot leads to the conclusion that the major phase consists of the $SnSe_2$ with hexagonal structure (Fiche No. 23-0602). A minor phase of $SnSe_2$ with cubic structure (Fiche No. 38-1055) was revealed. The background of the diffraction pattern indicates the presence of a significant content of amorphous phase as seen from the broad peak situated in the range: theta = 4÷13 ^{o}.
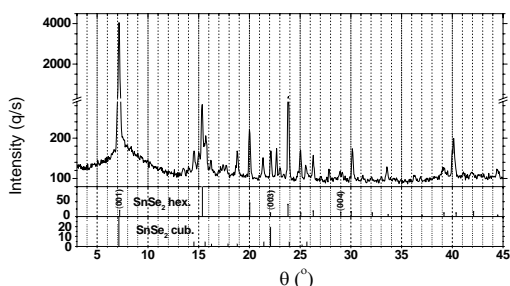

Fig. 1. X-ray diffraction pattern on the polycrystalline $SnSe_2$ ingot.

2.2. Pulsed laser deposition of $SnSe_2$ films.

Pulsed laser deposition is a modern method to deposit thin homogeneous and stoichiometric films started from a solid target. This method has been previously used to prepare thin films of oxides [45], semiconductors [46], superconductors and optical glasses [47]. Recently the method was applied to chalcogenide glasses as well [48]. The ultraviolet ablation is efficient due to the high energy of the UV radiation quantum. Nevertheless, particulate generation is a problem for the quality of the depositited films [49].

The pulsed laser deposition was carried out with a KrF* excimer laser. The laser source generated pulses having the wavelength λ= 248 nm with pulse duration τ_{FWHM}> 7 ns and 1 Hz repetition rate. The pulses were focused on the target through an MgF_2 cylindrical lens with the focal distance of 30 cm. The incidence angle to the target was 45°. The laser spot was set within 3 mm^2. The maximum output energy was 110 mJ/pulse corresponding to a fluency of ~3.6 J/cm^2. During laser irradiation brightly colored plume plasma was observed. The shape of this plume is forward directly and slightly divergent. The experiments were performed in a stainless steel vacuum chamber, which was evacuated down to 2 × 10^{-6} Torr. The target was rotated with the frequency of 0.4 Hz during the PLD process. The substrate for film deposition was a (100) oriented silicon wafer placed parallel to the target surface and situated at a distance of 4 cm from the target. The number of pulses applied during the deposition process was 50000. The estimated thickness of the film was 1 micrometer.

The films prepared by PLD look homogeneous, grey color, bright and without macroscopic defects.

2.3 Pulsed electron deposition of $SnSe_2$ films

Thin $SnSe_2$ films were also deposited by an alternative method: electron ablation and subsequent deposition. The target ($SnSe_2$ disk) was subjected to an electron beam accelerated, with an applied high voltage of 17 kV. The substrate (111 oriented silicon wafers) was placed at a distance of 37 mm from the irradiated target. The working gas in the deposition chamber was argon, with the pressure in the range $10^{-2} – 10^{-1}$ mbar. The electron spot on the target had a diameter of 10 mm. The target was rotated during deposition. There have been 18000 pulses applied with a frequency of ~2.5 Hz, which produced a thickness of 1 μm.

3. Results

3.1 Structural results on thin $SnSe_2$ films.

The structure of the $SnSe_2$ films was investigated by X-ray diffraction.

