AN EXPERIMENTAL STUDY OF InBi:Te CRYSTALS

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Introduction:

Semiconductors always offer wide scope of research due to its their various applications. It is possible to manipulate their properties and hence functionality in devices. There is good amount of work done to develop materials for Infrared (IR) detectors using narrow gap semiconductors. Over the last few decades, MCT (mercury cadmium telluride) system has been important for IR detector devices. However, this system bears a drawback of thermal and lattice instabilities due to the weak Hg-Te bond. In this respect low band gap III-IV compound materials can prove to be more advantageous for IR technology.

In recent years, growth of III-IV group pseudo binary crystals has increasingly became become a subject of significant research in view of demands of IR technology [1-4]. As a detector material InBi/InSb system is nonhazardous and suitable for narrow band gap applications as in IR optical devices. It has been observed that the materials studied so far in InBi:Te system are all Te rich quasi binary or ternary alloys. There are very few reports available on Indium rich alloys that too not related to the present investigation [4]. It is matter of great interest to investigate various narrow gap materials, such as, bismuth telluride based alloys including n-type Bi₂(Te,Se)₃ and p-type (Bi, Sb)₂Te₃. These materials are not only good thermoelectric devices that are available for near room temperature applications, but also useful for improving their figure of merit (ZT) values through structural and compositional modifications [5-6].

Among the pseudo binaries of interest in the present case, $InBi_{1-x}Te_x$ has been the least studied in this respect. This report is the first of its kind on InBi with Te as dopant. We have grown single crystals of $InBi_{1-x}Te_x$ (x= 0, 0.05, 0.10 & 0.15). The XRD, EDAX, FESEM (Field Effect Scanning Electron Microscopy), thermoelectric power and Hall measurement, Fourier transform infrared (FTIR) spectroscopy techniques have been employed to characterize various parameters of these grown crystals.

Motivation:

Recently there has been extensive interest in infrared detectors operating in the $8-12\mu m$ wavelength region where minimum atmospheric absorption is present. The atmosphere has clear transmission

windows in the MWIR and LWIR bands, making it very attractive for terrestrial applications. Covering the near infrared (IR) region becomes important for military as well as for industrial control, medical diagnostics and other civilian needs [1-5]. Usually the more developed III-V materials are preferred to group II-VI low band gap semiconductors and play major role in development of detector technology. This is because group III-V semiconductors exhibit very useful and tunable physical properties. Study of Bi based semiconductors has been very much carried out by researchers. InBi, among the III-V semiconductors, has sufficiently narrow band gap suitable for the above mentioned application. It crystallizes into the zinc-blende structure and has melting point ≈ 110 °C. It has no band gap or very nearly zero band gap. By doping Te in InBi, the band gap can be increased significantly [6-8]. This would make single crystals of InBi_{1-x}Te_x (x = 0, 0.05, 0.10 & 0.15) useful in various detectors. Hence the band gap of single crystals of InBi_{1-x}Te_x (x=0, 0.05, 0.10 & 0.15) was taken up in this study.

Objectives and Scope of the Work:

Since it is important to grow the said doped crystals with fairly large size, purity and perfection, it was intended to grow crystals of $InSb_{1-x}Bi_x$ using a suitable technique. The characterizations of the crystals and of the films obtained there from were taken up in order to investigate effect of doping on various characteristics.

The work reported in the present thesis thus includes crystal growth, X-ray diffraction (XRD), energy dispersive analysis by X-rays (EDAX), FESEM, thermoelectric power, optical band gap, Hall Effect and the Vickers indentation for the evaluation of microhardness hardness of the crystals. The materials included in the study are InBi_{1-x}Te with varied x. The thesis is presented in two parts.

Brief Information of Proposed Chapters of Thesis:

Part-1 of the thesis consists of two chapters. **Chapter 1** gives a general introduction to the basic background of the present work and importance of the optoelectric materials, thermoelectric materials and their applications. It also includes reports on optical, electronic and mechanical properties of these materials. Thus based on literature survey, this chapter describes the present status of research work going on in the field of crystal growth and characterization of materials.

This chapter also explains the objectives of present research problem.

Chapter 2 deals with the experimental techniques used in the present work. The techniques include the crystal growth, XRD, EDAX, FESEM, FTIR, thermoelectric power measurement, optical microscopy, hardness indentation, optical band gap and Hall Effect measurements.

Part 2 of the thesis consists of three chapters. **Chapter 3** deals with the results for growth of $InBi_{1-x}Te_x$ crystals. Various methods of crystal growth in general and of crystal growth from melt in particular have been discussed. Fairly large good quality crystals of $InBi_{1-x}Te_x$ (x = 0, 0.05, 0.10 & 0.15) were obtained with the zone melting method at growth rate of 3 mm/hr and temperature gradient around 45°C/cm. In this growth technique, the growth velocity was varied also and it was found that increase in growth velocity decreases the crystal perfection. Hence the growth velocity was optimized to yield good quality crystals useful for characterizations. EDAX analysis shows that the crystals obtained were stoichiometric and homogenous. The X-ray diffractrometry indicates substitution of Te by Bi in the InBi structure. Using FESEM Color mapping of crystals has been studied.

