

SUMMARY

Group V-VI semiconducting compounds have attracted attention of many research workers for the last several years because of their useful opto electronic and thermoelectric characteristics. Most of the work on these materials reported in literature is focussed on transport properties such as electrical resistivity, Hall effect, thermoelectric power etc. Little information is available in crystal growth, microhardness and defect structure of these compounds. The V-VI binary compounds and their psuedobinary solid solutions are highly anisotropic and crystallize into homologous layered structures parallel to c-axis. Among these, Bi_2Te_3 is the most potential material for thermoelectric devices such as thermoelectric generator, Peltier cooler and I.R Sensors with best figure of merit. There have been various studies on bulk and thin film characterization of Bi_2Te_3 including transport properties. Adding of indium to Bi_2Te_3 has been observed to change its properties considerably. It was found that as the concentration of indium increases the conductivity type changes from p-type to n-type. The work carried out by the author includes crystal growth, dislocation etching and hardness of the crystal of $\text{Bi}_{2-x}\text{In}_x\text{Te}_3$ as well as optical band gap and electrical resistivity. Thermoelectric power measurement, Hall measurement, optical

bandgap and resistivity measurements on crystals and thin films of $\text{Bi}_{2-x}\text{In}_x\text{Te}_3$ ($x = 0.1$ to 0.5) were also carried out.

The thesis is presented in two parts (part A and part B). Part A gives general introduction to the subject under study. A brief survey of earlier work reported which provides the basic background for present work is included. Chapter 1 discusses various methods of crystal growth in general and of crystal growth from melt in particular. General aspects of chemical etching of a crystal surface and its use as a tool to reveal line perfections, i.e. dislocation, in crystals are briefly described. Hardness and indentation creep of crystals are the main focus of the present study. Chapter 2 gives a qualitative survey of various techniques and empirical theories involved in this field. Chapter 3 deals with a brief review of studies carried out by previous workers, such as electrical and thermal transport properties, optical properties and energy bandgap. Chapter 4 gives the details of the experimental techniques used during the course of the present work. The techniques include crystal growth, chemical etching, optical microscopy, hardness indentation, electrical resistivity, thermoelectric power measurement and thin film preparation. Chapter 5 gives general information on Bi_2Te_3 and $\text{Bi}_{2-x}\text{In}_x\text{Te}_3$ ($x = 0.1$ to 0.5) crystals with regard to the structure and various electrophysical properties available in literature.

Part B of the thesis consists of four chapters. Chapter-6 includes results of growth and dislocation etching of $\text{Bi}_{2-x}\text{In}_x\text{Te}_3$ ($x = 0.1$ to 0.5) crystals. The crystals

were grown by the Bridgman Stockbarger method and zone melting method. Fairly large, good quality crystals of $\text{In}_{0.1}\text{Bi}_{1.9}\text{Te}_3$, $\text{In}_{0.2}\text{Bi}_{1.8}\text{Te}_3$ and $\text{In}_{0.5}\text{Bi}_{1.5}\text{Te}_3$ can be obtained by zone melting method at the rate of 0.4 cm/hr. and temperature gradient around 70°C/cm. The crystal orientation at any In concentration was observed to depend on the growth velocity. With increasing velocity the cleavage plane tends to orient parallel to the ingot axis. The layer mechanism of growth is operative at low growth speed in the zone melting method. As the growth velocity increases, the crystal perfection decreases. As the number of zone passes increases the crystal quality improves, i.e., dislocation density decreases. A new dislocation etchant was developed, viz., 3part saturated solution of I_2 in methanol + 0.3 part HCl (70%) + 0.3 part HNO_3 (70%), which is capable of revealing dislocations intersecting and lying in the cleavage plane. It also reveals dislocation motion.

Chapter-7 deals with the hardness study of $\text{Bi}_{2-x}\text{In}_x\text{Te}_3$ ($x = 0.1$ to 0.5) crystals. The variation of hardness with applied load has been studied in detail. As the concentration of indium increases, the load independent hardness increases. The work hardening capacity of $\text{In}_{0.5}\text{Bi}_{1.5}\text{Te}_3$ crystals has been observed to be the highest among the three crystals. The surface anisotropic variation of hardness is consistent with the six fold axis of symmetry in the crystals. The creep study indicates that as indium concentration increases the temperature softening parameter increases and also creep activation energy increases.

Chapter-8 deals with the electrical characterization of $\text{In}_x\text{Bi}_{2-x}\text{Te}_3$ ($x = 0.1$ to 0.5) crystals. The resistivity activation energy values are found to be 0.015, 0.0198 and 0.028 eV for $\text{In}_{0.1}\text{Bi}_{1.9}\text{Te}_3$, $\text{In}_{0.2}\text{Bi}_{1.8}\text{Te}_3$ and $\text{In}_{0.5}\text{Bi}_{1.5}\text{Te}_3$ crystals respectively. The thermoelectric power in all the crystals was found to increase with temperature. The measurements indicate $\text{In}_{0.1}\text{Bi}_{1.9}\text{Te}_3$ crystal to be p-type with carrier concentration $4.78 \times 10^{19} \text{ cm}^{-3}$ while $\text{In}_{0.2}\text{Bi}_{1.8}\text{Te}_3$ and $\text{In}_{0.5}\text{Bi}_{1.5}\text{Te}_3$ crystals are of n-type with carrier concentrations $3.23 \times 10^{19} \text{ cm}^{-3}$ and $7.57 \times 10^{18} \text{ cm}^{-3}$, respectively. The carrier concentration in these crystals decreases with indium concentration. The optical band gap is found to decrease from 0.14 eV to 0.1 eV with indium concentration varying from 0.1 to 0.5.

Chapter-9 deals with the growth of thin films of $\text{Bi}_{2-x}\text{In}_x\text{Te}_3$ ($x = 0.1$ to 0.5). The film thickness dependence of the band gap of $\text{In}_x\text{Bi}_{2-x}\text{Te}_3$ with $x = 0.1$ to 0.5 indicates the optical transitions to be governed by quantum size effect within the thickness range studied. The variation of electrical resistivity, carrier mobility and carrier concentration of the $\text{In}_{0.1}\text{Bi}_{1.9}\text{Te}_3$ and $\text{In}_{0.5}\text{Bi}_{1.5}\text{Te}_3$ films with different thickness can be explained in terms of size effect. The metal semiconductor contact study reveals that Ag and Sn metals provide good ohmic contact, while Al provides non-ohmic contact to $\text{In}_{0.1}\text{Bi}_{1.9}\text{Te}_3$ films forming a Schottky barrier cell.