Available online at www.scholarsresearchlibrary.com

Scholars Research Library

Archives of Physics Research, 2012, 3 (1):15-20
(http://scholarsresearchlibrary.com/archive.html)

ISSN : 0976-0970
CODEN (USA): APRRC7

Characterization of InSbBi Bulk Crystals Grown at Various Growth-rates by Vertical Directional Solidification (VDS)

D. S. Maske[1,2*], P. S. More[2], M. D. Deshpande[2,4], R. Choudhary[2] and D. B. Gadkari[2,3]

[1]*Department of Physics, D. G. Ruparel College, Mumbai*
[2]*Department of Physics, Mithibai College, Mumbai*
[3]*Dept of Physics, University of Mumbai, Mumbai*
[4]*Department of Physics, Jai Hind College, Mumbai*

ABSTRACT

The VDS technique was used for the crystal growth of $InSb_{1-x}Bi_x$*. The source materials were filled with argon in a quartz ampoule of cone angle <200 at one end at pressure 200 torr. The ampoules were synthesized for 40-50 hrs at 850°C temperature. Five growths of* $InSb_{1-x}Bi_x$ *bulk semiconductor crystal were carried out at the growth rate varying from 2 to 6 mm/hr and various values of x. Temperature gradient at the solid liquid interface was in the range of 18 °C/cm to 20 °C/cm. The grown ingots were sliced to 450 – 600 µm thickness along the axis and perpendicular to the axis. One growth resulted in p-type semiconductor while the other four resulted in n-type semiconductor. The growth rate of 2 mm/hr show good quality single crystal with maximum mobility up to 44500* $cm^2/V\ s$ *at room temperature (300°C), while the higher growth rate produce poor crystal quality (polycrystalline) material. The result of second growth (x=0.05) shows that the material is semiconductor having resistivity* $5.45 \times 10^{-4}\ \Omega$ *cm. Linear variation of the Hall voltage with the applied magnetic field shows that the crystal is good semiconductor. The lattice constant of the sample InSbBi-2 found to be changed by 21 A° as compared to the pure InSb. Calculation of energy band gap from the variation of resistivity with the temperature show reduction of the energy band gap up to 0.138 eV as compared with the energy band gap of the pure InSb (0.172eV) at room temperature. No appreciable change in the parameters tested after 6 months reveals that the material parameter does not change with time.*

Key words: Directional solidification, Growth from melt, Single crystal growth, Semiconducting III-V materials.

INTRODUCTION

The semiconductor technology has been in progress to grow ternary materials of III-V and II-VI compounds in the field of detection of IR (infrared) [1]. The optoelectronic devices, especially, low-wavelength (8-12µm) photo detectors for near infrared region and their operations at room temperature are of most importance in the devices used in military, medical diagnostics, pollution monitoring, industrial process controls, etc [2]. So far this field is being dominated by Mercury-Cadmium- Telluride (MCT). But this material has some serious drawbacks, such as: (i) material parameters change with time [3], (ii) thermal instability, (iii) poor compositional uniformity over a large area due to high Hg- vapour pressure and (iv) weak Hg- bond, hindering the further development of infrared technology [4, 5], (v) epitaxial growth and other processing steps are more difficult in II / VI alloys than III / V alloys. Thus, as far as detector operations in near IR are concerned, problems mentioned above have turned out to be the real challenges. These problems seem to be less severe for III / V alloys as compared to II / VI alloys. The only reason due to which II / VI alloys are still preferred is inability of conventional III / V alloys to reach higher end of near IR (12 µm) at the common operating temperature of 77 K [6]. Owing to these problems, $InSb_{1-x}Bi_x$ seems to be a strong contender to HgCdTe, which can operate even at room temperature. Incorporation of small amount of impurity of Bi into the host InSb lattice, changes the band gap from 0.172 eV of InSb to -1.5 eV of a semimetal InBi [7] to cover the NIR region (8–12 µm). Recent studies showed that, it is relatively difficult to grow ternary and quaternary large single crystals of high quality. The problems reported in such growths are: (i) constitutional super cooling appear in front of the growth interface which results to sudden transition from single to polycrystals (ii) local compositional inhomogeneity in the solid leads to cracking of the crystals [8]. These problems can be reduced by controlling the growth parameters. It is desirable to have a high temperature gradient at the melt-solid interface and/or at a slower growth rate [9]. This paper reports the effect of growth-rate on quality of $InSb_{1-x}Bi_x$ bulk crystals grown by VDS technique.

