Bull. Mater. Sci., Vol. 22, No 1, February 1999, pp. 15–16. © Indian Academy of Sciences.

Effects of anisotropy and annealing on microhardness of $In_xBi_{2-x}Te_3$ ($x = 0{\cdot}1$ to $0{\cdot}5$) single crystals

G R PANDYA, S R BHAVSAR* and P H SONI
Department of Physics, Faculty of Science, The MS University of Baroda, Vadodara 390 002, India

MS received 15 October 1998

Abstract. The crystals of $In_xBi_{2-x}Te_3$ ($x = 0{\cdot}1$ to $0{\cdot}5$) have been grown by zone-melting method. In order to study anisotropy exhibited by the (0001) plane of the crystals, the directional hardness was determined by producing indentations at various azimuthal orientations of the indentor with respect to the surface over a range 0–180°. The crystal was rotated about the indentor axis in steps of 15° while keeping applied load and loading time constant at 50 g and 20 sec, respectively. For annealing study, the sample was kept at a temperature of 375°C. It was observed that softening of crystal takes place and the hardness decreases to a considerable extent.

Keywords. Anisotropy; annealing; hardness.

1. Introduction

The V–VI group compounds are low band gap semiconductors and known to find applications ranging from photoconductive targets in TV cameras to IR detectors (Arivuoli *et al* 1988). Among these, Bi_2Te_3 is the most potential material for thermo-electric devices (Jansa *et al* 1992). It crystallizes into hexagonal structure. Its melting point is about 573°C and has a direct band gap of about 0·16 eV. There has been an ample study reported on crystal growth and polycrystalline thin films of both pure and indium doped Bi_2Te_3 apart from the semiconducting, optoelectronic and thermoelectric properties (Drabble 1963; Sagar and Faust 1967; Testradi and Burstein 1972; Há *et al* 1994). It has been shown that on exceeding a certain limiting concentration of indium in Bi_2Te_3 the conductivity changes from *p*-type to *n*-type, for $x = 0$–$0{\cdot}32$ (Jansa *et al* 1992). However, there are very few reports on microhardness of single crystals of Bi_2Te_3. This is particularly so in the case of indium doped crystals. Microhardness is a general macroprobe for assessing the bond strength, in addition to being a measure of the bulk strength. In this work the Vickers microhardness of $In_xBi_{2-x}Te_3$ ($x = 0{\cdot}1$–$0{\cdot}5$) single crystals as a function of applied load, temperature and orientation on the cleavage surfaces have been reported.

2. Experimental

The single crystals were obtained from stoichiometric mixtures of the respective elements of 5 N purity, using zone-melting method. The vacuum pressure used to seal the quartz ampoules containing the charge was of the order of 10^{-4} Pa and the growth velocity and the furnace gradient were kept at 3 5 mm/h and 45°/cm, respectively.

The specimens were in the form of 2–3 mm thick (0001) cleavage slices obtained at ice temperature to minimize deformation. A Vickers projection microscope with diamond pyramidal indentor was used to produce indentations on the (0001) plane and later on measure the same. The indentation diagonals were measured to an accuracy of 0·125 mm.

In order to study anisotropy exhibited by (0001) plane of the crystals, the directional hardness was determined by producing indentation at various azimuthal orientations of the indenter with respect to the surface over a range 0–180°. The crystal was rotated about the indentor axis in steps of 15° while keeping the applied load and loading time constant at 50 g and 20 sec, respectively.

For annealing study, the sample was sealed in an ampoule at 10^{-4} Pa. It was kept in the furnace at temperature of 375°C for about 48 h and gradually cooled down to room temperature following which microhardness was calculated using the standard formula. At least three indentations for each loading time were produced. The results present averages of the data obtained.

