Optimization of growth conditions for SnSe$_2$ thin films

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Bulk SnSe$_2$ was prepared by melting the constituents in stoichiometric proportions and thin films of this material were grown by a flash evaporation technique. X-ray and electron diffraction methods were used for characterization of the bulk material and the films. The effect of substrate temperature on the structural properties, composition and electrical resistivity of the films have been studied. It was found that single-phase polycrystalline stoichiometric films of SnSe$_2$ can be grown in the substrate temperature range 398 to 623 K. The films deposited at 523 K had the minimum electrical resistivity.

1. Introduction

A widespread interest in the structural, optical, electrical and superconducting properties of the transition metal dichalcogenide layer compounds has evolved during the past few decades. Tin diselenide is a layered semiconductor of the IV–VI family which crystallizes in CdI$_2$-type C6 lattice structure. The optical properties of these crystals have been reported by many authors [1–5], as have the resistivity of these crystals perpendicular to the C-axis, and Hall effect measurements [1–3, 6]. Several authors have reported structural properties of SnSe$_2$ crystals [7–9]. It appears from a survey of the literature that so far, SnSe$_2$ thin films have received relatively less attention compared to other IV–VI compounds. Hence, the present investigation was undertaken on the growth and structural characteristics of SnSe$_2$ thin films which, in turn, may throw some light on the fabrication of the devices.

Experimental techniques

2.1. Material synthesis

The SnSe$_2$ material was prepared by mixing pure (99.999%) individual elements in stoichiometric proportions in a sealed quartz ampoule evacuated to a pressure about 10^{-4} Pa. The sealed ampoule was placed in a furnace at the required temperature and was rotated by an electric motor to ensure complete mixing and reaction of the constituents. The rotation of the tube commenced when the temperature of the furnace reached about 940 K and continued for 12 h. The ingot thus obtained on breaking the ampoule was crushed to a fine powder for use in energy dispersive analysis of X-rays (EDAX) as well as X-ray diffraction analysis (XRD). The XRD analysis was carried out using an X-ray diffractometer with CuKα radiation.

2.2. Film preparation

SnSe$_2$ thin films were deposited by a flash evaporation method in a vacuum of the order of 10^{-4} Pa. The evaporation of the material was carried out from a molybdenum boat maintained at a sufficiently high temperature, about 1200 K, in order to evaporate the material instantaneously. The deposition rate was measured to be about 2 nm sec^{-1} in all the experiments and the thickness of the deposits was kept at 120 nm in all cases. Thoroughly cleaned glass slides were used as the substrates. The films were grown at substrate temperatures varying between 300 and 700 K. The films were carefully stripped off the glass substrate for structural studies. The structural properties of the films were examined using an electron microscope (EM 400 Philips) while compositional analysis was carried out using EDAX (PW 9100) attached to the EM 400. The dark electrical resistivity was measured at room temperature using the four-probe method and high-impedance electrometers. Vacuum-deposited silver films with silver-pasted leads provided ohmic contacts.

3. Results and discussion

Different parts of the SnSe$_2$ ingot were examined by the EDAX analysis. It was observed from the analysis that the ingot was nearly stoichiometric and homogeneous in nature. The material was then characterized by the X-ray powder diffractogram. Fig. 1 shows the X-ray diffractogram of bulk SnSe$_2$. The d-spacings were calculated and compared with the standard values [10]; they are listed in Table I. The calculated d-spacings are in good agreement with the standard values. The very strong and sharp (1 0 1) peak indicates a highly preferred orientation of the crystallites.

