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Spray pyrolysis deposited tin selenide thin films for thermoelectric applications

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HIGHLIGHTS

- Influence of substrate temperature on the deposition of SnSe has been shown.
- Seebeck measurements at 275°C–375 °C confirms n-type conductivity.
- Higher seebeck coefficient has been observed at 350 °C deposited film.
- Decrease in band gap was observed on increasing Tsub and size of the crystallites.

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ABSTRACT

Tin selenide thin films were prepared by spray pyrolysis technique using tin (II) chloride and selenourea as a precursor compounds using Se:Sn atomic ratio of 1:1 in the starting solution onto glass substrates. Deposition process was carried out in the substrate temperature range of 250 °C–400 °C using 1 ml/min flow rate. The films were investigated using X-ray diffraction, field emission scanning electron microscopy, Raman spectroscopy, optical absorption and thermoelectric studies. The X-ray diffraction patterns suggest that the major phase is hexagonal-$SnSe_2$ was present when the deposition was carried out in 275–375 °C temperature range, while for the films deposited in the below and above to this range, Sn and Se precipitates into some impure and mixed phase. Raman scattering analysis allowed the assignment of peaks at ~180 cm^{-1} to the hexagonal-$SnSe_2$ phase. The optical absorption study shows that the direct band gap of the film decreases with increase in substrate temperature and increasing crystallite size. The thermo-electrical measurements have shown n-type conductivity in as deposited films and the magnitude of thermo EMF for films has been found to be increasing with increasing deposition temperature, except for 350 °C sample. 350 °C deposited samples shows enhance thermoelectric value as compared to other samples. Thermoelectric study reveal that although sample deposited between 275 °C and 375 °C are structurally same but 350 °C sample is thermoelectrically best.

1. Introduction

The thermoelectric effect (TE) enables direct and reversible conversion between thermal and electrical energy, and provides an effective route to use the waste heat from automobiles or factories, or conversely to cool down electronic devices for example. The efficiency of thermoelectric materials is dictated by the dimensionless figure of merit, ZT (where Z is the figure of merit and T is absolute temperature), which governs the Carnot efficiency for heat conversion [1]. $ZT = S^2T/\rho\kappa$, where ρ, S and κ are the electrical resistivity, Seebeck coefficient and thermal conductivity, respectively. To obtain highly efficient TE devices, low ρ, high S and low κ must be associated simultaneously [2].

Thin chalcogenide films have recently gained considerable attention due to their interesting physical (optical and electrical) properties and their technological applications. Among various chalcogenide films e.g. PbTe, PbSe, Bi_2Se_3, Bi_2Te_3, etc [3] are well studied system. 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. Tin selenide offer a range of optical band gaps suitable for various optical and optoelectronic

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applications. Tin monoselenide (SnSe) and tin diselenide ($SnSe_2$) are promising candidates for solar cell applications, memory switching devices, etc [4,5]. SnSe has an orthorhombic crystal structure and is a p-type semiconductor with an optical band gap of nearly 1.0 eV [6]. $SnSe_2$ has a hexagonal crystal structure of the type CdI_2 characterized by layers of Sn–Se–Sn bonded by van der Waals forces and has been identified as an n-type semiconductor with a direct band gap energy of 1.59 eV [7].

In a recent report [8] by a group of researchers of North-western University has shown that Tin selenide (SnSe) has the highest Carnot efficiency for a thermoelectric cycle ever found and has shown it potentially for a possible material for use in generating electricity from waste heat. In their Nature article, the team describes work they've conducted on SnSe single crystal and how their discovery might lead to even more efficient materials. Apart from that it has been reported that SnSe is the world's least thermally conductive crystalline material [9], this property may boost the thermoelectric effect as it is inversely propositional and very few crystalline compound exist which has low thermal conductivity.

Always it is crucial to prepare high-quality films with good structural and optical properties for the fabrication of efficient devices. SnSe and $SnSe_2$ semiconducting film have been prepared by several techniques such as pulsed laser deposition, chemical vapour deposition, electro deposition, Sputtering, chemical bath deposition, flash deposition, atomic layer deposition, hot wall epitaxy, ultrasonic spray pyrolysis, etc [10–18]. Among other techniques, Spray pyrolysis technique is considered a simple and a relatively low cost technique for the preparation of thin film compounds.

In this work we report the deposition of tin selenide thin films by spray pyrolysis technique at different substrate temperature. Thin film deposition process was carried out in the substrate temperature range of 250 °C–400 °C. Films were characterized by x-ray diffraction, Raman spectroscopy, scanning electron microscopy, optical measurements, and thermoelectric measurement, etc. It has been seen that, there is a specific temperature range (275–375 °C) in which $SnSe_2$ phase form as a major phase. Below and above this range Sn and Se precipitates into some impure and mixed phase.

