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Effect of deposition time on lead selenide thermoelectric thin films prepared by chemical bath deposition technique

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ABSTRACT

A series of lead selenide (PbSe) films was deposited at constant bath temperature with various deposition time (3–5 h) using simple chemical bath deposition techniques, to study the effect of deposition time on its structural and thermoelectric properties. The as-deposited film was analyzed through X-ray diffraction, SEM, Energy dispersive X-ray analysis, Raman spectroscopy and Seebeck coefficient measurement. The improvement of crystallinity of the PbSe films was studied using X-ray diffraction and Raman scattering. The structural parameters, such as the lattice constant (a), crystallite size (D), dislocation density (δ) and microstrain (ε) were evaluated from the XRD spectra. Average crystallite size was calculated from Scherrer's formula and it was found to be increased from 19.65 to 23.97 nm as the deposition time was varied from 3 h to 5 h. The dislocation density and microstrain were found to vary inversely with the crystallite size, whereas the lattice constant increases with an increase in crystallite size. SEM images show that the morphology of particles strongly depends on the deposition time. The possible growth mechanism for the variation in the morphology is discussed. The thermoelectric measurements have shown n-type conductivity in "as deposited films" and the magnitude of Seebeck coefficient is found to be increasing with an increase in deposition time.

1. Introduction

Thermoelectric energy conversion, which directly transforms heat into electricity/energy, has drawn much attention in recent years and has found applications in a variety of areas such as renewable and clean energy, small scale cooling systems for electronic devices, thermoelectric power generation, micro refrigerator devices, etc [1,2]. Thermoelectric behaviour can be evaluated with Seebeck coefficient (S) which represents the rate of voltage variation per unit temperature change ($\Delta V/\Delta T$) for the materials. This coefficient is very low in metals measuring up to few μV/K and much larger for semiconductor typically few 100 μV/K [3]. Performance of thermoelectric devices is evaluated by material's figure of merit ($ZT=S^2\sigma T/\kappa$), a dimensionless quantity and power factor by $S^2\sigma$, where S is the Seebeck coefficient, T is the temperature, σ and κ are electrical and thermal conductivity respectively [3].

Binary semiconductors are considered as important technological materials because of their potential applications [1–4]. In recent years the synthesis of semiconductor thin films by chemical deposition of colloidal semiconductors has been used frequently for various purposes. Now a days lead chalcogenides has also shown utmost characteristics for the use of a thermoelectric material in cooling and power generation devices.

Lead selenide (PbSe), a member of the family of $A^{IV}B^{VI}$ is important for its narrow band gap ($Eg=0.27$ eV) [5], and

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has a large exciton Bohr radius (46 nm), that offers the opportunity to achieve strong size quantization at the relatively large crystal size [6,7]. PbSe finds wide range of applications in long and mid-wavelength infrared detectors, mid-infrared lasers, optical amplifiers, as thermoelectric materials, and as Pb^{2+} ion selective sensors [8–11].

PbSe can be synthesized by using various techniques such as Vacuum evaporation [12], Microwave heating [13], Pulsed laser deposition [14], Electro-chemical atomic layer epitaxy [15], Electro-deposition [16], and Chemical bath deposition method [17,18]. Chemical bath deposition is a versatile technique for deposition of semiconductor and oxide thin films. Due to its feasible low cost and easy production, it has widely been researched. Recent developments show substantial increase in thin film synthesis rate via chemical bath deposition technique. To the best of our knowledge, synthesis and characterization of PbSe thin films with respect to deposition time by chemical bath deposition technique is not often reported.

In this work, PbSe thin films were deposited on glass substrates by chemical bath deposition method at a temperature of 75 °C on a hot plate. Chemical bath deposition is the simplest way to deposit thin films of some chalcogenides that are known to have selective characteristics suitable for thermoelectric application. The structural, morphological and thermoelectric properties of the deposited film were studied with respect to various deposition times. Various parameters like crystallize size, lattice parameter, etc were also calculated. Possible growth mechanism for the variation in the morphology is also discussed. Thermoelectric measurement confirms n-type semiconducting nature.