Figs 2a, b and c show the transmission electron micrographs and the corresponding electron diffraction patterns of SnSe$_2$ films deposited at 300, 523 and 673 K, respectively. Fig. 2a shows that the thin films deposited at 300 K were amorphous and fine grained in nature. It was observed that these as-grown amorphous thin films changed to polycrystalline due to electron beam heating. This has been attributed to the electron charge or thermal gradient set up in the poorly
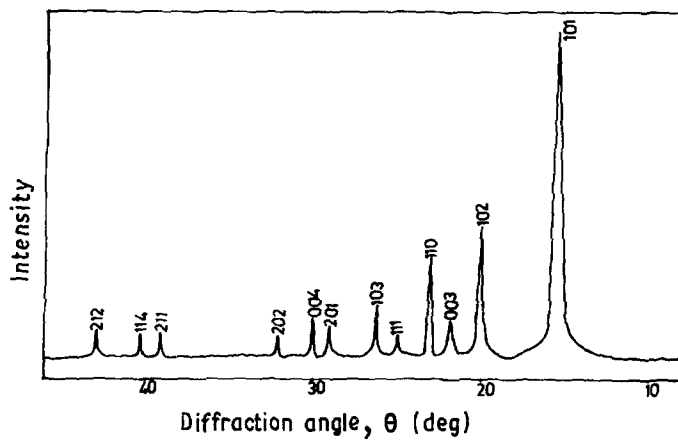
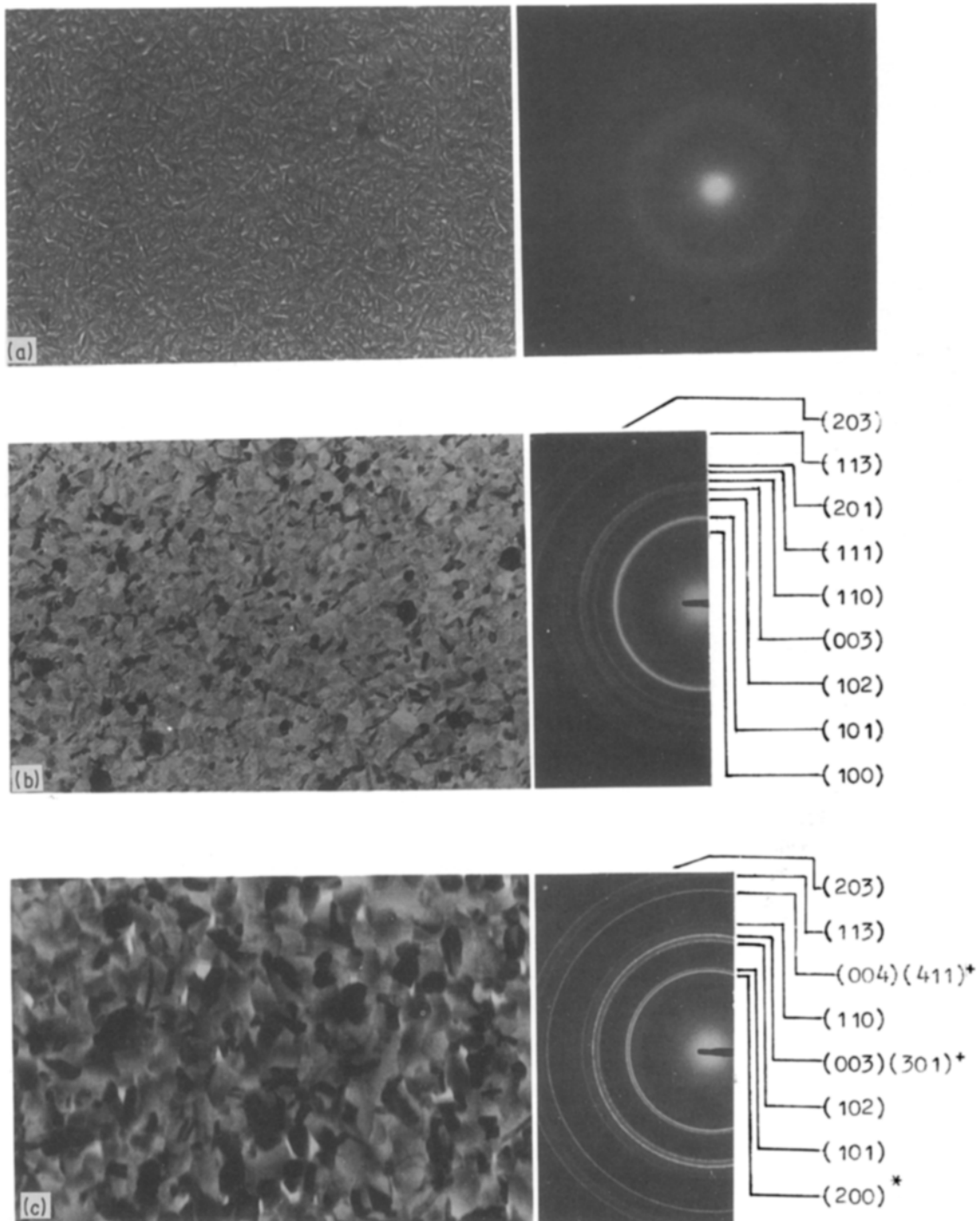Figure 1 X-ray diffractograms of SnSe₂ bulk materials.