MATERIALS AND METHODS

The VDS technique consists of a single vertical furnace of a quartz tube (10 cm diameter, 100 cm length and closed at both the ends with Wilson seal) as the growth chamber. Microcontroller based arrangements are made to control the temperature and movements (vertical and rotational) of the ampoule in the growth chamber. Highly pure (6N) Indium, antimony and Bismuth were used as the source materials for the growth of ternary semiconductor crystals. Stoichiometric composition of the source materials (InSbBi) were filled with argon at pressure (200 torr) in a quartz ampoule of 10 mm diameter and the cone angle $< 20^o$. The ampoules were synthesized for 50 hr at 850 ^oC temperature. Five growths of $InSb_{1-x}Bi_x$ bulk semiconductor crystal were carried out at a growth rate varying from 2 to 6 mm/hr and various values of x (0.05 to 0.1).

Temperature gradient at the solid liquid interface was in the range of 18 °C/cm to 20 °C/cm. The grown ingots were sliced to 500μm thickness along the axis and perpendicular to the axis to obtain mirror finish substrates by carborundum powder. The substrates were characterized by etching and microstructure, Hall measurements, XRD, EDAX, XRF, and optical FTIR to optimize the growth rate to improve quality of the crystal.

RESULTS AND DISCUSSION

One of the important aspects of the good quality crystal growth is the detachment of the ingot from the ampoule wall. The as grown ingot of the crystal grown at the rate of 2mm/hr in the ampoule (fig.1) show completely detached growth in the top region (1.2 cm) of the ingot, while in the lower portion the ingot was weakly attached with the ampoule wall. More attachment was observed in the region of pockets on the ingot surface. Top portion of the ingot (end-cap) was found to be spherical in nature with 1.2 cm radius of curvature. The nature of spherical end cap was same in all the five ingots grown at different growth rates.

Microstructures and SEM images

Observation of the polished surfaces of the wafers using high resolution optical microscope show that the surface morphology of the crystals is different in the crystals grown at different growth rates. Crystals grown at low growth rate were almost free from micro cracks while higher growth rate show increase in the micro cracks on the surface (fig.2). After etching (CP4) major portion of the surface was found to be homogenous for the growth rates of 2-3 mm/hr. Surface of the crystal grown at 4mm/hr growth rate show micro cracks. The presence of twin lamellae were observed in the crystals grown at the growth rate 5mm/hr and 6mm/hr. The surface morphology on the two sides of each twin is almost same. Solidification at the faster rate lead to thermal stresses which results to secondary nucleation and dislocation. The uniform dislocation in the crystal forms lamellae. Maximum surface defects were observed on the surface of the crystal grown at 6mm/hr. Similar observations were obtained by SEM images of the surfaces of the wafers. The SEM observations also show the presence of more regions of Bi segregation in the crystals grown at 4, 5 and 6mm/hr. Hence in higher growth rates Bi is not mixed (incorporated) uniformly in the ingot but it remains segregated in the form of separate pockets. Crystal grown at the low growth rate (2mm/hr) shows very much reduction in segregation of Bi.

Data from EDAX and XRF was used to find composition of indium, antimony and bismuth along the axis of the ingot (fig 3). Overall observations show that the presence of Bi in the ingot is more in case of higher growth rates while presence of Bi found to be low as well as non uniform in crystal grown at low growth rates.