3. Results and discussion

The surface anisotropic variation of H_v in the three cases are represented in figure 1 in the form of plots of H_v vs orientation angle, θ. The four-fold symmetry of the

*Author for correspondence

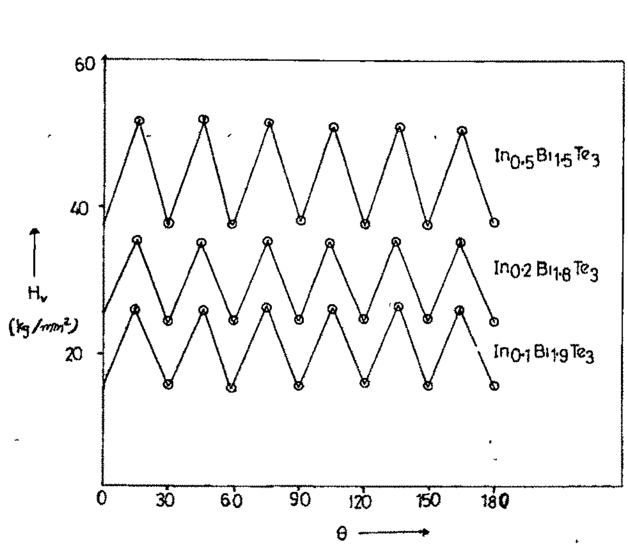

Figure 1. Plots of H_v vs θ.

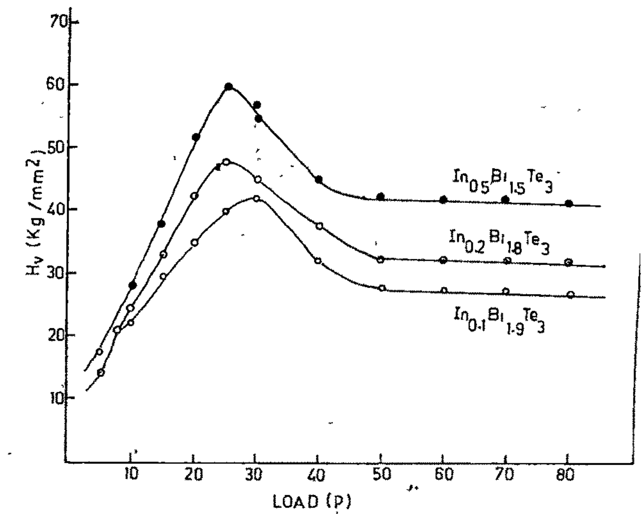

Figure 2. Plots of H_v vs P.

indentor and six-fold symmetry axis normal to the cleavage plane combine to result into twelve-fold symmetry. This is evident in the plot (Pandya *et al* 1977). The hardness values repeat at every 30° interval.

Figure 2 shows the plots of H_v vs load (P) obtained for samples annealed at 375°C. In the low load range the hardness remains dependent on load while at higher load it remains particularly independent of load. The complexity observed in the load dependence of hardness closely parallels many a report on variety of crystals (Buckle 1951; Bhatt *et al* 1983; Jani *et al* 1994). The hardness peaks are in turn explained in terms of the resulting deformation induced coherent regions. Beyond a certain depth of penetration, which corresponds to the expanse of the coherent region and to the load at the peak hardness, the indentor penetrates the virgin layers which easily favour nucleation and multiplication of dislocations (Braunovic 1973; Pandya *et al* 1977; Vyas *et al* 1995). It is observed (figure 2) that the hardness is independent of load for loads beyond 50 g and represents the true hardness of the bulk of the crystal. Accordingly, the hardness values of $In_{0.1}Bi_{1.9}Te_3$, $In_{0.2}Bi_{1.8}Te_3$ and $In_{0.5}Bi_{1.5}Te_3$ crystals are 27, 32 and 41 kg/mm^2, respectively. It is observed that softening of crystal takes place and the hardness decreases to a considerable extent as a result of annealing. Annealing is known to decrease dislocation density and to free immobile dislocation tangles, thus causing the plastic softening of the crystals.

Acknowledgement

The authors are grateful to the UGC, New Delhi, for the DRS grant.