Figure 2 Transmission electron micrographs and the corresponding electron diffraction patterns of SnSe₂ thin films deposited at (a) room temperature (300 K), (b) 523 K, and (c) 673 K. *The *d*-value matches Sn₂Se₃. † The *d*-value may match Sn₂Se₃ × 57 600.
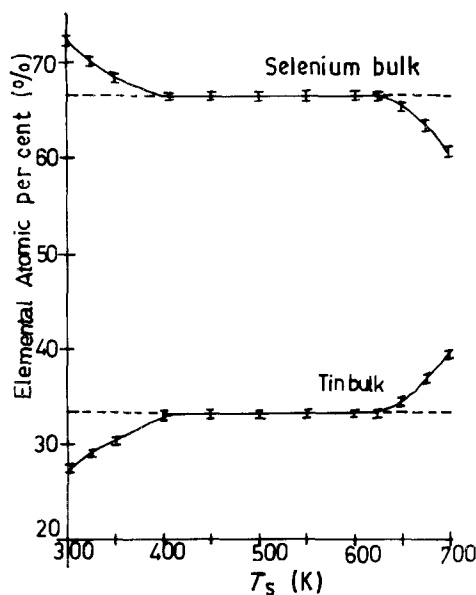
Figure 3 Variation of elemental atomic per cent of tin and selenium with substrate temperature (T_s) for $SnSe_2$ thin films.

Figure 4 Variation of electrical resistivity (ϱ) of $SnSe_2$ thin films with substrate temperature (T_s).

conducting film when subjected to the electron beam [11]. Therefore, all films were examined under low beam current.

Fig 2b shows that the thin films deposited at 523 K were polycrystalline. The calculated d-values from the electron diffraction pattern are in good agreement with the standard values, which are listed in Table I. The electron diffraction patterns revealed that the (1 0 1) plane is a highly preferred orientation. Similarly, the d-values of the films deposited in the substrate temperature range 398 to 623 K are also in good agreement with the standard d-values, which revealed that $SnSe_2$ films thus grown are single-phase polycrystalline in nature.

Fig. 2c shows that the thin films deposited at 623 K are also polycrystalline in nature, but the presence of additional reflections may be seen. These reflections
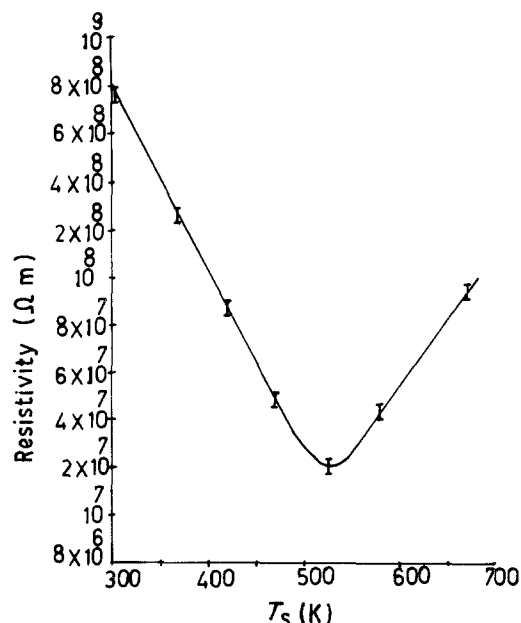
TABLE I Comparison between the standard and the experimental diffraction data for $SnSe_2$ bulk and films