Hall coefficient, resistivity and mobility

Results of the various measurements are summarized in the table 1. Resistivity measurements were performed by four point probe as well as van der Paw method. Polarity of the Hall voltage showed that one of the crystals InSbBi-3 is p-type semiconductor and the other four crystals are n-type semiconductors. Crystals grown at low growth rates show linear variation of the Hall voltage with the applied magnetic field (from 1 X 10^3 gauss to 5 X 10^3 gauss) confirming homogenous crystal growth. Hall coefficient decreases with the increase in the growth rate. Semiconductor crystals grown by VDS technique exhibit high mobility [10,11]. Mobility of the InSbBi crystal grown at 2mm/hr is 44500 cm^2/V-s, indicating good crystal quality with electron concentration 2.6 X 1017 cm^{-3}.

Optical FTIR pattern of the wafers of InSbBi crystals were obtained by PERKIN-ELMER FTIR-SGX in transmission mode. The FTIR curves (fig.4) of the wafers from the top region of InSbBi-2 grown at 2mm/hr, indicate the energy band gap of 0.16 eV while the band gap calculated from the variation of resistivity with the temperature is 0.155 eV. The energy band gap of pure InSb grown by the same method and calculated from the resistivity variation with temperature is 0.172 eV. This slight reduction in the band gap shows small amount of Bi incorporated in InSb lattice. Though the presence of more Bi is shown in the crystals grown at higher growth rates (5mm/hr), edge of the FTIR curve do not show appreciable reduction in the band gap. This shows that in the crystals grown at higher growth rates, Bi is not incorporated in the crystal lattice.

X-ray diffraction (XRD) pattern of the wafers of the crystals grown at the growth rates 2mm/hr and 5mm/hr are shown in fig 5. The wafers used for obtaining XRD were cut along the axis of the ingot. The patterns indicate that, the good crystal growth with single peak orientation (4, 2, 2) observed for the growth rate 2mm/hr. Laue pattern of a vertically cut wafer showed perfectly symmetrical spots confirming single crystal growth. However in all the other growths the crystals are polycrystalline.

Table 1. Bi composition, Mobility and Hall measurements of the InSbBi samples grown at different growth rates

Sr. No.	Sample Name	Bi composition x	Growth Rate mm/Hr	Mobility Cm^2/Vs	Hall coefficient cm^3/Coul
1.	InSb	0	5	59000	100
2.	$InSb_{1-x}Bi_x$ -1	0.065	6	854.2	0.75
3.	$InSb_{1-x}Bi_x$ -2	0.05	2	44500	24.25
4.	$InSb_{1-x}Bi_x$ -3	0.07	4	5800	7.8
5.	$InSb_{1-x}Bi_x$ -4	0.06	3	4500	4.5
6.	$InSb_{1-x}Bi_x$ -5	0.062	5	1530	1.48

