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Microscopic and Elemental Mapping of InSbBi Substrate of Bulk Crystal Grown by VDS

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Abstract- III-V ternary bulk crystal (ingot) using Indium, Antimony and Bismuth as the source materials ($InSb_{1-x}Bi_x$) was grown by the vertical directional solidification (VDS) technique and the grown ingot was sliced into wafers. Further the well-polished wafers were used for the surface characterization of the grown crystal. The resistivity measurement indicated that the wafers were n-type semiconductors with the resistivity 1.00 X 10^{-3} ohm-cm. These wafers were lapped and polished to get mirror finish surface. After cleaning the wafers were etched by using CP4 (HNO_3:HF:CH_3COOH::5:3:3) and the modified CP4 (HNO_3:HF:CH_3COOH:H_20::5:3:3:10) etchants. The microstructures and defects on the surface of the wafers (substrates) were studied using metallurgical microscope. SEM and EDAX techniques were used for the further analysis of the microstructures observed by the microscope. Most of the surface is having uniform configuration with some defects like grain boundaries, dents, black spots etc. EDAX analysis of the black spots indicate Bi rich domains. Distribution of the compositional elements was studied by elemental analysis of the surface. High resolution SEM analysis of a dent shows formation of nano-crystals of size ~ 150nm.

Index Terms- bulk crystal growth, microstructures, elemental mapping, Bi rich domins

I. Introduction

Development of new class of semiconductor materials using the properties of a group V semimetal bismuth (Bi) is of substantial interest in semiconductor technology. These include materials for development of optoelectronic, thermoelectric and electronic devices. Thus understanding and engineering of Bi containing III-V semiconductors become significant in the development of novel semiconductor materials for their applications. One of these novel materials is Bi doped indium antimonide (InSbBi) because, incorporation of a small amount of Bi atoms in common III-V compounds; for example, arsenides and antimonides, reduces the energy band gap by a large amount.**[1, 2]**. In principle, due to addition of Bi, the band gap of InSb can, be reduced from 0.17 eV (InSb) to -1.5 eV (the semi-metal InBi) at 300 K **[3]**.

Among the III-V semiconductors, bulk crystal of InSbBi is the most studied material because, its energy gap can be reduced (below 0.17eV) by adjusting their compositional ratio, to extend the wavelength range beyond 7.2 µm (LWIR wavelength range) **[4, 5]**. During the study of bulk crystal growth of the III-V bismides, two major problems are reported in the literature. Constitutional super cooling appear in front of the growth interface which results to sudden transition from single crystal growth to polycrystals and local compositional inhomogeneity in the solid leads to cracking of the crystals **[6]**. These problems can be reduced by controlling the growth parameters **[7 , 8]**. However the resulting composition in the grown crystal is of great importance as far as the properties of the material are concerned. Scanning of etched surface of the substrate by optical microscope provide information about various compositional defects in the grown material. Elemental analysis is the qualitative detection and quantitative determination of the elements (atoms, molecules, ions) present in the sample. Elemental analysis performed by the energy dispersive x-ray spectroscopy on different areas of the samples specifies compositional uniformity of the material.

II. Experimental

Vertical Directional Solidification (VDS) technique was used for the melt growth of an ingot of InSbBi semiconductor without seed. This technique is having easy and precise control on the growth parameters to produce good quality bulk semiconductor crystals **[9, 10]**. Highly pure (6N) Indium, antimony and Bismuth were used as the source materials for the growth of ternary semiconductor crystals $InSb_{1-x}Bi_x$ where the stoichiometric composition factor was x=0.06. The grown ingots were cut perpendicular to the axis to obtain the substrates, which were cleaned, lapped and polished to mirror finish. Wafers from the different regions of the grown ingot were prepared to study the microstructure by chemical etching using CP4 (HNO_3:HF:CH_3COOH::5:3:3) and the modified CP4 (HNO_3:HF:CH_3COOH:H_20::5:3:3:10) etchant. Each sample (wafer or part of the wafer) was first dipped in the etchant for ~15 seconds, and then it was immediately dipped in HCL for few seconds for cleaning. Further the sample was cleaned with warm TCE,

