

Electrical properties of $\text{SnTe}_x\text{Se}_{1-x}$ sintered films

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The solid solutions of $\text{SnTe}_x\text{Se}_{1-x}$ series have been prepared by mechanical alloying method. The sintered films of the material were prepared and their electrical properties were investigated. The resistivity and Hall measurements were performed using Vander-Pauw technique in order to determine Hall-coefficient, carrier concentration and mobility of the samples. The gradual variation is observed in the properties with compositional changes. The average crystallite size determined by using Scherrer formula was found to be 25-50nm.

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1. Introduction

The IV-VI group semiconductors [1] have been the interesting materials for their manifold technological applications. Attention of many researcher has been focused to semiconductors with defect structure lying in the categories of self doping compounds. Metal chalcogenides belonging to this category may include SnSe , SnTe and their compounds $\text{SnTe}_x\text{Se}_{1-x}$. Metal chalcogenides are called p-type semiconductor due to stronger self compensation of p-type conduction. It means that the levels related with foreign atoms introduce additional lattice defects which have compensation acceptor levels. These acceptor level trap loosely bound electrons but do not have any effect on lattice structure and band structure of such compounds. The binary or ternary compounds in the form of thick films are particularly interesting due to the possibility of having a series of materials where the transport properties vary as a function of composition. Thick films are of practical importance as there is a considerable deviation from the bulk behaviour and some times new phenomena are observed in film state. Tin Selenide, Tin Telluride and their solid solutions evolved to be the materials of considerable interest in recent years on account of their utility in optoelectronics [3-6], holographic recording systems [7,8], electronic switching [9,10] and infrared generation and detection systems [11]. Tin Selenide is an efficient solar material for photovoltaic applications with an energy gap of about 1 eV [12-15] and tin telluride with the energy gap of about 0.33 eV [16]. SnTe exhibits very high p-type conductivity as the result of Sn vacancies that gives rise to double ionized acceptors [20]. However in order to obtain variable conduction properties immediate to those of binary systems (SnSe and SnTe), solid solution series of

$\text{SnTe}_x\text{Se}_{1-x}$ with $0 \leq x \leq 1$ have been prepared in form of sintered films and gone through electrical characterization. Very few experimental data is available for the middle members of the series formed with one cation (Sn) and two anions (Se, Te) in the form of series $\text{SnTe}_x\text{Se}_{1-x}$ though extreme members have been studied in detail.

2. Experimental details

The samples are taken in thick film form. The material is prepared by mechanical alloying and the alloys films of $\text{SnTe}_x\text{Se}_{1-x}$ are prepared using the screen printing method. The constituent elements of high purity (99.99%) were taken (Sn, Se and Te) in stoichiometric proportion and mixed properly in agate mortar and pestle for 10 minutes at room temperature to allow Sn, Se and Te to react completely with continuous vibrational shaking to ensure homogeneity of the sample. Thick films of $\text{SnTe}_x\text{Se}_{1-x}$ have been prepared by screen printing method followed by sintering process. In appropriate proportion Stannic Chloride $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ was added as adhesive and ethylene glycol as binder. The paste thus formed was screen printed on glass substrates that 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 thick films were dried at 120°C for 4 hours in open atmosphere. Finally the films were sintered at a temperature of 200°C for 10 minutes. The films of different thickness were prepared.

3. Electrical characterization

The electrical properties of a material have great importance to determine whether the material is congruent with our necessities or not. The resistivity (conductivity), Hall co-efficient, carrier concentration and the mobility of the carriers are the most important electrical properties which are affected by the factors viz. film thickness, substrate temperature, environmental conditions and purity of the material to be deposited, inhomogeneity of the film, structural and compositional variations in the film. The electrical properties of thus prepared samples were investigated. The electrical resistivity of these films was determined at room temperature by Vander Pauw technique [21]. The Hall Effect measurements of the samples were carried out at different magnetic field intensities. The number of free charge carriers (holes) was calculated from R_H data ($n=1/R_H e$) where e is electron charge and n is number of free charge carriers. The Hall mobility of the charge carriers was calculated by $\mu_H = R_H \sigma$ for seven different compositions of $\text{SnTe}_x\text{Se}_{1-x}$ ($0 \leq x \leq 1$). All the measurements were repeated three times to confirm the reproducibility of the results within experimental accuracy. X-ray diffraction analysis of the samples has been performed using Philips PW 1820 diffractometer employing Cu- α radiation.