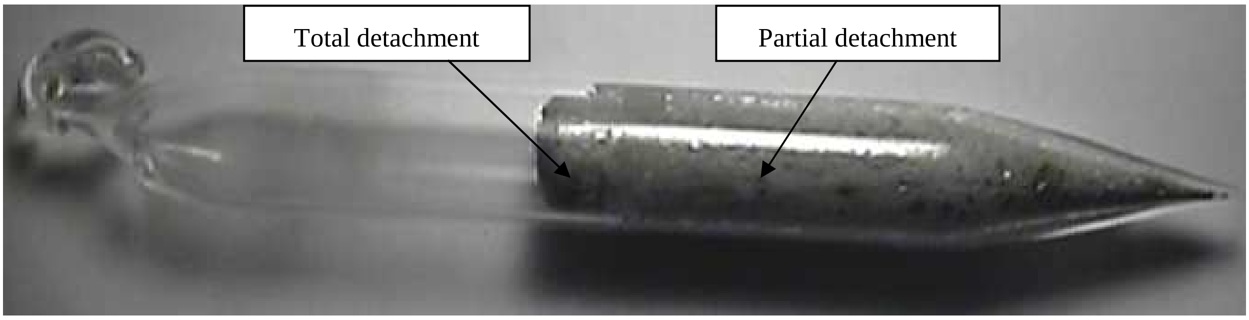

Fig. 1 **$InSb_{1-x}Bi_x$ ingot in the ampoule.**

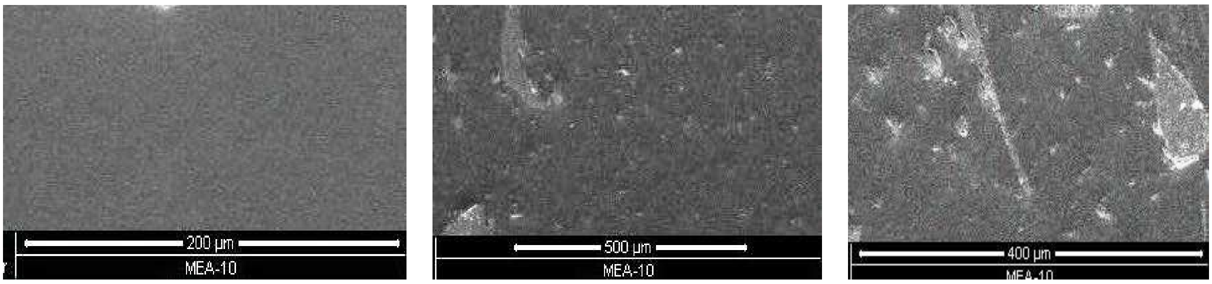

Fig. 2 SEM of the crystals grown at (a) 2 mm/hr, (b) 4 mm/hr, (c) 6 mm/hr.

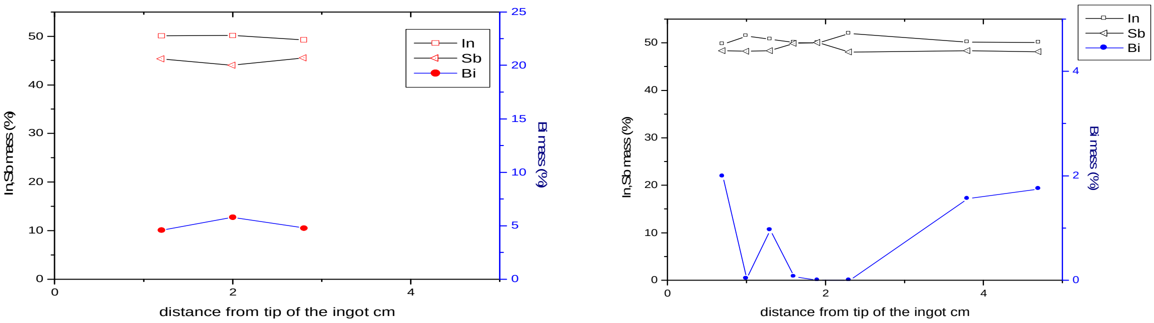

Fig. 3 Composition of Bi along the length of InSbBi-5 and InSbBi-2.

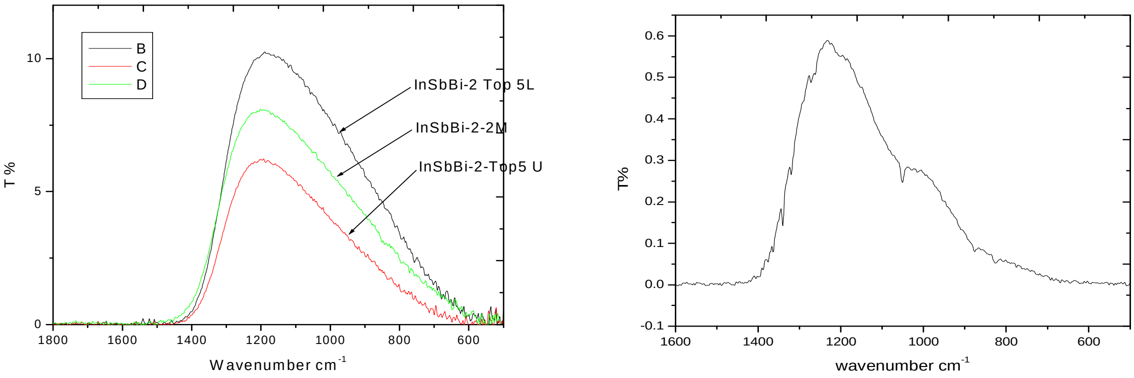

Fig. 4 FTIR curves of the wafers grown at 2mm/hr and 5mm/hr.

