CHAPTER VII

SnTe THIN FILMS PREPARED BY REACTIVE EVAPORATION

7.1. INTRODUCTION

The electrical and optical properties of SnTe have received considerable attention in recent years owing to the narrow band gap (0.33 eV) of this material and its potential use as an IR detector material /1-3/. Crystalline and non-crystalline SnTe films have been grown and their electrical, optical and structural properties have been reported. Several authors have reported the influence of subsidiary bands on the transport properties of SnTe single crystals and epitaxial films /4-13/. The preparation of epitaxial films of SnTe on NaCl, KBr and KCl by different methods and studies of their structural, galvanomagnetic and optical properties have been reported by many workers /14-19/. Ota and Zemel /15/ and Samantary and Chaudhuri /20/ have reported the effect of film thickness, the substrate material and temperature and the evaporation time on the electrical transport properties of SnTe thin films. Goswami and Jog /17/ prepared the epitaxial films on NaCl and mica substrates by resistive heating and have studied the
structural properties by electron diffraction. Zheleva /19/ prepared the epitaxial films on NaCl, PbS and mica substrates by closed-hot-wall technique and has studied their structural properties. The effect of non-stoichiometric excess of tin on the electrical transport properties /21/ and of thermal treatment on the composition and crystal structure /22/ of SnTe films have also been investigated.

SnTe is a IV-VI compound, which has got the NaCl structure. In perfectly stoichiometric and chemically pure form it would be an intrinsic semiconductor. In practice, however, the bulk and thin film form is always deficient in tin. This is due to the low chemical diffusion constant of tin vacancy concentration /23/. As a result, the material is extrinsic with a carrier concentration of two holes per tin vacancy. Consequently, all samples of SnTe behave as heavily doped degenerate p-type semiconductors. Lorenz and Jepsón /24/ have calculated that the energy necessary to create an ionized Sn-vacancy is only about 5K Cal/g-atom. In order to explain why this energy is so small, they proposed that the energy level of Sn-vacancy acceptor lies below the top of the valence band. The model is generalised to state that the metal vacancy acceptor level in a semiconductor will be below the top of the valence band whenever the more metallic component does not exhibit
its highest valence in the compound.

In all the earlier mentioned cases SnTe thin films were prepared from p-type SnTe ingots prepared by fusing stoichiometric proportions of tin and tellurium. Therefore it was thought interesting to investigate the electrical transport properties of SnTe films prepared using the three temperature method.

In the work reported here SnTe thin films were prepared by co-evaporation of the constituent elements to avoid incongruent evaporation from a single source and the consequent lack of stoichiometry. The temperature dependences of the electrical transport properties such as, conductivity $\sigma$, the Hall coefficient $R_H$, and Hall mobility $\mu_H$ of these films were studied in the temperature range 100-450K. The effect of annealing on these properties has also been investigated. These results are interpreted in terms of a model involving two valence bands.

7.2. EXPERIMENTAL DETAILS

As explained in chapter 3, in the three temperature method the components of the binary alloy are evaporated from separate sources with the substrate kept at a given temperature. It has been reported for many materials that a stoichiometric interval exists within a limited range of flux and substrate temperature /25,26/.
It has been found that good stoichiometric films of SnTe are obtained with the following parameters:

- Tin flux: $4.1 \times 10^{14}$ to $2.4 \times 10^{15}$ atoms cm$^{-2}$s$^{-1}$
- Tellurium flux: $7.4 \times 10^{15}$ to $2.2 \times 10^{16}$ atoms cm$^{-2}$s$^{-1}$
- Substrate temperature: $568 - 598$ K.

Tin and tellurium (purity $99.999\%$) were used as evaporants. Tin was evaporated from a helical filament made of molybdenum wire and tellurium from a conical glass crucible with molybdenum wire windings. The coating was performed in a Hind High Vacuum coating unit under a vacuum of the order of $10^{-6}$ torr. The substrates used were optically flat glass slides of dimensions $3$ cm x $1.1$ cm x $0.2$ cm which were cleaned ultrasonically and then subjected to ion bombardment. The substrate temperature was measured using a chromel-alumel thermocouple in contact with the substrate. The flux rate from each source could easily be adjusted by controlling the current through each filament. The tin source was shielded to minimise heating of the substrate by radiation.