References

Arivuoli D, Gnanam F D and Ramasamy P 1988 *J. Mater. Sci. Lett.* **7** 711

Bhatt V P, Patel R M and Desai C F 1983 *Cryst. Res. & Technol.* **18** 1173

Braunovic M 1973 *The science of hardness testing and its research applications* (eds) J H Westbrook and H Conard (Ohio: ASM) p. 329

Buckle H 1951 *Rev. Metall* **48** 957

Drabble J R 1963 *Progress in semiconductors* (eds) A F Gibson and R E Burgess (New York: John Wiley & Sons Inc.) Vol. 7, p. 47

Ha H P, Cho Y W, Byun H Y and Shim J D 1994 *J. Phys. Chem. Solids* **55** 1233

Jani T M, Pandya G R and Desai C F 1994 *Cryst. Res. & Technol.* **29** 1

Jansa L, Lostak P, Sramkova J and Horak J 1992 *J. Mater. Sci.* **27** 6062

Mott B W 1956 *Microindentation hardness testing* (London: Butterworths Scientific Publications) Ch. 1

Pandya N S, Bhatt V P, Vyas A R and Dandya G R 1977 *Indian J. Pure & Appl. Phys.* **15** 750

Sagar A and Faust Jr J W 1967 *J. Appl. Phys.* **38** 482

Testardi L R and Burstein E 1972 *Phys. Rev.* **B6** 460

Vyas S M, Pandya G R and Desai C F 1995 *Indian J. Pure & Appl. Phys.* **33** 191

Indian Journal of Engineering & Materials Sciences
Vol. 6, August 1999, pp. 237-238

Note

Microhardness study of $In_xBi_{2-x}Te_3$ (x = 0 to 0.5) crystals

G R Pandya, C F Desai, S R Bhavsar & P H Soni
Physics Department, Faculty of Science, M S University of Baroda, Vadodara 390 002, India
Received 16 November 1998; accepted 5 May 1999

The crystals of $In_xBi_{2-x}Te_3$ have been grown using the zone-melting method. Vickers microhardness measurements have been carried out on the cleavage surface of the crystals at room temperature and with constant loading time. The load dependence of hardness has been studied on the single crystals with x = 0 to 0.5 with applied load varying from 5 to 80 g. The hardness has been observed to increase with indium concentration. The results have been subjected to Mayer's equation and implications have been discussed. The load independent hardness obtained in the high load range has been observed to increase with the indium concentration.

The V-VI group compounds are semiconductors and find applications in television cameras, photoconducting targets, thermoelectric devices and IR spectroscopy[1]. $In_xBi_{2-x}Te_3$ solid solutions are used for the construction of cooling elements and generators operating in the temperature range close to 300 K[2]. It has been shown that on exceeding a certain limiting concentration of indium in Bi_2Te_3, the conductivity changes from p-type to n-type[3] .There are a few reports on microhardness study of Bi_2Te_3 crystals[4]. In this paper , microhardness and its load dependence in the case of $In_xBi_{2-x}Te_3$ (x = 0 to 0.5) crystals have been presented.

Experimental Procedure

For the growth of $In_xBi_{2-x}Te_3$ (x = 0 to 0.5) crystals, the stoichiometric amounts of indium, bismuth and tellurium all 99.999% pure, were sealed in a quartz ampoule under a pressure of 10^{-4} Pa. The ampoule was placed at 50 °C higher than the melting point of the charge and was continuously rocked and rotated for 48 h by a motorized arrangement, for effecting proper homogenization and reaction. It was then cooled to room temperature under ambient conditions. The ingot thus obtained was zone-leveled. The temperature gradient of the furnace was 70°C/cm. Fifteen alternate passes were given to obtain crystals of good quality, at the speed of 0.4 cm/h. The crystals thus obtained were cleaved along (0001) planes at ice temperature to minimize deformation.

The microhardness indentations and measurements were carried out using Vickers pyramidal indentor and a micrometer eye-piece attached to the Vickers projection microscope. For the identations, cleavage slices of 2 to 3 mm thickness were used. The indentations were made under different loads from 5 to 80 g, keeping the azimuthal orientation of the indentor fixed to avoid anisotropic variations. The indentation time was kept constant at 20 s. At least three indentations were produced at each applied load and they were repeated on three samples. The results present average of the hardness values obtained. All necessary precautions were taken to see that the experimental error in the indentations and measurements are as small as possible.