Chapter 4 discusses the results of optical band gap of crystals of $InBi_{1-x}Te_x$ (x = 0.05, 0.10 & 0.15). This chapter includes study of optical properties of $InBi_{1-x}Te_x$ (x = 0.05, 0.10 & 0.15) crystals using absorption spectra obtained using FTIR spectrometer. The value of optical band gap is calculated from the plots of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ for all crystals. Thermo electric power has been measured and described in this chapter. The thermoelectric power and the band gap of crystals were evaluated. The band gap obtained of $InBi_{1-x}Te_x$ (x = 0.05, 0.10 & 0.15) crystals was about 0.2 eV (direct band gap). There are no observable indirect transitions in the crystals

Chapter 5 deals with hardness studies on $InBi_{1-x}Te_x$ (x = 0, 0.05, 0.10 & 0.15) crystals. The variation of hardness with applied load has been studied in detail. Particularly, the observed complex low load dependence of hardness has been explored. The results indicate that the hardness peaks obtained in the low load range may be explained in terms deformation induced coherent regions. The hardness values of $InBi_{1-x}Te_x$ (x = 0, 0.05, 0.10 & 0.15) single crystals have been obtained on average about 115 MPa. Micro hardness is a load dependent quantity and the variation is quite

prominent in the low load range, while only for sufficient high applied loads it becomes virtually independent of load. The peaks observed in H_v versus load (P) plots may be explained in terms of deformation induced coherent regions. The indentor penetration through surface region work hardens the crystal and due to work hardening, as the penetration progresses with increasing load, the crystal hardness increases. Only in the interior of the crystal the work hardening saturation prevents hardness from increasing and saturates the hardness to true bulk value. The Mayer index is not truly constant but may be different in various load ranges. There is applied load dependence of hardness observed but the bulk micro hardness is found to be quite independent of the applied load. In the cold-worked crystals, the load independent hardness value significantly increases in the case of the as-cleaved samples. In the annealed sample, the load independent hardness value is less than that of the as-cleaved sample. The annealing treatment very significantly improves perfection of all the crystals.

Future Scope of work:

Materials such as InBi and its alloys are unique and can be used for cooling and energy generation applications. Because of their high Seebeck coefficient, low electrical resistivity and relatively low thermal conductivity, tellurium alloys (p-type Bi₂Te₃ and n-type Sb₂Te₃) are widely used in the thermoelectric devices. As semiconductor technology advances, radiation is becoming increasingly important in improving crystal properties. In ion beam treatment, microstructural changes in crystals may take place and take place irreversibly, which in turn may change their chemical, optical, mechanical and electrical properties. It can be used to change, in a controlled way, the physical properties of thin films or to modify the near-surface characteristics of a bulk crystal. The ion beam irradiation effects on microstructure and resulting property modification may be explored for suitability in applications. So ion beam treatment can be used on these crystals to modify their properties.

Further, photoconductivity and electrical properties of thin film, mechanical creep and effect of high temperature quenching on micro hardness of the crystals can also be studied to supplement study of other properties and their modifications.

References:

- U. Roy, D. Glassco, Characterization of InBi single crystal by etching and indentation, J of Crystal Growth, 16, 227-234 (1972). https:// doi:10.1016/0022-0248(72)90207-2
- [2] V. P. Bhatt, C. F. Desai, Temperature dependence of Vickers microhardness and creep of InBi single crystals. Bull Mater Sci., 4, 23-28 (1982). https://doi: 10.1007/BF02744461
- [3] H. U. Walter, Growth of InBi Single crystals, J. of Crystal Growth, 19, 351-355 (1973).
- [4] D. Shah, G. Pandya, S. Vyas, M. Jani, B. Jariwala, Single Crystal growth of InBi_{1-x}Se_x by syringe pulling method, J Crystal Growth, **312**, 1085-1089 (2010).
 https://doi:10.1016/j.jcrysgro.2009.12.052
- [5] C. J. Ajayakumar, A. G. Kunjomana, Influence of Te doping on the dielectric and optical properties of InBi crystals grown by directional freezing, International Journal of Minerals, Metallurgy and Materials 21,503-509 (2014). https://doi:10.1007/s12613-014-0935-4
- [6] C. J. Ajayakumar, A. G. Kunjomana, Directional solidification and characterization of InBi_{1-x}Sb_x Crystals, J Mater Sci: Mater Electron, 27, 7467-7477 (2016). https://doi:10.1007/s10854-016-4724-x
- [7] S. Jin, M-S Kim, S. Kanayama, H. Nishikawa, Microstructure and mechanical properties of indium-bismuth alloys for low melting –temperature solder, J Materials Science, 29, 16460-16468 (2018). https://doi: 10.1007/s10854-018-9738-0
- [8] N. Nanda, P. H. Soni, Growth and characterization of $InB_{i0.95}T_{e0.05}$ and $InB_{i0.90}T_{e0.10}$ crystals, Optical Materials, **136**, 113430, 1-7 (2023). https://doi.org/10.1016/j.optmat.2023.113430