When the substrate temperature had stabilized at the required value, the current through the tellurium source was switched on and the tellurium was allowed to melt in the crucible with the shutter placed over the tin
and tellurium sources. The tin source current was then switched on. After adjusting the flux rate from the two sources by varying the source current, the shutter was removed. Tellurium atoms were unable to stick to the substrate independently at the elevated temperature. The tin atoms reaching the substrate reacted with those tellurium atoms present on the substrate and the compound film was deposited. The films obtained in this way were metallic grey in colour and opaque. Highly reproducible films were obtained under these conditions. Films deposited at substrate temperatures below 568K were found to contain tellurium rich regions, and those deposited at temperatures above 598K were found to have a non-uniform thickness.

X-ray diffraction patterns of the film - substrate system were obtained and it was found that the diffracttion lines compared well with the literature data /27/. Fig.7.1 shows the diffraction patterns obtained, using Cu Kα radiation. The corresponding (hkl) planes are indicated. From the x-ray diffraction patterns it could also be found that these films had grains oriented such that (111) planes were parallel to the substrate surface.

X-ray powder patterns of the films were also obtained using a Debye-Scherrer powder camera. Fig.7.2 shows the patterns obtained using Cu Kα radiations.
Fig. 7.1: X-ray diffraction patterns of SnTe films using Cu $K_{\alpha}$ radiation.
Fig. 7.2: X-ray powder patterns obtained using Cu K$_\alpha$ radiation and the corresponding (hkI) planes.
The corresponding (hkl) planes are also indicated.

The film thickness was measured using multiple-beam interferometry. The films prepared for electrical measurements were 4000 - 5000 Å thick. The systems described in chapter 3 were used to measure the conductivity $\sigma$, and the Hall coefficient $R_H$. Satisfactory contacts to bridge shaped samples were made using silver paste. The ohmic nature of the contacts was verified throughout the temperature range by the linearity of the current-voltage (I-V) characteristics. The sample was mounted on a copper block which was the cold finger of a vacuum cryostat containing liquid nitrogen. This had provisions for electrical connections, film heating and temperature measurements. The temperature was measured using a chromel-alumel thermocouple in contact with the substrate. The error in this measurement was only 3K. The conductivity of the film was measured by passing a known current through the film and measuring the voltage across the film. A stabilized magnetic field was applied across the sample and the Hall voltage developed was measured using a digital multimeter (Hewlett-Packard Model 3465A). The length to width of the samples used for the Hall measurements was greater than four so that the influence of film geometry was negligible. The conductivity
and Hall coefficient measurements were repeated many times and were found to be reproducible.

7.3. RESULTS AND DISCUSSIONS

The electrical measurements were carried out on freshly prepared films and on films which had been annealed for six hours after deposition without breaking the vacuum. The electrical characteristics such as Hall coefficient, Hall mobility and conductivity were calculated as in the case of PbS films, explained in chapter 5. The properties of the freshly prepared films agreed well with those reported by earlier workers /14, 21/.

The dependence of the Hall coefficient on temperature (log $R_H$ versus $10^3/T$) for annealed and unannealed films is shown in fig.7.3. It can be seen that for any particular temperature $R_H$ increases with annealing. This is because the tin vacancies, which are the predominant defects in SnTe, are annealed out and therefore the number of carriers resulting from the deviation from stoichiometry is reduced /23/. It should also be noted that $R_H$ remains constant at low temperatures for both annealed and unannealed films. This is characteristic of an extrinsic degenerate semiconductor. It can also be seen that $R_H$ increases with temperature at higher temperatures as has
Fig. 7.3: Variation in the Hall coefficient $R_H$ with the temperature ($\log R_H$ vs. $10^3/T$): $\circ$, unannealed; $\bullet$, annealed.
been reported for epitaxial films /14,21/. This could be explained as follows. A set of subsidiary maxima in the valence band plays an important role in the conduction process in SnTe samples /28/. The main and subsidiary maxima of the valence band are identified as light hole \( L \) valence band and heavy hole \( \Sigma \) valence band. It had become traditional to refer to the subsidiary maxima as a second valence band /29,30/, but the band calculations have made it quite clear that both sets of maxima belong to the same valence band. In SnTe samples above 150K significant numbers of holes begin to be thermally generated in the \( \Sigma \) valence band region /23,29,30,31/. At lower temperature, holes appear near \( \Sigma \) valence band only when the total density of holes exceeds \( 2 \times 10^{20} \text{ cm}^{-3} /30,32,6/ \). At higher temperatures Hall coefficient increased with temperatures due to the onset of hole transfer from light hole \( L \) valence band to the heavy hole \( \Sigma \) valence band.