acetone and methanol and washed in distilled water. Finally the sample was dried thoroughly to make it ready to study microstructures. Scanning of the surface of the wafer from the ingot of the crystal growth of InSbBi by optical microscope indicate that, most of the surface is having uniform texture indicating defect free growth of the material (Figure 1.a, c) except few black spots or inclusion and grain boundaries shown in Figure 1:(b,d). The average density of such defects, calculated using computer software is 8.3 X $10^3/cm^2$. Figure 1.b shows two textures separated by a fine grain boundary. This indicate growth of two grains of the same material with different orientations.

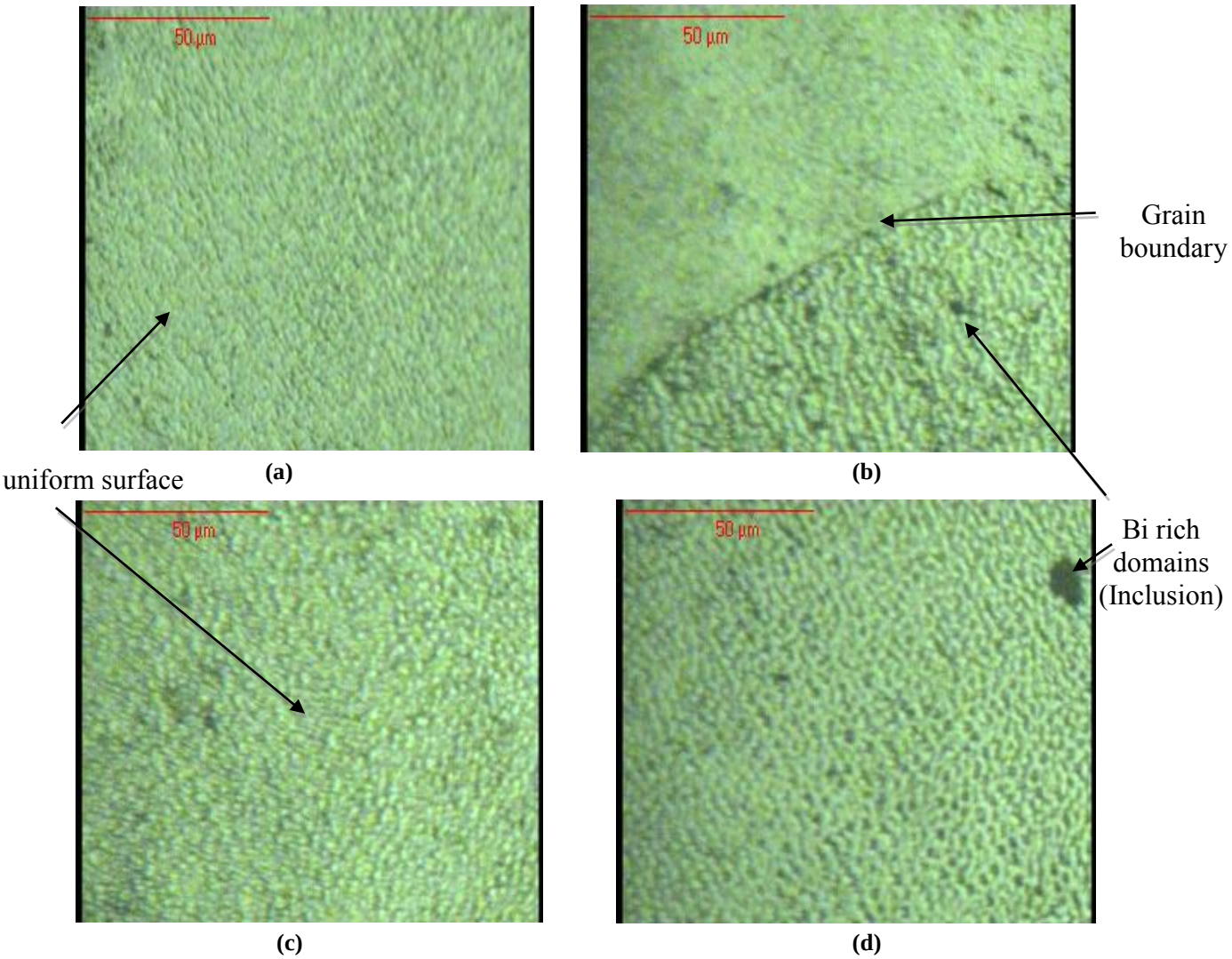
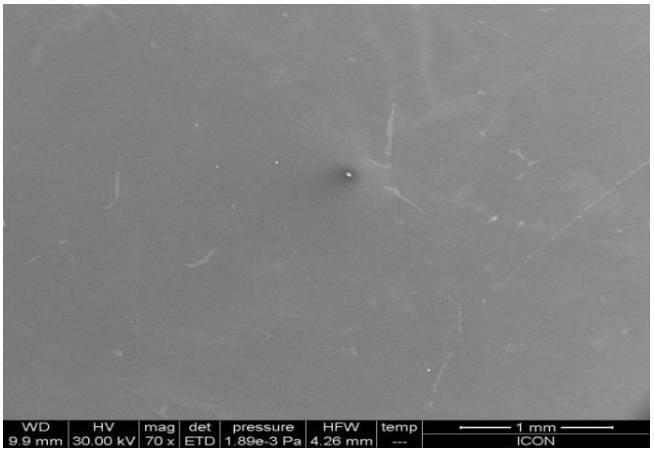