4. Results and discussion

All the films prepared by any technique are invariably associated with some growth defects or imperfection [16-19] such as lattice defects, twinning, disorders in atomic arrangement, dislocation grain boundaries, foreign atom inclusion etc.

Surface states of a film also play a dominant role in modifying its electrical properties. The plot of resistivity and mobility of the samples against the composition x is shown in Fig.1 and Fig. 2.

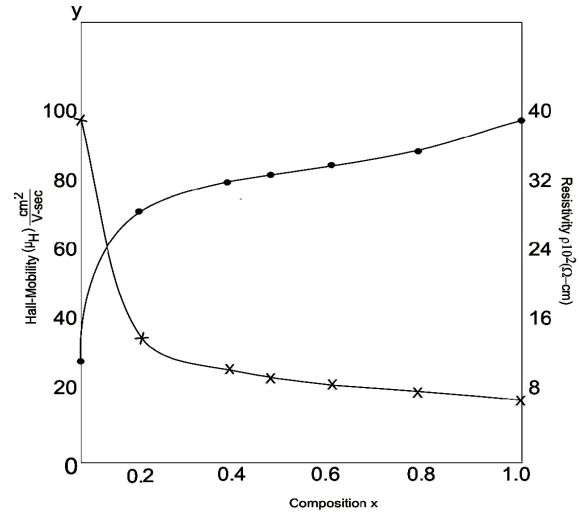


Fig 1. Variation of resistivity and Hall mobility with composition x .

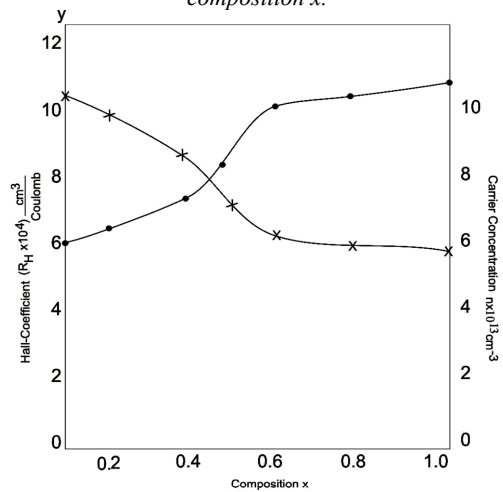


Fig. 2. Variation of Hall effect and carrier concentration with composition x .

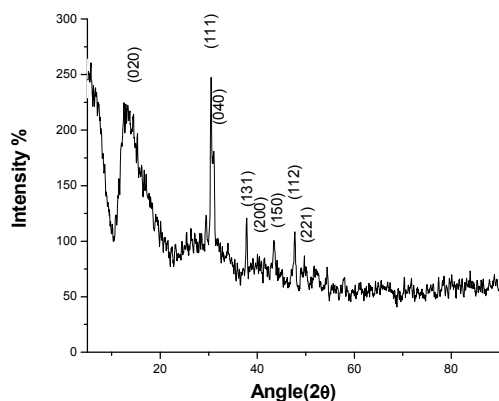
The resistivity of pure SnSe ($x=0$) film is found to be maximum while that of SnTe film ($x=1$) is minimum. The resistivity of the middle samples lies in between the two extreme cases which is justifiable and supports the formation of proposed solid solutions $\text{SnTe}_x\text{Se}_{1-x}$ series. The high resistivity of the samples as compared to earlier reported results [15,16] is due to the difference in preparation method of the samples and can be accounted for the smaller grain size in films and the presence of greater number of defects such as structural disorders, dislocations, surface imperfections, etc. The mobility of the films increased from 26.7 to 95 $\text{cm}^2/\text{volt-sec}$. The carrier concentration was changed from 6×10^{13} to 10.9×10^{13} per cm^3 as x changed from 0 to 1. As the mobility is proportional to conductivity ($\sigma = ne\mu_H$) the mobility variation shows the reverse trend to that of resistivity.