The X-ray patterns recorded with CuK_α radiation exhibited no diffraction lines. Characteristic curves for the amorphous phase are evidenced in both types of films. Fig. 3 and 4 show the diffraction curves recorded on PLD and PED films.
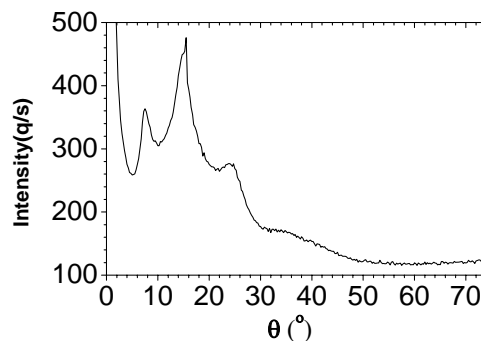

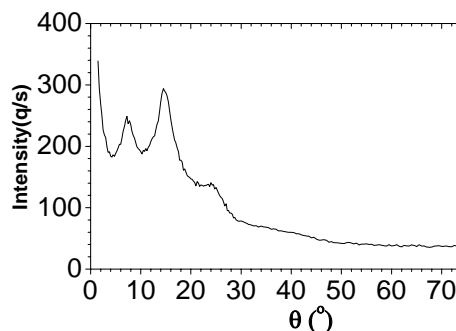*Fig. 2. X-ray diffraction pattern of the PLD films of $SnSe_2$.*

Fig. 3. X-ray diffraction pattern on PED $SnSe_2$ film.

The PLD film of $SnSe_2$ shows in the structure factor a very small peak at the angle of theta = 16° ascribed to the

hexagonal phase of tin di-selenide. The PED film is completely amorphous.

The radial distribution functions of PLD and PED films were calculated. The resulting curves are shown in Fig. 4 and Fig. 5.
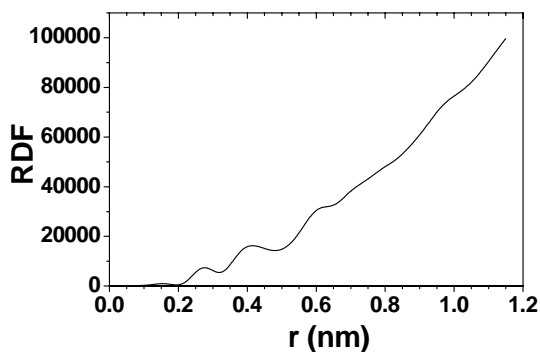

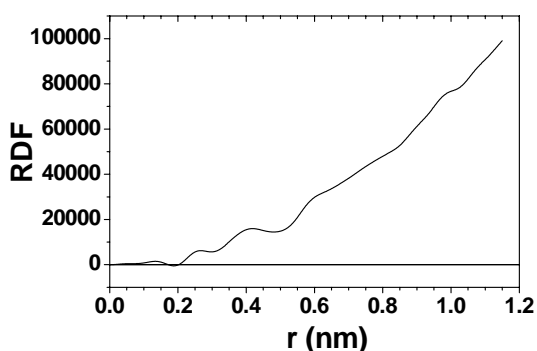*Fig. 4. The radial distribution curves for an amorphous PLD film.*

Fig. 5. The radial distribution curves for an amorphous PED film.

Both radial distribution functions seem to be very similar if one compares the positions of the first peaks (see Table 1).

Table 1. The structural data obtained from RDF of PLD and PED amorphous films.

Film	first peak		second peak		third peak	
	r_1 (Å)	A_1 (e.u.)	r_2 (Å)	A_2 (e.u.)	r_3 (Å)	A_3 (e.u.)
PLD	2.690	4703.5	3.984	22246	6.030	59144
PED	2.575	3095.1	3.981	28505	6.050	32792

According to the position of the first peak, r_1 = 2.690 Å, the Sn-Se bonds are dominant. Taking into account the ratio of the positions of the first two peaks, r_2/r_1= 1.481, and because the r_2/r_1 ratio in the case of tetrahedral bonding is 1.63, one may conclude that Sn atoms are not bonded tetrahedrally in the network.

As regarding the length of the various bonds, one can estimate them from the covalent and ionic radii of the appropriate atoms. Thus, the Sn-Se covalent bond is characterized by the length 1.40 + 1.17 = 2.57 Å, while for the ionic Sn $^{4+}$-Se^{2-} bond the length is 0.67 + 1.93 = 2.60 Å. For the ionic bond: Sn^{2+} - Se^{2-} the bond the length is: 1.02 + 1.93 = 2.95 Å.