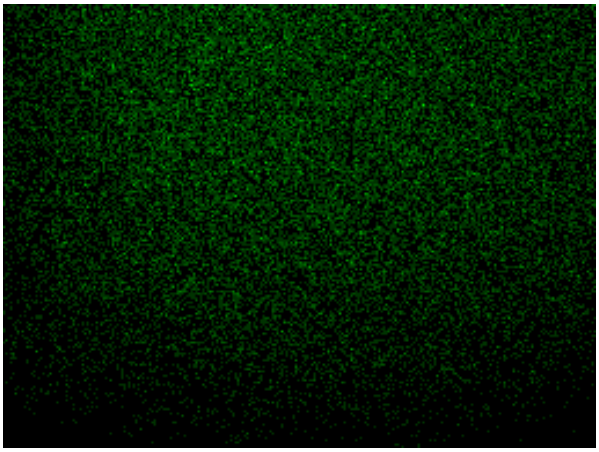
Figure 1. Microstructures on the etched surface of the InSbBi substrate.

III. Elemental (EDAX) Mapping:

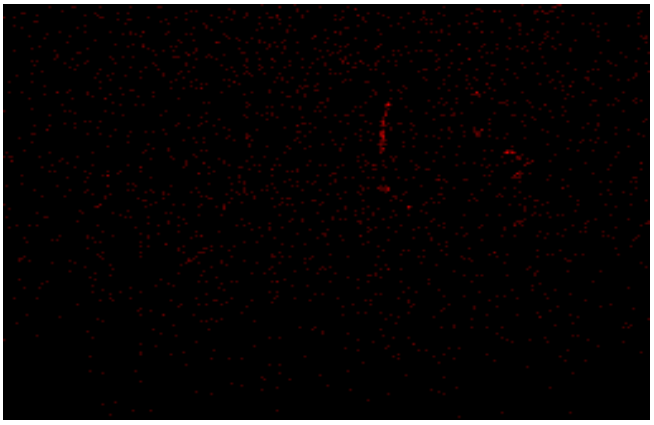
A wafer from middle region of the ingot was used for the elemental mapping. Figure 2.(a) show SEM image of the substrate in which most of the region is having minimum defects exhibiting good crystal quality. Figure 2: (b, c, d) show mapping of the elements indium, bismuth and antimony by green, red, and blue respectively on the surface of the substrate. All the three mapping images indicate that, the compositional distribution of the three materials is almost uniform throughout the grown material as indicated by the uniform regions observed in the microscopic analysis. This is one of the requirement of the device grade semiconductor crystal. However few non uniformities indicated in the mapping were further analyzed by high resolution SEM. Compositional analysis of such spots by EDAX shown in Figure 3. (b) indicate that, such regions are having excess amount of bismuth (Bi ~ 30% of the total InSbBi composition) and they are treated as Bi rich domains or inclusions. These inclusions are created when less amount of Bi gets incorporated in InSb lattice and remaining amount forms Bi pockets or inclusions as shown by a black spot in Figure 1.(b), (d).