2. Experimental procedure

2.1. Synthesis of PbSe thin films

Analytical grade chemicals such as lead acetate [$Pb(CH_3COO)_2 \cdot 3\,H_2O$] tri sodium citrate (TSC), selenium metal powder, sodium sulphite and potassium hydroxide were used for deposition of PbSe thin films. Sodium selenosulphate was obtained by refluxing 5 g Selenium powder and 12 g sodium sulphite in 100 ml double distilled water for 24 h at 90 °C. The mixture was kept under constant stirring throughout the reflux process. After 24 h of stirring, the solution was filtered off to remove the unreacted selenium. The selenosulphate solution was transferred in air tight bottle. It is recommended to make small volumes of selenosulphate stock solution to be used within 3–4 day [19,20]. The concentration of the resulting solution was found to be 0.2 M.

$$Na_2SO_3 + Se \rightarrow Na_2SeSO_3 \quad (1)$$

The PbSe thin films were deposited on glass substrates at constant deposition temperatures and various deposition times using chemical bath deposition technique. Before the deposition, the glass substrates were cleaned to remove the greasy contaminants and debris present on its bare hard surface [21]. The deposition bath was prepared in 100 ml beaker by the addition of 0.2 M lead acetate [$Pb(CH_3COO)_2 \cdot 3\,H_2O$] solution. Appropriate amount of TSC was added to this solution. Finally, freshly prepared sodium selenosulphate (Na_2SeSO_3) solution was added to the bath.

The pH of the solution bath was set about 11 by drop wise addition of potassium hydroxide and the temperature of the bath was maintained at 75 °C. In this manner, a set of four samples was prepared by depositing PbSe at various time intervals (3, 3.5, 4 and 5 h).

2.2. Film characterization:

X-ray diffraction (XRD) patterns of the films was recorded using Pan analytical XRD ($\lambda = 0.15406$ nm) instrument, to determine the structural information and qualitative analysis of the as-grown films. Scanning electron microscopy (SEM) along with energy dispersive X-ray analysis (EDAX) images were recorded on a JEOL-SEM for direct observation of the surface morphology and the quantitative analysis of the deposited films. SEM micrographs were recorded in high as well as low magnification. Raman spectra of the films were recorded on a RENISHAW in Via microscope. The thermoelectric capacity is measured by a locally fabricated experimental set up supplied by M/s Pushpa Scientific, Hyderabad. Using this set up, we may achieve a maximum temperature gradient up to 150 °C across two end of the sample.

3. Results and discussion

3.1. Film growth

The lead selenide films were prepared from an aqueous alkaline bath containing Pb^{2+} and Se^{2-} ions. Lead acetate and sodium selenosulphate were the source of Pb^{2+} and Se^{2-} ions, respectively, during the time that TSC was used as complexing agent. At a fixed temperature the film growth rate is dependent on the rate of release of Pb^{2+} ions from the complex state and the decomposition of sodium selenosulphate. For deposition of PbSe, Pb^{2+} ions complexed with TSC were allowed to react with Se^{2-} ions that were generated by decomposition of $Na_2S_2O_3$. The mechanism of film formation can be understood from the following reactions: The deposition process is based on the slow release of Pb^{2+} and Se^{2-} ions in the solution. The complexing agent TSC controls the Pb^{2+} concentration and slowly releases Pb^{2+} ions into the solution. The proposed reaction mechanism for formation of PbSe thin films is as follows:

$$[Pb(TSC)_n] \overset{75\ ^\circ C}{\Longrightarrow} Pb^{2+} + n(TSC) \quad (2)$$

$$Na_2SeSO_3 + 2OH^- \overset{75\ ^\circ C}{\Longrightarrow} Na_2SO_4 + Se^{2-} + H_2O \quad (3)$$

$$PB^{2+} + Se^{2-} \overset{75\ ^\circ C}{\Longrightarrow} PbSe \quad (4)$$

PbSe thin film is formed when the ionic product of Pb^{2+} and Se^{2-} ions exceeds the solubility product of PbSe ($\approx 10^{-38}$ at 300 K) [16].

3.2. Structural studies

The structural identification of PbSe films was carried out using XRD technique in the $20^\circ \le 2\theta \le 90^\circ$ angular range as