The compositional dependence of Hall co-efficient R_H and carrier concentration is shown in Fig. 2. The sign of the Hall co-efficient indicates that the films are p-type. The curve for Hall co-efficient reveals a gradual decline in R_H values with stoichiometric proportion. These variations

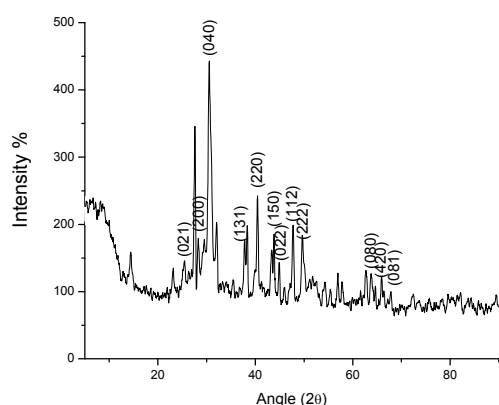
can be attributed to the change in nature of chemical bonding between the cation (Sn) and anion (Te or Se) as the stoichiometry of anion atoms changes in films of the series SnTe_xSe_{1-x}.

The carrier concentration for the samples is found to be maximum for SnTe ($x=1$) and minimum for SnSe ($x=0$). For the intermediate ternary alloys formed with one cation (Sn) and two anions (Se and Te) the carrier density rises gradually. Smaller hole concentrations in these samples are due to enhanced lattice defects created by implantation of certain acceptor levels, connected with foreign atoms which trap the loosely bound electrons [15].

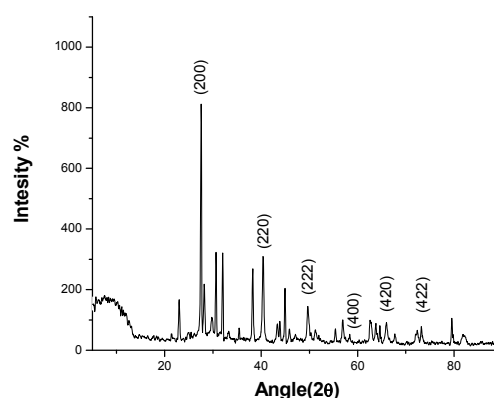
The X-ray Diffractogram of the samples [shown in Fig. 3(a), (b), (c)] confirms the formation of binary and ternary solid solutions. The investigation of XRD for middle samples manifests that the variation in stoichiometry of anion atoms (Se & Te) in SnTe_xSe_{1-x} series changes only the direction of preferred orientation but does not induce any structural phase transition.



(a)



(b)



(c)

Fig. 3. (a) XRD pattern of SnSe; (b) XRD pattern of SnTe_{0.5}Se_{0.5}; (c): XRD pattern of SnTe.

The crystallite size was calculated by Scherrer formula

$$D = \frac{0.94\lambda}{\beta \cos \theta}$$

where, D is the grain size (in Å), β is the Full Width at Half Maximum (FWHM) of the particular peak, θ is the Bragg's angle and λ is the wave-length of X-Ray. Using this relation the average value of the composite size is found to be 25~50 nm for various compositions of solid solutions. The middle compositions of the SnTe_xSe_{1-x} solid solution series show smaller crystallite size than extreme members of the series i.e. SnSe and SnTe. This may be attributed to the Se or Te atoms going to interstitial sites in solid solutions as some peaks appearing in one composition are being suppressed in the other composition and vice-versa.

5. Conclusions

The electrical studies for sintered films of SnTe_xSe_{1-x} series have been performed. The simple technique of mechanical alloying is found to be more successful at binary composition through in solid solution SnSe_{1-x}Te_x the bonding may be incomplete. The results obtained are found to be comparable with the earlier work within experimental limitations. It may be possible to control crystallite size and reduce grain boundary effects by improving the fabrication process.

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