It is remarkable that in the free SnSe molecule the inter-nuclear distance is 2.3256 Å. It seems that the true coordination of Sn is less than four and some positive charge is characteristic for tin. From the area under the first peak of the RDF (A_1 = 4703 e.u.) one gets an average of 2.766 atoms in the first coordination sphere. If one compares this value with the mean coordination for the case of tetravalent tin and divalent selenium in the compound, which is 3, one concludes that the mean coordination of tin is smaller than 4, or some tin atoms are three-coordinated. The second peak in RDF shows an area of A_2 = 22246 e. u. If one calculates the A_2 area in the case of the 4-2 model, one gets 33872 electronic units. For the case of 3-2 model of SnSe₂ one gets the value of 24248 e.u. This means that the most probable model is the model 3-2 i.e. three-valent tin linked to di-valent selenium in a continuous random network.

Because the tin takes a quasi-planar trivalent configuration, the formation of quasi-layers in the amorphous tin selenide is very probable. The distance between these quasi-layers was obtained from the position of the first sharp diffraction peak (FSDP). One obtains the value of the "d_{FSDP}" situated at theta=7.8°: 5. 674 Å. If one apply the factor 1.23 [50] one gets the true interlayer-distance of ~7 Å. The thickness of the package of quasi-layers (d_q) in small clusters (amorphites) was calculated from the width of the FSDP. For PLD films d_q = 26.8 Å while for PED films d_q = 19.1 Å. A rough value of 30 Å was obtained. This means an average of ~4.7 quasi-layers in PLD and ~3.4 quasi-layers in PED films are orderly packed in SnSe₂ layered amorphous clusters.

Fig. 6 shows the difference between the reduced radial distribution curve of PLD films and that of PED film. One observes very small differences at the limit of the experimental errors in the measured data.
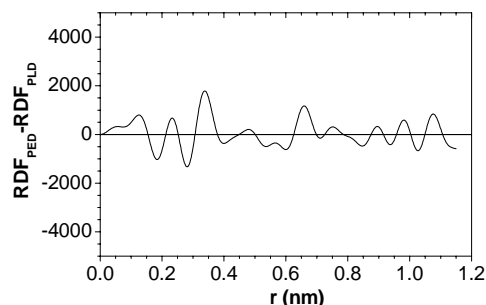

Fig. 6. The difference between the RDFs curves of PLD and PED films.

3.2. Microhardness

The microhardness was determined in polycrystalline SnSe₂ ingot, as well as in the PLD and PED films with a

PMT-4 apparatus provided with a diamond prism (alpha =136 ^{o}).

The microhardness measurements on both type of amorphous films show close values one to another, while different values from that of polycrystalline SnSe$_2$. The polycrystalline ingot exhibits a hardness of 10 kgf/mm^2 (10 Vickers). The PLD films are characterized by a microhardness of 94 kgf/mm^2 (94 Vickers), while the PED films show a lower microhardness: 80 kgf/mm^2 (80 Vickers). In the literature is reported the microhardness in single crystals of SnSe$_2$ (with layered structure) [51]. The microhardness value varies between 35.42 kgf/mm^2 in the direction parallel to the layers and 72.8 kgf/mm^2 perpendicular to the layers.

3.3 Electrical measurements

The electrical conductivity in SnSe$_2$ films was measured using a Keithley Instrument. The conductivity is high ($\sigma = 0.1$ Ω^{-1}cm^{-1}) and this value places SnSe$_2$ in the group of semiconducting - semi-metallic materials. The activation energy for conduction for a PLD film is situated between 0.055 eV for temperatures around the room temperature and 1.587 eV for temperatures around 200 ^{o}C. In the literature an optical band gap of $1\div1.27$ eV has been determined [39] in thin SnSe$_2$ or composite films of SnSe$_2$+SnSe.