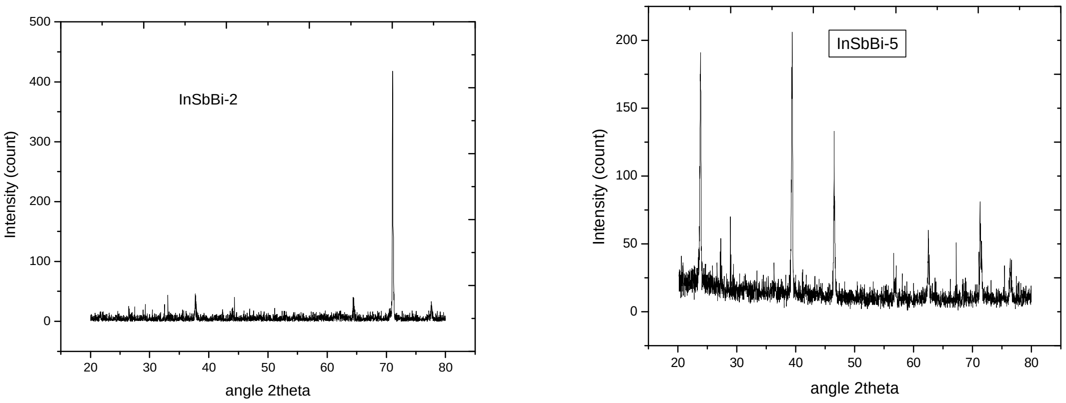

Fig. 5 XRD patterns of the crystals grown at 2mm/hr and 5mm/hr.

CONCLUSION

Crystals grown at the low growth rate show less incorporation of Bi but very good quality single crystal and higher growth rates show good amount of presence of bismuth but poor crystal quality polycrystalline material. Detachment was observed in all the growths. Maximum mobility up to 44500 cm^2/V s at room temperature was observed in the crystal grown at the rate of 2 mm/hr. Thus, to have good quality InSbBi semiconductor crystal, the optimized growth rate is 2 to 3 mm/hr when the temperature gradient at the solid liquid interface is in the range of 18 ^{o}C/cm to 20 ^{o}C/cm.

REFERENCES

[1] M. C. Wagener, J. R. Botha, A.W.R. Leitch, *J. of Crystal Growth*, **2000**, 213, 51-56.
[2] Y. Z. GAO, T. Yamaguchi, *Crystal Res. Technol*. 34, **1999**, 3, 285-292.
[3] M. Oszwaldowski, T. Berus, J. Szade, K. Jozwiak, I. Olejniczak, P. Konarski. *Cryst. Res. Technol* 36 **2001** 8-10, 1155-1171
[4] J. J. Lee, M. Razeghi, *Journal of Crystal Growth*, 221, **2000**, 444 – 449
[5] J. J. Lee, J. D. Kim and M. Razeghi, *Appl. Phys. Lett*., **1998**, 73 (5) 602-604
[6] K. T. Huang, C.T. Chiu, R.M. Cohen and G. B. String fellow. *J. of Applied Physics*. **1994**, 75, 6, 94/75(6)/285717
[7] M. C. Wagener, R.E. Kroon, J. R. Botha, A.W.R. Leitch. *Physica B* **1999**, 273-274, 919-921
[8] P. S. Dutta, *J. of Crystal Growth*, **2005**, 275, 106-112
[9] P. S. Dutta, H. J. Kim and A Chandola, *Trans Indian Inst. Met*. **2007** Vol. 60, 2, 155-160
[10] D B Gadkari, P Shashidharan, K B Lal and B M Arora *Bull. Mater. Sci*., **2001**, Vol. 24, No. 5, 475–482
[11] D. B. Gadkari, K. B. Lal, & B. M. Arora. *Journal of Crystal Growth*, **1997**, 173, 585-588