AN EXPERIMENTAL STUDY OF $InSb_{1-X}Bi_X$ SINGLE CRYSTALS AND THIN FILMS

Synopsis of the Thesis to be Submitted

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Introduction:

Though intensive research is still going on on the primitive elemental semiconductors Ge and Si, at present much more attention is being paid to compound semiconductors, viz., binary, ternary and quaternary ones. Among the binary compounds, the group II-IV, IV-VI, III-V and V_2-VI_3, semiconducting compounds have been receiving considerable attention due to their important photoconducting, photovoltaic, electrooptic and general electronic properties. Their pseudobinary and ternary compounds have also found their significance. For the study of basic semiconducting properties, it is of primary importance that these properties be measured on bulk single crystals. The single crystals themselves are also most frequently required directly or indirectly for device fabrication. The performance of the devices principly depends on the bulk crystalline characteristics. The important characteristics are purity, perfection and homogeneity of the crystal. Because of this, the field of crystal growth carries no less significance than the crystals themselves. In most of the applications the semiconductors are used in the form of single crystals or thin films or both at a time. These materials have been subject of study by quite a number of workers. Most of these studies are concerned with thin films and their opto-electronic characterization.

Motivations:

Recently there has been extensive interest in the infrared detectors operating in the 8-12μm 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 prefrred 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 attunable physical properties. Study of Sb based semiconductors has been very much carried out by researchers. InSb, among the III-V semiconductors, has sufficiently narrow band gap suitable for the said application. It crystallizes into the zinc-blende structure. It has a band gap 0.18 eV and its melting point is ≈ 527 °C. By doping Bi in InSb the bandgap can be reduced by fair margin [6-8]. This would make single crystals of $InSb_{1-x}Bi_x$ useful in various detectors. Hence the band gap of single crystal $InSb_{1-x}Bi_x$ was taken up in this study.

Objectives and Scope of the Work:

Since it is imporatnt to grow the said doped crystals with fairly large size, purity and perfection, it was intended to 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 effects of doping on various characterisctics.

The work reported in the present thesis thus includes crystal growth, thermoelectric power, optical band gap and hardness measurements on the crystals followed by optical band gap and I-V characterisations of their thin films. The materials included in the study are $InSb1_{-x}Bi_x$ 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 thermoelectric materials and their applications. A brief survey of earlier work reported on growth and micro

hardness of the crystals (InSb in particular) is given. It also includes reports on optical and electronic properties of these materials.

Chapter 2 deals with the experimental techniques used in the present work. The techniques include the crystal growth, thin film preparation, thermoelectric power, optical microscopy, hardness indentation, optical band gap and I-V characteristics measurements.

Part 2 of the thesis consists of three chapters. Chapter 3 deals with the results of growth of $InSb_{1-x}Bi_x$ single crystals. The crystals were grown using Bridgman-Stockbarger method. Various methods of crystal growth in general and of crystal growth from melt in particular have been discussed. Fairly large good quality crystals of $InSb1_{-x}Bi_x$ (x=0.01,) were obtained with the Bridgman-Stockbarger technique at the ampoule lowering rate of 3.5mm/hr and temperature gradient around 45˚C/cm. The $InSb_{1-x}Bi_x$ In the growth technique, the growth velocity was varied 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 crystals obtained were stoichiometric and homogenous. The X-ray diffractrometry study indicates the substitution of Bi at the antimony sites in InSb. The band gap obtained of $InSb_{1-x}Bi_x$ crystals are about 0.16 eV (all direct). There are no observable indirect transitions in the crystals.

Chapter 4 deals with hardness studies on $InSb_{1-x}Bi_x$ 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 $InSb1_{-x}Bi_x$ single crystals have been obtained about 4360 MPa. Microhardness is a load dependent quantity and the variation is quite prominent in the low load ranges and 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 at 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 different load ranges.

Chapter 5 discusses the results on optical band gap of thin films of $InSb_{1-x}Bi_x$. These also include the effect of film thickness on optical band gap. The results are discussed invoking the size effect operative in the thickness range used. The band gap of $InSb_{1-x}Bi_x$ thin films are on an average 0.143 eV (direct), respectively, for film thickness around 1500 Å. At smaller thickness the band gap is larger than the bulk values. The film thickness dependence of the band gap of $InSb_{1-x}Bi_x$ indicate the optical transition to be governed by quantum size effect within the thickness range studied.