2. Experimental procedure

Spray pyrolysis involves the application of a fine mist of very small droplets containing the reactants onto the hot substrates in the atmospheric conditions. The critical operations of the spray pyrolysis technique are the preparation of uniform and fine droplets and the controlled thermal decomposition of these droplets. A schematic view of the apparatus is shown in Fig. 1. The tin selenide

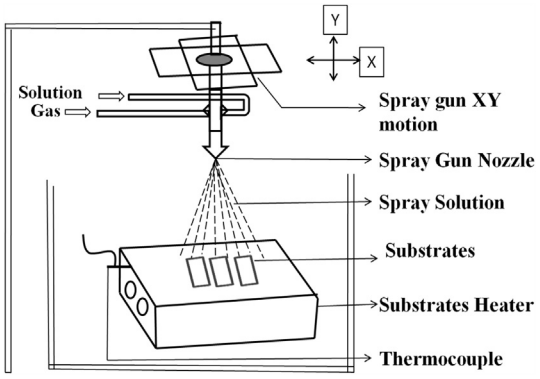

Fig. 1. The schematic view of the apparatus of spray pyrolysis system.

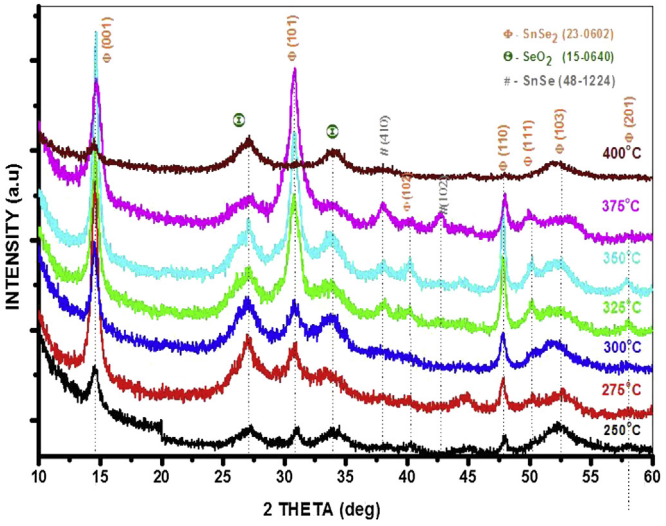

Fig. 2. XRD pattern of tin selenide films prepared at different substrate temperature.

Table 1
Crystallite sizes and optical band gap values at various substrate temperatures.

S. No	Substrate temp (°C)	Crystallite size (nm)	Optical band gap (eV)
1	250	14.96	1.78
2	275	15.21	1.67
3	300	15.90	1.65
4	325	17.34	1.52
5	350	18.81	1.42
6	375	19.48	1.20

thin films were prepared by spraying a 1:1 ratio of aqueous solution of 0.05 M selenourea ($SeC(NH_2)_2$) and 0.05 M of tin (II) chloride ($SnCl_2$) on the high cleaned glass substrate. All reagents used in this work were of analytical grade. The solution was properly mixed using magnetic stirrer for ~2 h before loading into the spray pyrolysis system. The final solution was sprayed onto a 4 × 3 cm glass substrate kept at 15 cm below the spray nozzle. Here the spray rate for all the samples was set at 1 mL/min. In this manner, a set of samples were prepared by depositing tin selenide at different

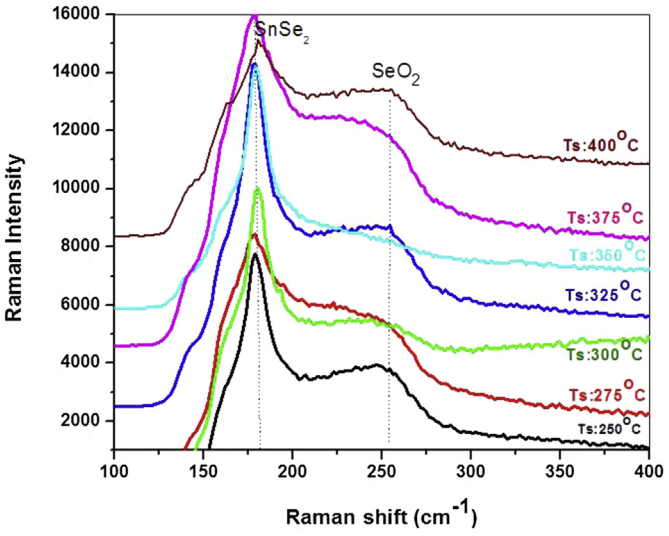

Fig. 3. Raman spectra of tin selenide films prepared at different substrate temperature.