hkl	Standard d (nm)	Experimental d (nm)		
		Bulk (Fig. 1)	$T_s = 523$ K (Fig. 2b)	$T_s = 673$ K (Fig. 2c)
2 0 0	0.3275	–	–	0.3269 (2 0 0*)
1 0 0	0.3299	–	0.3285	–
1 0 1	0.291	0.291	0.2905	0.2908
1 0 2	0.225	0.2245	0.225	0.2245
0 0 3	0.205	0.205	0.2054	0.2054 (3 0 1†)
1 1 0	0.191	0.190	0.1903	0.1905
1 1 1	0.182	0.1815	0.1824	–
1 0 3	0.174	0.1738	–	–
2 0 1	0.159	0.1581	0.1585	–
0 0 4	0.154	0.1541	–	0.1535 (4 1 1†)
2 0 2	0.145	0.1448	–	–
2 1 1	0.122	0.1214	–	–
1 1 4	0.119	0.183	–	–
1 0 5	0.151	0.1509	–	–
2 1 2	0.15	0.1489	–	–
1 1 3	0.139	–	0.1385	0.1388
2 0 3	0.128	–	0.1275	0.1283

†d-values may be matches with Sn_2Se_3.
*d-values match Sn_2Se_3.

(2 0 0) were identified as a formation of Sn_2Se_3 phase, and are listed in Table I. The formation of additional reflections may be due to decomposition of single-phase $SnSe_2$. Similar observations are also observed in films deposited at a substrate temperature higher than 623 K. It is revealed from all the micrographs (Fig. 2) that crystallite size increases with increasing substrate temperature.

The compositional analyses of the films grown at different substrate temperatures is shown in Fig. 3. The range bar represents data taken on four separate films prepared under the same experimental conditions and five analysis points on each film. It may be observed from Fig. 3 that the $SnSe_2$ films were stoichiometric when grown in the substrate temperature range 398 to 623 K, while films deposited at substrate temperatures below 398 K are selenium-rich, and films deposited at substrate temperatures above 623 K are selenium-deficient.

The possible mechanism for the growth of $SnSe_2$ films deposited at different substrate temperatures is as follows. At room temperature, the deposition of the vapour flux arriving at the substrate results in the formation of selenium-rich films, as is evident from the composition data of the film (Fig. 3). Irrespective of whether $SnSe_2$ evaporates in a molecular fashion or in the dissociated form, on arrival at the substrate, it forms the compound of $SnSe_2$ and excess of selenium is maintained in the films. An increase in substrate temperature results in a decrease of the volatile selenium in the films, because at higher substrate temperatures, the excess selenium re-evaporates at a faster rate than the compound in accordance with vapour-pressure dependence on the temperature. The vapour pressure of the compound remains comparatively smaller than that of individual elements over the temperature range from 398 to 623 K, which leads to the formation of stoichiometric of $SnSe_2$ films. For films deposited at temperatures above 673 K, the possibility of decomposition and re-evaporation of the films

slowly increases, which leads to a deficiency of selenium. Fernandez-Samuel et al. [12] have reported similar phase changes and decompositions of as-grown tin diselenide thin films by applying pulse annealing treatment.

The variation of the electrical resistivity of $SnSe_2$ films with the substrate temperature is shown in Fig. 4. It is observed that the resistivity decreases with increasing substrate temperature and reaches a minimum value at 523 K and again it increases at substrate temperatures above 523 K. The decrease in the resistivity may be explained using Petritz's barrier model [13]. Because the crystallites do not grow sufficiently large at low temperatures, the intercrystalline barriers are wide, offering a high resistance to the motion of charge carriers, while at higher substrate temperatures, large crystallite sizes are obtained which ultimately decrease the intercrystalline barriers. The charge carriers, therefore, have to cross comparatively narrow intercrystalline barriers and this results in a decrease of resistivity. The resistivity of the films deposited at substrate temperatures above 523 K increased, this may be due to the deviation from stoichiometric composition of the film, as well as the formation of an additional phase of Sn_2Se_3 present in the film.

4. Conclusions

In the present study, the substrate temperature has been found to have significant influence on the quality, orientation and composition of the $SnSe_2$ thin films, as follows.

1. The flash evaporation of stoichiometric bulk $SnSe_2$ yields an amorphous, selenium-rich and high-resistive films deposited at substrate temperatures below 398 K.

2. The films deposited in the substrate temperature range 398 to 623 K are single phase, polycrystalline and stoichiometric. The films deposited at the sub-strate temperature have minimum electrical resistivity ($\approx 10^7 \Omega$ cm).

3. At higher substrate temperature (> 673 K) the films are non-stoichiometric, highly resistive and mixed phases.

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