STRUCTURAL AND ELECTRICAL CHARACTERIZATION OF SINTERED SnTe FILMS

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The effective deposition techniques of good quality SnTe films over a large area have been of increasing interest in many optoelectronic applications exp. infrared detectors and solar cells. Tin telluride was prepared by mechanical alloying technique and the films were deposited by an inexpensive and commerciably viable sintering technique on glass substrate. The structural and electrical properties of these films have been examined to investigate the utility of the material for different device applications. The resistivity, carrier concentration and Hall mobility of the films were calculated using Vander-Pauw method. The temperature dependence of resistivity was also investigated. The energy band gap has been determined from the absorption spectra of the films. The X-ray diffraction patterns of sintered SnTe films revealed the formation of polycrystalline material with randomly oriented grain. The lattice parameter for the films was found to be in good agreement with ASTM data and average grain size was determining as 28.75 nm. From the XRD traces it has been observed that the films were nano crystalline.

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Keywords: Mechanical alloying, Sintering, Absorption spectra, Lattice parameter, Grain size

1. Introduction

The large area capability and ease of scaling up with complete control of material handling offers potential application of sintering in industrial production of coatings and optoelectronic devices [1]. Metal chalcogenides of the chemical formula IV-VI have received considerable attention because of their interesting physical properties. Narrow gap semiconductors are highly desirable for photovoltaic, thermovoltaic and thermoelectric devices as well as numerous optical applications [2-5].

Tin chalcogenide SnTe is a narrow gap semiconductor that crystallizes in rock salt structure with a direct band gap 0.35 eV. It has found application in mid infrared (3-14μm) detection, photo detectors, and thermoelectric devices [6-10]. SnTe has recently been accused of having new, previously unexpected properties. They placed SnTe among the most promising material for thin film photovoltaics [11].

In view of the strong trend towards material preparation techniques with composition control possibilities mechanical alloying was adopted to prepare SnTe and the films were prepared by screen printing technique followed by sintering of the films. Screen printing is an economical technique with good reproducibility. This technique permits the preparation of polycrystalline films for large area applications. It is extremely simple and commercially viable compared to other vacuum based expensive methods. In this work, we report for the first time, to the best of our knowledge, a systematic study of electrical, optical and structural properties of sintered SnTe films deposited onto glass substrates.

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2. Experimental details

In the present investigation SnTe material was prepared by taking high purity (99.99%, Sigma Aldrich) tin and tellurium powder in elemental form. The calculated amounts taken in stoichiometric proportion were mixed together at room temperature with the help of Agate mortar and pestle for ten minutes at room temperature to allow Sn and Te to react completely with continuous vibrational shaking to ensure homogeneity of the material. 10% weight of SnCl₄·2H₂O (stannic chloride) was added to SnTe powder as adhesive and an appropriate amount of ethylene glycol as a binder. The paste thus prepared is screen-printed onto glass substrates. The glass slides have been cleaned thoroughly by HCl, embryo powder, soap solution and washed with distilled water. The substrates were dried at 80 °C in oven. Thus prepared samples of SnTe were dried at 120 °C for 4 hours in open atmosphere. The reason of drying the sample at lower temperature was to avoid the cracks in the samples. For good stability of the films it is necessary that stannic chloride and ethylene glycol should be removed in the samples. The thickness of the samples was measured by Xi-100 non contact optical profiler. The prepared sintered films were characterized by X-Ray diffraction study using Bruker AXS D8 Erz Nr 7K P2025 Karlsruhe (Germany) diffractometer employing CuKα radiation (λ = 1.5405 Å) in the range 0.2KC/S at the speed of 20/min. It is important to mention that these films are deposited under similar conditions several times to confirm the reproducibility of the results.

3. Result and discussion

3.1 Electrical Characterization

The electrical properties are greatly dependent on various deposition parameters such as film composition, thickness and substrate temperature. The electrical resistivity and the temperature dependence of resistivity (conductivity) was studied for the films using four probe method. The activation energy has been determined from the slope of the resistivity versus temperature curve using the equation

\[ \rho = \rho_0 \exp (-\Delta E/kT) \]

where \( \rho_0 \) is constant (pre exp. factor), \( \Delta E \) is activation energy for conduction process and K is Boltzman’s constant. Further we may write

\[ \log \rho = \log \rho_0 - \Delta E/kT \]
\[ \log \rho = (- \Delta E/kT)(1000/T) + \log \rho_0 \]

A curve has been plotted between resistivity (\( \rho \)) and 1000/T which is found to be straight line having the slope (\( \Delta E/kT \)) and intercept \( \log \rho_0 \). This indicates that the films are semiconducting in nature and conduction is through thermally activated process. The activation energy of SnTe films comes out to be 0.098 eV.
At room temperature, the resistivity of SnTe semiconducting films was measured by four probe Vander Pauw’s technique [12]. Actually it is the $R_{sh}$ which is measured from this method and resistivity of the samples was determined by the relation

$$\rho = R_{sh} \times t$$

where $t$ is the thickness of the film. The electrical resistivity comes out to be $6 \times 10^2$ (Ω-cm). As the prepared films have nanocrystalline structure and has large number of grain boundaries. So the high value of resistivity of SnTe may be attributed to the smaller grain size and high density of surface imperfections such as grain boundaries, dislocations etc. Carrier concentration is determined by using the relation

$$n = \frac{1}{R_H} e$$

where $e$ is electron charge and $n$ is number of free charge carriers per unit volume. It is found to be $10.9 \times 10^{13}$ cm$^{-3}$. The grain boundary scattering seem to be responsible for the low carrier density. The hall mobility of the charge carriers was calculated by the equation

$$\mu_H = \frac{R_H}{\sigma}$$

The sign of the hall co-efficient suggests that the films are of p-type.