Results and Discussion

Fig.1 shows the plots of Vickers hardness (H_V) versus applied load (P) for different indium concentrations in pure Bi_2Te_3. The graph displays three distinguishable regions. In the low load region the hardness has complex load dependence and it can be explained in terms of the depth of penetration of the indentor and consequent strain hardening of the

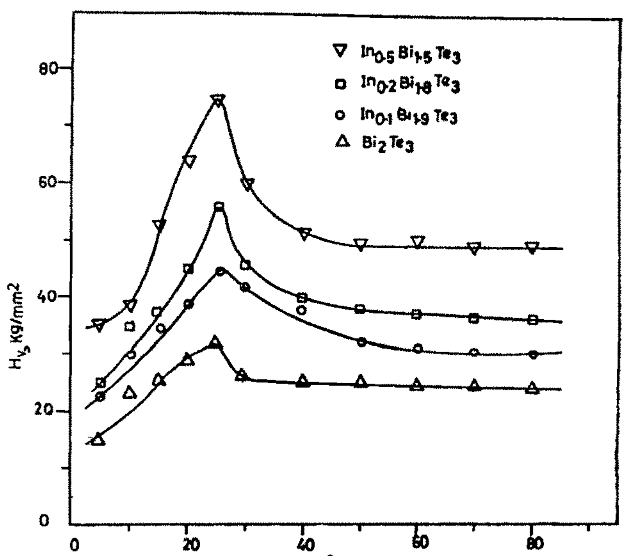

Fig. 1—Plots of H_v versus load (P)

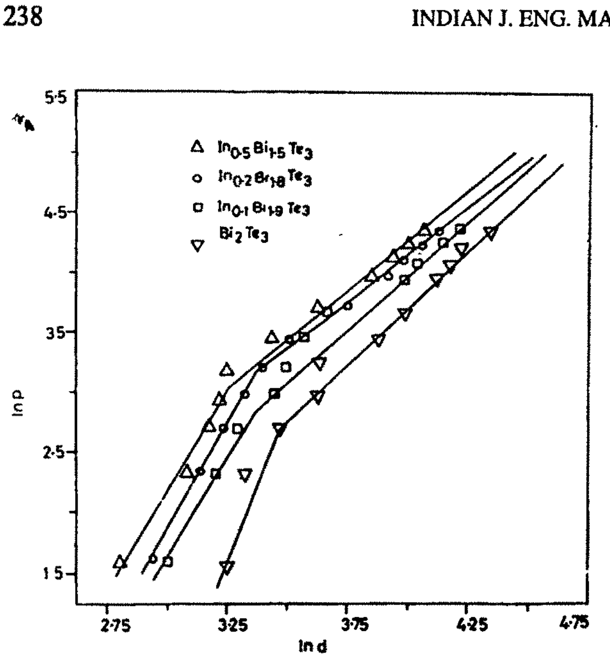

Fig. 2—Plots of ln P versus ln d

surface layers. The hardness shows empirical divisions into: the one, at loads less than that at the hardness peak and the other, beyond it in the intermediate load range. With the increase in the load, penetration depth increases and hence the plot reflects distinctive responses of the corresponding depth zones. A plausible explanation of the hardness variation in the above mentioned low and intermediate load ranges can be given in terms of deformation induced coherent regions[5,6]. The coherent region in the present case extends to a depth of penetration of the indentor produced by the load at the hardness peak, e.g., 25 g for $In_xBi_{2-x}Te_3$. In the higher load range the hardness tends to be independent of applied load, particulary at loads higher than 50 g. In this respect, the average hardness obtained may safely be taken to represent the bulk, since at higher loads the presentation depth of the indentor is well beyond the surface layers. Hence the hardness sensed is that of the interior bulk of the sample, the effect of surface layers being none or negligible.

The data obtained were analyzed using Mayer's equation[7-9]

$$P = ad^n \qquad \ldots (1)$$

Where P is the applied load, d is the diagonal length of the identation mark (Fig. 2) and a and n are constants for the material under test. Using plots of ln P versus ln d, the constant n called Mayer index, was calculated for all the In concentrations. There are two distinct regions obtained, one representing the low load region (LLR) and the other, the high load region

Table 1—Mayer's index and hardness values at different indium contents

x of indium	n_1	n_2	Hardness (H_v) kg/mm^2
0	5.60	2.08	25
0.1	3.08	1.93	31
0.2	4.00	1.98	37
0.5	3.23	1.92	50