4. Conclusions

Thin amorphous films based on SnSe$_2$ composition were prepared by PLD and PED methods. Fully amorphous samples were obtained. The structure of these amorphous films, as determined by X-ray diffraction, consists of a random packing of quasi-layers with four-fold coordinated tin atoms mixed with three-fold coordinated ones and two-fold coordinated selenium.

Acknowledgement

References

[1] Jai Singh, Koichi Shimakawa, Advances in Amorphous Semiconductors (Adv. In Condensed Matter Series, **5**, Eds. D. D. Sharma, G. Cotliar, Y. Tokura), Taylor and Francis, 2003.

[2] Photo-induced Metastability in Amorphous Semiconductors, Ed. Alexander V. Kolobov, Wiley-VCH, 2003.

[3] Mihai A. Popescu, Non-Crystalline Chalcogenides (Solid State Science and Technology Library, Vol. 8), Kluwer Academic Publishers, 2000.

[4] Semiconducting Chalcogenide Glass I, Glass formation, Structure, and stimulated Transformations in Chalcogenide Glasses (Semiconductors and Semimetals, Treatise Editors: Robert K. Willardson and Eicke R. Weber, Vol. **78**), 2004.

[5] I. Ohlidal, D. Franta, M Frumar, J. Jedeleský, J. Omasta, J. Optoelectron. Adv. Mater. **6**(1), 139 (2004).

[6] V. Balitska, O. Shpotyuk, Chalcogenide Letters **1**(5), 67 (2004).

[7] M. Štábl, L. Tichý, J. Optoelectron. Adv. Mater. **6**(3), 781 (2004).

[8] V. Balan, C. Vigreux, A. Pradel, J. Optoelectron. Adv. Mater. **6**(3), 875 (2004).

[9] J. K. Olsen, H. Li, P. C. Taylor, J. Ovonic Research **1**(1), p. 1 (2005).

[10] A. Zakery, J. Optoelectron. Adv. Mater. **7**(3), 1143 (2005).

[11] N. Starbov, K. Starbova, J. Optoelectron. Adv. Mater. **7**(3), 1197 (2005).

[12] N. Mateleshko, V. Mitsa, M. Veres, M. Koos, A. Stronski, Chalcogenide Letters **1**(11) p. 139 (2004).

[13] A. Andries, J. Optoelectron. Adv. Mater. **7**(6), 2931 (2005).

[14] P. Petkov, V. Vassilev, T. Petkova, B. Monchev, L. Aljihmani, J. Optoelectron. Adv. Mater. **7**(4), 1965 (2005).

[15] A. V. Kolobov, P. Fons, J. Yominaga, A. i. Frenkel, A. l. Ankundinov, T. Uruga, J. Ovonic Research, **1**(1), 21 (2005).

[16] M. Popescu, J. Ovonic Research **1**(6), 69 (2005).

[17] M. Popescu, J. Optoelectron. Adv. Mater. **7**(4), 2189 (2005).

[18] J. Dikova, J. Optoelectron. Adv. Mater. **7**(6), 2045 (2005).

[19] K. Shimakawa, J. Optoelectron. Adv. Mater. **7**(1), 145 (2005).

[20] Y. Ikeda, K. Shimakawa, Chalcogenide Letters **2**(12) 125 (2005).

[21] D. Platikanova, D. Arsova, E. Skordeva, J. Optoelectron. Adv. Mater. **7**(1), 337 (2004).

[22] J. Hegedus, K. Kohary, S. Kugler, J. Optoelectron. Adv. Mater. **7**(5), 2231 (2004).

[23] N. A. Hegab, H. E. Atyia, J. Ovonic Research **2**(3), 9 (2006).

[24] P. Boolchand, Chalcogenide Letters **3**(3), 29 (2006).