Table 2 comprises the experimental results obtained for various electrical parameters and forbidden band width of SnTe sintered films.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Calculated Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical parameters</td>
<td></td>
</tr>
<tr>
<td>Thickness (t)</td>
<td>132 µm</td>
</tr>
<tr>
<td>Resistivity ($\rho$)</td>
<td>$6 \times 10^2$ Ω-cm</td>
</tr>
<tr>
<td>Hall coefficient ($R_{H}$)</td>
<td>$5.7 \times 10^4$ cm$^3$/coulomb</td>
</tr>
<tr>
<td>Carrier concentration ($n$)</td>
<td>$10.9 \times 10^{13}$ cm$^{-3}$</td>
</tr>
<tr>
<td>Hall mobility ($\mu_{H}$)</td>
<td>95 cm$^2$/V-sec</td>
</tr>
<tr>
<td>Band gap</td>
<td>0.35 eV</td>
</tr>
<tr>
<td>Grain size</td>
<td>28.75 nm</td>
</tr>
</tbody>
</table>
3.2 Structural characterization

X-Ray diffraction patterns provide important information about the nature and structure of the prepared sample. The XRD traces of SnTe sintered films are shown in fig.1. All the peaks appearing in the whole 2θ range of the pattern are identified and corresponding (hkl) planes are indicated. It refers to the complete miscibility of the constituent elements and formation of a single phase. Additionally, ‘d’ spacing values and average grain size from XRD data are useful to study the crystalline quality of the films. The spacing between the lattice planes is calculated using Bragg’s equation [13]

\[ 2d \sin \theta = n\lambda \]

where ‘d’ is the interplaner spacing in the lattice, \( \theta \) gives the direction of propagation of scattered beams and \( \lambda \) is the wavelength of the X-radiation used (\( \lambda = 1.5405 \) Å and \( n = 1 \) here). The ‘d’ values are closer to ASTM data implying a good crystallinity for SnTe films. For cubic crystal of unit size the lattice parameter is related to the miller indices by the equation

\[ a = d / (h^2+k^2+l^2)^{1/2} \]

Table 2: X-ray diffraction data of SnTe sintered films

<table>
<thead>
<tr>
<th>S.No.</th>
<th>2θ(deg)</th>
<th>sin θ</th>
<th>d(Å)</th>
<th>d*(Å)</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28.190</td>
<td>0.243</td>
<td>3.167</td>
<td>3.163</td>
<td>200</td>
</tr>
<tr>
<td>2</td>
<td>40.283</td>
<td>0.344</td>
<td>2.234</td>
<td>2.237</td>
<td>220</td>
</tr>
<tr>
<td>3</td>
<td>49.884</td>
<td>0.421</td>
<td>1.833</td>
<td>1.826</td>
<td>222</td>
</tr>
<tr>
<td>4</td>
<td>58.278</td>
<td>0.486</td>
<td>1.582</td>
<td>1.581</td>
<td>400</td>
</tr>
<tr>
<td>5</td>
<td>65.968</td>
<td>0.544</td>
<td>1.416</td>
<td>1.414</td>
<td>420</td>
</tr>
<tr>
<td>6</td>
<td>73.222</td>
<td>0.596</td>
<td>1.290</td>
<td>1.291</td>
<td>422</td>
</tr>
</tbody>
</table>

The lattice parameter calculated from observed XRD traces is found to be in good agreement with standard ASTM values as shown in table 1. The grain size of the SnTe films comes out to be 28.75 nm. In this way, they are called nanocrystalline or nanostructured due to the fact that it shows a structural coherence limited to just few nm. Also the width of the peaks observed refers to the limited atomic ordering [14].
3.3 Optical characterization

The optical absorption spectrum of the films deposited on glass substrates was recorded in
the wavelength range 800 to 3500 nm using Varian Cary 5000 UV-VIS-NIR spectrophotometer.
Fig 2 shows the $(\alpha h \nu)^2 \ vs \ energy \ (h \nu)$ plot for the films deposited at room temperature. The plot is
linear indicating the direct band to band transition in the films. The energy band gap has been
determined by extrapolating the graph to $\alpha = 0$, which is found to be 0.35 eV. This value is in good
agreement with the value obtained for single crystals [15].

![Energy band gap determination of SnTe sintered films.](image)

4. Conclusions

SnTe material was prepared by mechanical alloying. The technique employed for film
preparation is very simple, commerciably viable and yields reproducible and more consistent
results than the other sophisticated techniques. The XRD confirms the formation of SnTe as well
as its nm range of structural periodicity. The films were semiconducting in nature with the
activation energy 0.098 eV and electrical resistivity $6 \times 10^2 \Omega$-cm. The forbidden band width of the
films comes out to be 0.35 eV here. These studies explore the feasibility of employing the material
in industrial production line of thermoelectric generators and infrared detectors.

References

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Chapter 7.