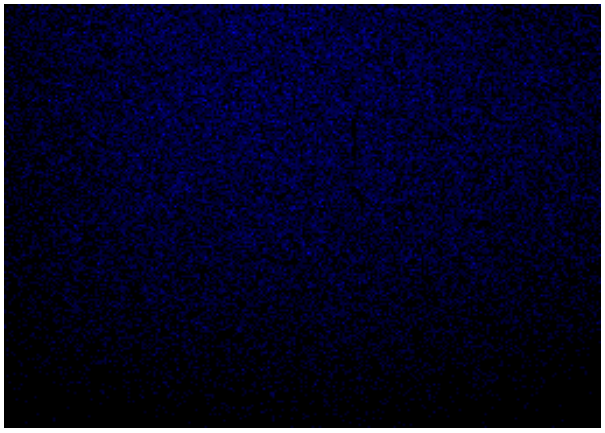
(a) SEM of the surface of InSbBi-4 wafer



(b) Indium mapping for InSbBi-4 wafer

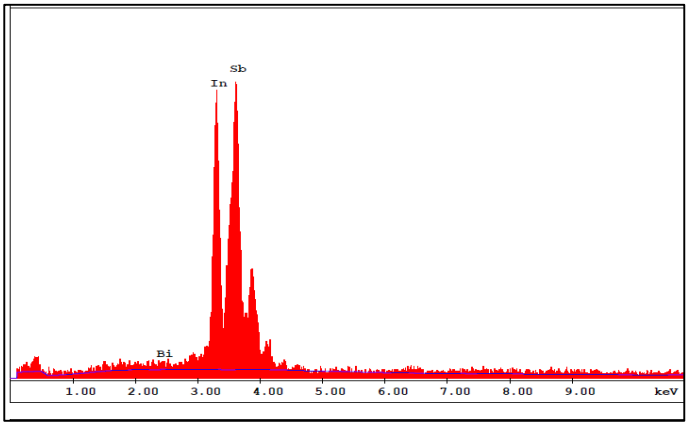


(c) Bismuth mapping for InSbBi-4 wafer



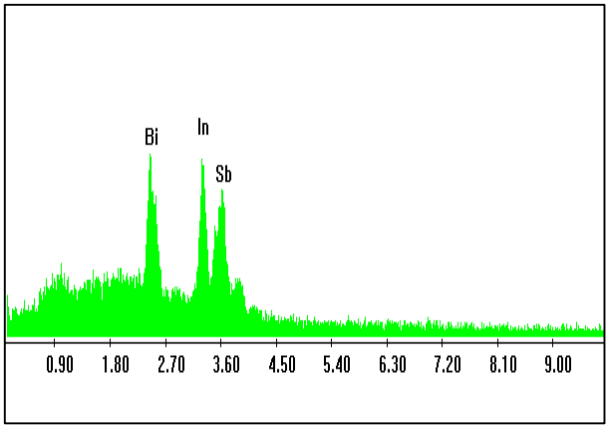
(d) Antimony mapping for InSbBi-4 wafer

Figure 2: SEM and Elemental mapping of InSbBi



Element	Wt %	At %
Bi	2.97	1.7
In	47.46	49.52
Sb	49.57	48.78

Figure 3: (a) EDAX of uniform region of the substrate



Element	Wt %	At %
Bi	29.75	19.24
In	40.91	48.17
Sb	29.34	32.59

Figure 3: (b) EDAX of Bi rich domain on the substrate

IV. Analysis of Black Spots (Inclusions) observed in the microstructures

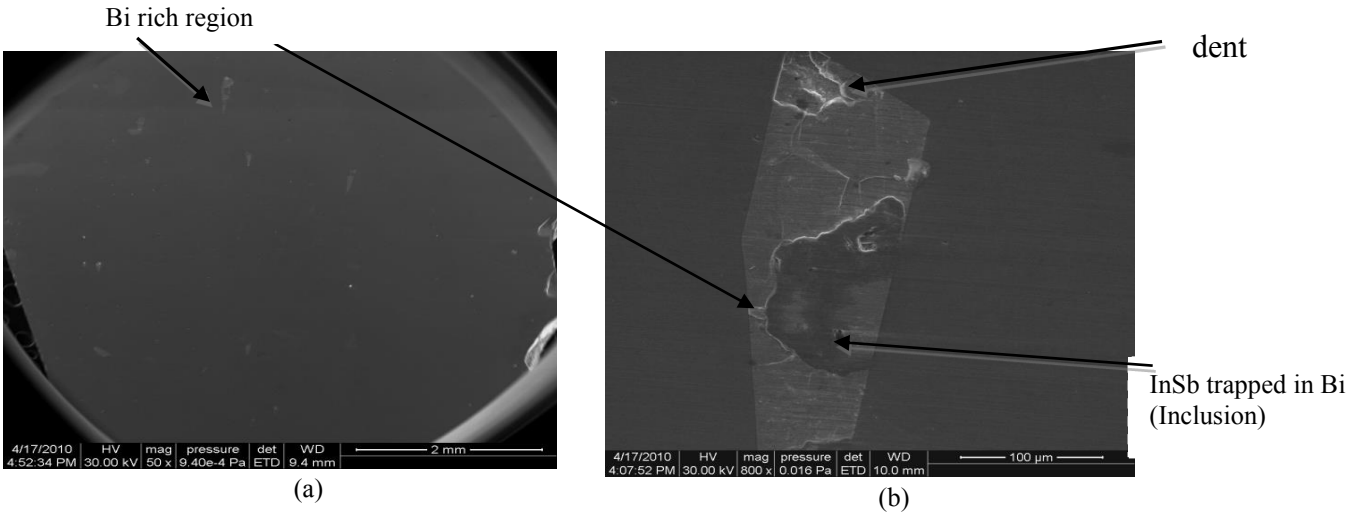


Figure 4. (a) SEM showing small defect. (b) magnification of the small inclusion