The energy separation \( \Delta E_g \) between the light and heavy hole valence bands was found out by studying the variation of Hall coefficient in the high temperature region.

The change in Hall coefficient relative to its low temperature limit can be expressed as /33/
\[
\frac{R_T - R_L}{R_L} = (1 - \frac{1}{b})^2 \frac{m^*_2}{m^*_1}^{3/2} \exp \frac{-\Delta E_g}{kT}
\]

where \( R_T \) is the Hall coefficient at temperature \( T \), \( R_L \) is the low temperature value of Hall coefficient which can be obtained by extrapolating the low temperature values from the regions where \( R_H \) remains constant (Fig. 7.3), \( b \) is the ratio of the mobility of light holes to that of the heavy holes, \( m^*_1 \) and \( m^*_2 \) are the effective masses of light and heavy holes and \( k \) is the Boltzmann's constant.

The dependence of \( \frac{R_T - R_L}{R_L} \) on inverse temperature is shown in fig. 7.4. The values of \( \Delta E_g \) for unannealed and annealed films were calculated from the slopes of the corresponding plots. The calculated values from the graph are, \( \Delta E_g = 0.147 \text{ eV} \) for unannealed film and \( \Delta E_g = 0.133 \text{ eV} \) for annealed film and these are in good agreement with the reported values /10,11/. If we consider the temperature variations of \( \frac{m^*_2}{m^*_1} \) and \( b \), the values obtained for \( \Delta E_g \) will be slightly different.

The dependence of the d.c. conductivity on temperature (\( \log \sigma \) versus \( 10^3/T \)) is shown in fig. 7.5. As the temperature is increased and conductivity decreases because the defect scattering is higher in these films owing to the high carrier concentrations. At any particular temperature the conductivity is higher in the
Fig. 7.4: Variation in $\frac{R_T - R_L}{R_L}$ with temperature $(\log \frac{R_T}{R_L}$ vs. $10^3/T)$: ○, unannealed; ●, annealed.
Fig. 7.5: Variation in the d.c. conductivity $\sigma$ with temperature ($\log \sigma$ vs. $10^3/T$): 0, unannealed; o, annealed.
unannealed samples because of the comparatively high carrier concentrations in the unannealed films. In the low temperature regions the conductivity is found to be a weak function of temperature in both samples. At higher temperatures the concentration of light holes will be decreased owing to light hole conduction to the heavy hole valence band, and the effect of these heavy holes, which have lower mobility, will be increased. This is the reason for the abrupt change in the variation in conductivity at about 200K.

The variation in the mobility with temperature ($\mu_H$ versus $T$) is shown in fig. 7.6. In both cases (unannealed and annealed) the mobility decreases with increasing temperature, and at a given temperature $\mu_H$ is greater in the annealed sample than in the unannealed sample. The boundary regions between crystallites in polycrystalline films should exert a pronounced effect on the various properties of the thin films. The boundary region should be effective in scattering the current carriers and this should lead to a reduction in the carrier mobility. Since the substrate temperature and the temperature at which the films are annealed are the same in the films studied, the effect of carrier scattering at the grain boundaries and the consequent reduction in the mobility will be the same. In other words the relative
Fig. 7.6: Variation in the Hall mobility $\mu_H$ with temperature ($\mu_H$ vs. $T$): O, unannealed; *, annealed.
effect of the boundary scattering on mobility is not affected by the annealing process. No change in the grain size of the specimens is observed after annealing. Fig. 7.7 shows photomicrographs of the surface of the unannealed and annealed films. However, the contribution of defect scattering to the reduction in mobility is higher in unannealed films with high carrier concentrations. The slow rate of decrease in carrier mobility at high temperatures observed in both the annealed and the unannealed films is due to the onset of heavy hole conduction.

7.4. CONCLUSIONS

Using the co-evaporation technique, polycrystalline films of SnTe have been prepared for the first time. The electrical transport properties (Hall coefficient, d.c. conductivity and Hall mobility) of unannealed and annealed films are measured in the temperature range 100 - 450K and these agree well with the values reported by earlier authors. The carrier concentration and conductivity decreases after annealing whereas the Hall mobility increases. Energy separation $\Delta E_g$ between light and heavy-hole valance bands have been found out in case of unannealed and annealed films and are in good agreement with the earlier reported data.
Fig. 7.7: Optical micrographs of SnTe thin films; 
(a) unannealed; (b) annealed.
(Magnification, 3800X)
REFERENCES