Future Scope of work

Indium Antimonide and its alloys are unique materials. They are excellent thermoelectric material, and are as important to the thermoelectric industry – for cooling and energy generation applications – as silicon is important to the electronic industry. Indium Antimonide may increase significantly the speed of microchips and be the basis for the next generation technology known as "Spintronics". Spintronics is a new, very promising (although still in its infancy) technology in which the intrinsic spin of electrons, rather than the value of a voltage like in today's electronics, is used to store and transport information to be interpreted as either a "1" or a "0". The materials most apt to use in the field of Spintronics are what experts call topological insulators, something that scientists have been searching for years and have now finally found in bismuth telluride. Topological

insulators, something that scientists have been searching for years and have now finally found in bismuth telluride. Topological insulators have the property of opposing no resistance at all to an electrical flow next to their surface, thus allowing for minimal heat dissipation. Integration of efficient solid state thermoelectric micro devices with microelectronics is desirable for both local cooling and thermoelectric micro generation. Tellurium alloys (p-type Bi_2Te_3 and n-type Sb_2Te_3) are well-established room-temperature thermoelectric materials that are widely used in the thermoelectric industry due to their high Seebeck coefficient, low electrical resistivity and relatively low thermal conductivity.

Thin-film planar technology can scale down conventional bulk thermoelectric devices to the micron size range or even to nanothin film. Thin-film technology allows for an enlarged choice of the type of substrate, for the possibility of patterning the devices to micro or sub-micro dimensions and for easy integration with standard Si technology.

Application of radiation in semiconductor technology is of great importance in achieving some desired improvement in crystal properties. Ion beam treatment provides a unique way to modify the chemical, structural, optical, mechanical and electrical properties of crystal by causing irreversible changes in their macromolecular structure. 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 affects the crystal structure by cross-linking as well as by degradation. So ion beam treatment can be used for these crystals to modify their properties.

Further, photoconductivity and electrical properties of thin film, chemical etching, creep and quench micro hardness of crystal can be studied.

References:

1. M. Razeghia, Eur. Phys. J. Appl. Phys. **23**, pp. 149-205 (2003).

2. D. A. Miller, S. D. Smith, A. Johnston, App. Phy. Lett. **35**, 658 (1976).

3. S. G. Pandya, M. Kordesch, Nano Res. Lett. **10**, 258 (2015).

4. P. Norton, Opto-electron. Rev. **10** (3), 159-174 (2002).

5. Yuxin Song, Yi Gu, Jun Shao, Shumin Wang, WangSpringer Series in Materials Science **186**, 143 (2013).

6. S. Premila Mohan, P. MoorthyBabu, P. Santhanaraghavan, Ramasamy, Mater. Chem. Phys. **66**, pp. 17-21 (2000).

7. J. J. Lee, J. D. Kim, M. Razeghi, App. Phy. Lett. **70**, 3266 (1997).

8. D. S. Maske, M. Joshi, D. B. Gadkari, Int. J. Sci. and Res. Publ. **3** (2), 14126 (2013).

9. P. Mohan, S. M. Babu, P. Santhanaraghavan, P. Ramasamy, J. Mater. Sci. letters **20**, pp. 241–244 (2001).

10. M. K. Rajpalke, W. M. Linhart, K. M. Yu, M. Birkett, J. Alaria, J. J. Bomphrey, S. Sallis, L. F. J. Piper, T. S.Jones, M. J. Ashwins, T. D. Veal, Appl. Phys. Lett. **105**, 212101 (2014).

11. P. H. Soni, S. R. Bhavsar, G. R. Pandya and C. F. Desai, Indian J. of Pure and Applied Physics, **46** (11), pp. 806-808 (2008).

12. V. Damodardas, D. Karunakaran, J. Appl. Phys. **54**, 5252 (1983).

13. K. L. Chopra, *Thin Film Phenomena*, McGraw Hill, New York (1969).

14. M. Singh, K. C. Bhahada, Y. K. Vijay, Indian J. Pure Appl. Phys. **43**, 129 (2005).

Proposed Plan of Chapters in Thesis

PART-I

1. **Introduction**
2. **Experimental Techniques**

PART-II

3. **Crystal Growth**
4. **Microhardness**
5. **Thin film**

Future Scope of work

List of Publications Based on the Research Work:

1. "Optical band-gap of $InSb_{0.97}Bi_{0.03}$ thin films"
   Ketan Chaudhari, P. H. Soni, A. Mahadik, Vacuum, 154, pp. 49-51 (2018).
2. "Band gap variation in $InSb_{1-x}Bi_x$ (x=0, 0.04, 0.05) thin films"
   Ketan Chaudhari, P. H. Soni, A. Mahadik, AIP Conf. Proc. 2220, 090019 (2020)