[25] S. Marian, K. Potje-Kamloth, D. Tsyulyanum, H. –D. Liess, Thin Solid Films, **359**, 108 (2000).

[26] D. Tsiuleanu, S. Marian, K. Potje-Kamloth, H. –D. Liess, Patent No. DE 100 19010 A1, 25.10.2001, Germany.

[27] K. P. Kornev, I. P. Korneva, J. Optoelectron. Adv. Mater. **7**(5), 2359 (2004).

[28] D. Lezal, J. Pedlikova, J. Zavadil, J. Optoelectron. Adv. Mater. **6**(1), 633 (2004).

[29] N. P. Eisenberg, M. Manevich, A. Arsh, M. Klebanov, V. M. Lyubin, Chalcogenide Letters **2**(4), 35 (2005).

[30] N. P. Eisenberg, M. Manevich, A. Arsh, M. Klebanov, V. M. Lyubin, J. Optoelectron. Adv. Mater. **7**(5), 2275 (2005).

[31] D. Lezal, J. Zavadil, M. Prochazka, J. Optoelectron. Adv. Mater. **7**(5), 2281 (2005).

[32] D. Strand, J. Optoelectron. Adv. Mater. **7**(4), 1679 (2005).

[33] M. L. Trunov, J. Optoelectron. Adv. Mater. **7**(5), 2235 (2004).

[34] D. Savastru, S. Miclos, R. Savastru, J. Optoelectron. Adv. Mater. **7**(4), 1909 (2004).

[35] A. Andriesh, J. Optoelectron. Adv. Mater. **7**(6), 2931 (2006).

[36] E. Mooser, W. B. Pearson, Phys. Rev. **101**, 495 (1956).

[37] R. M. Dongwoo Chu, R.W.B. Walser, T. H. Courteny, Appl. Phys. Lett. **24**, 479 (1974).

[38] G. Domingo, R. S. Itoga, C. R. Kannewurf, Phys. Rev. **143**(2), 143 (1966).

[39] K. Bindu, P. K. Nair, Semicond. Sci. Technol. **19**, 1348 (2004).

[40] V. P. Bhat, KI. Gireesan, J. Mater. Sci. Letters, **9**(3), 362 (1990).

[41] David B. Mitzi, US Patent No. 6,875,661, Issued on 4/05/2005.

[42] J. Sharma, G. Singh, A. Thakur, G. S. S. Saini, N. Goyal, S. K. Tripathi, J. Optoelectron. Adv. Mater. **7**(4), 2085 (2005).

[43] Max Hansen, Constitutions of binary alloys (second edition), Vol. 2, p. 1187, McGraw-Hill Book Company, 1958, New York, USA.

[44] http://www.webelements.com/webelements/compounds/text/Sn/Se2Sn1-20770096.html.

[45] H. Sankur, Mat. Res. Sci. Symposium, Proceedings **29**, 373 (1984).

[46] J. T. Cheung, Mat. Res. Sci. Symposium, Proc. **29**, 301 (1984).

[47] E. M. Vogel, E. W. Chase, J. L. Jackel, B. J. Wilkens, Applied Optics, **28**(4), 649 (1989).

[48] P. Nemec, M. Frumar, J. Optoelectron. Adv. Mater. **5**(5), 1047 (2003).

[49] E. György, I. N. Mihailescu, M. Kompitsas, A. Giannoudakos, J. Optoelectron. Adv. Mater. **6**(1), 39 (2004).

[50] M. Popescu in Proc. Adv. NATO Res. Workshop, Chishinau, Moldova Rep., 1996, Physics and Applic. of Non-Cryst. Semic. in Optoelectron., 1997, Kluwer Acad. Publ., pp. 215 – 232.

[51] E. Trifonova, I. Y. Yanchev, P. Manou, K. Kambas, Anagnostopoulos A. N., J. Mat. Sci. **31**(14), 3647 (1996).

*Corresponding author: fsava@infim.ro