(HLR). The slopes n_1 and n_2 of the straight lines are listed in Table 1, for all impurity concentrations. A careful study of these data would indicate that the exponent n_1 is greater than 2.0 in LLR. This implies fully softened state in the LLR - only a few surface layers are penetrated by the indentor and the measured hardness is only a characteristic of these layers, the fact responsible for the work hardening with the progressing penetration and hence for the observed deviation of n_1 from 2. The value of n_2 deviates maximum by about 10% from its standard value 2, whereas n_1 deviates by as much as 140% indicating highly load sensitive hardness for all impurity concentrations in LLR. n=2 for all concentration, implying nearly load independent hardness in the HLR. As is well-known, the load independent value of the hardness represents hardness of the bulk. Accordingly the hardness of $In_xBi_{2-x}Te_3$ is shown in Table 1. From the Table 1, it can be concluded that as indium concentration increases, the hardness increases.

Acknowledgement

The authors are thankful to U.G.C., New Delhi, for DRS research grant support.

References

1 Ha, H P, Cho Y W, Byun H Y & Shim J D, *J Phys Chem Solids*, 55(1994) 1233.
2 Birikholz Z, *Thermoelektrische Bauselement in "Amorfe and Polykristalline Halbleiter,"* edited by Heywang W (Springer, Berlin), 1984, 77.
3 Jansa L, Lostak P, Sramkova J & Horak J, *J Mater Sci*, 27 (1992) 6062.
4 Arivuoli D, Gnanam F.D, & Ramasamy P, *J Mater Sci Lett*, 7 (1988) 711.
5 Buckle H, *Rev Metal*, 48 (1951) 957.
6 Braunovic M, *The Science of Hardness of Testing and its Research Application*, edited by Westbrook & Conrad (ASM, Ohio), 1973, 329.
7 Jindal P. C. & Gurland J, *The Science of Hardness Testing and its Research Applications*, edited by Westbrook & Conrad (ASM, Ohio), (1973) 99.
8 Jain T M, Pandya G R, & Desai C F, *Cryst Res Technol*, 29 (1994) k3 - k8.
9 Mayer L, *Microhardness Testing*, (Butterworths Scientific Publications, London), 1956, Ch.4.

A STUDY ON CRYSTALS AND THIN FILMS OF $Bi_{2-x}In_xTe_3$ (x = 0.1 to 0.5)

A THESIS SUBMITTED TO

THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

PHYSICS

17th JANUARY-2000

UNDER THE GUIDANCE OF
DR. G.R.PANDYA
THE M.S.UNIVERSITY OF BARODA
VADODARA- 390 002.

BY
SAURABH BHAVSAR
THE M.S.UNIVERSITY OF BARODA
VADODARA- 390 002.

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 $Bi_{2-x}In_xTe_3$ 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 $Bi_{2-x}In_xTe_3$ (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, thermolectric power measurement and thin film preparation. Chapter 5 gives general information on Bi_2Te_3 and $Bi_{2-x}In_xTe_3$ (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 etcing of $Bi_{2-x}In_xTe_3$ (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 $In_{0.1}Bi_{1.9}Te_3$, $In_{0.2}Bi_{1.8}Te_3$ and $In_{0.5}Bi_{1.5}Te_3$ 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 $Bi_{2-x}In_xTe_3$ (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 $In_{0.5}Bi_{1.5}Te_3$ 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 $In_xBi_{2-x}Te_3$(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 $In_{0.1}Bi_{1.9}Te_3$, $In_{0.2}Bi_{1.8}Te_3$ and $In_{0.5}Bi_{1.5}Te_3$ crystals respectively. The thermoelectric power in all the crystals was found to increases with temperature. The measurements indicate $In_{0.1}Bi_{1.9}Te_3$ crystal to be p-type with carreir concentration 4.78 x 10^{19} cm^{-3} while $In_{0.2}Bi_{1.8}Tc_3$ and $In_{0.5}Bi_{1.5}Te_3$ crystals are of n-type with carrier concentrations 3.23 x 10^{19} cm^{-3} and 7.57 x 10^{18} 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 $Bi_{2-x}In_xTe_3$ (x = 0.1 to 0 5). The film thickness dependence of the band gap of $In_xBi_{2-x}Te_3$ 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 $In_{0.1}Bi_{1.9}Te_3$, and $In_{0.5}Bi_{1.5}Te_3$, 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 $In_{0.1}Bi_{1.9}Te_3$, films forming a Schottky barrier cell.