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Structure, properties and gas sensing effect of $SnSe_2$ films prepared by pulsed laser deposition method

M. Popescu [a,*], F. Sava [a], A. Lőrinczi [a], G. Socol [a,b], I.N. Mihăilescu [a,b], A. Tomescu [a], C. Simion [a]

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

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Abstract

Amorphous $SnSe_2$ films were prepared by pulsed laser deposition (PLD) from solid polycrystalline targets. The atomic scale structure has been revealed by X-ray diffraction. Hardness and electrical properties were measured. Strong gas sensing properties have been evidenced for the first time in heat treated films.

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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.

Mooser and Pearson [36] predicted that $SnSe_2$ would exhibit semiconductor behavior. SnSe is a semiconductor with the melting point of 860 °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 $3.6\ \Omega^{-1}\ cm^{-1}$, electron concentration of $10^{18}\ cm^{-3}$ 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

* Corresponding author. Tel.: +40 214930047; fax: +40 214930267.
E-mail address: mpopescu@infim.ro (M. Popescu).

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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. 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 to the melting point of $SnSe_2$ [43]. The temperature of synthesis was increased over a period of 8 h to 730 °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 2 mm thickness 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 theta range: 4–13°.

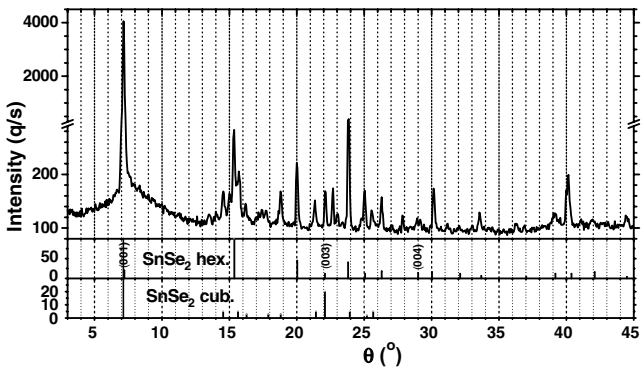

Fig. 1. X-ray diffraction pattern on the polycrystalline $SnSe_2$ ingot.

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.

The pulsed laser deposition was carried out with a KrF^* excimer laser. The laser source generated pulses having the wavelength $\lambda = 248$ nm with pulse duration $\tau_{FWHM} > 7$ 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 (1 0 0) 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 50 000. The estimated thickness of the film was 1 μm.

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

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 pattern recorded with Cu Kα radiation exhibited a characteristic curve for the amorphous phase (Fig. 2). The PLD film of $SnSe_2$ shows in the structure factor a very small peak at the angle theta = 16° ascribed to the hexagonal phase of tin diselenide.

The radial distribution function of PLD film was calculated. The resulting curve is shown in Fig. 3 and the structural data in Table 1.

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, $r_2/r_1 = 1.481$,