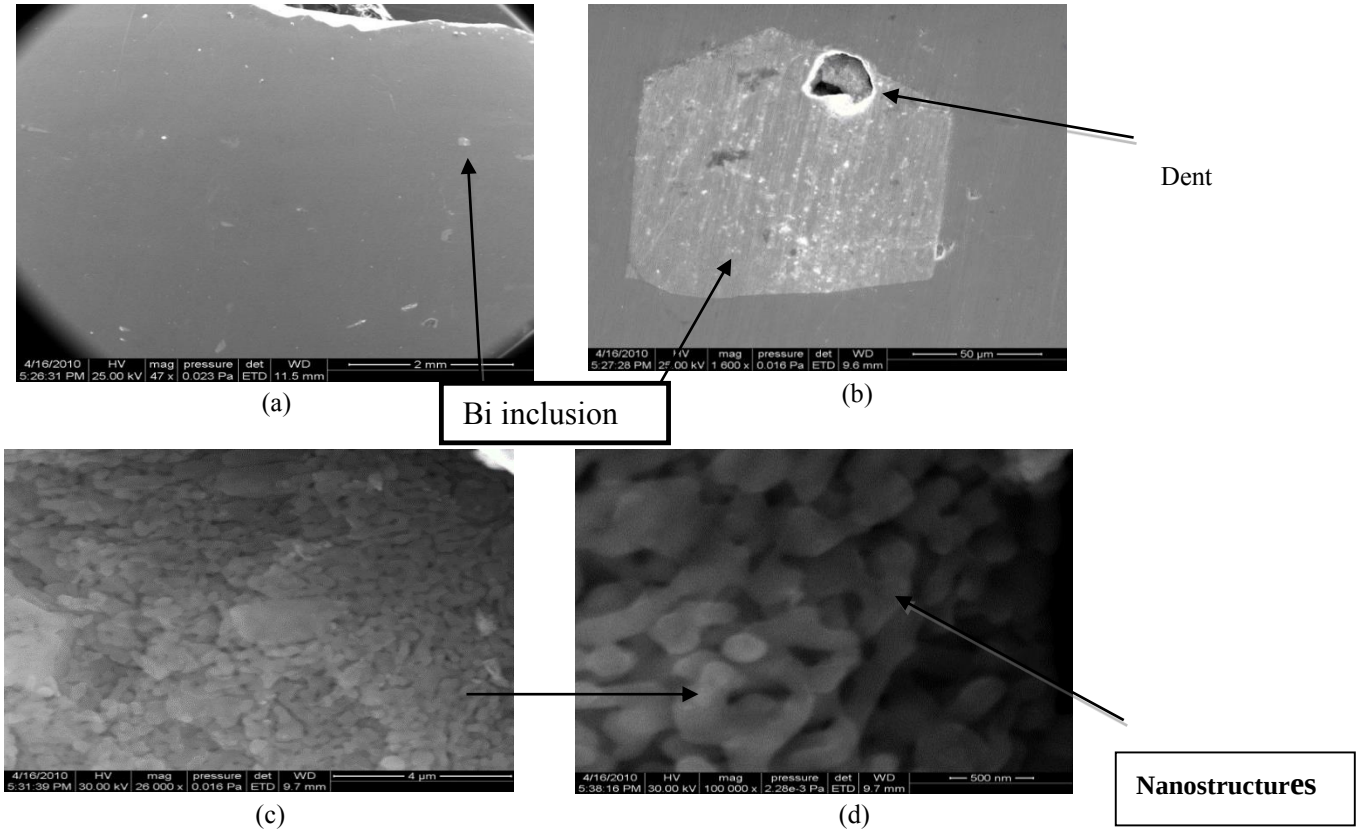


Figure 5. Nano- size structures observed in the defect(dent) region on the surface of InSbBi

Observation of the defects using SEM indicate growth of small grains with the Bismuth composition more than the expected (doped) value (At% shown in figure 3.b). These regions have different texture (more shining) so that the grain boundaries are clearly visible. Surface of such grains is not very smooth and uniform as shown by the SEM image in figure 4.(b) and Figure 5. (b). However the defects like cracks are observed in these Bi rich regions. Magnification of small Bi rich region observed on the wafer surface by the high resolution of SEM image indicate a dent as shown in fig 5.(b) (top left corner in the Bi rich grain).

V. Nanostructures in the Defect

A small Bi rich inclusion (defect) observed on the surface of the wafer was analyzed by high resolution SEM as shown in figure 5. (a, b). It showed a dent of width 25 µm at the corner of the inclusion. Scanning of the dent by increasing the resolution of SEM up to 2 µm scale (figure 5. c) showed small structures with the size smaller than 1µm present in the dent. Observation of these structures with the resolution of 500 nm scale (Figure 5. d) indicates presence of nanosize InSbBi structures. The nano structures observed are similar to nano tubes.

VI. CONCLUSION

Microscopic analysis of the surface of InSbBi crystal grown by VDS technique indicate good crystal quality semiconductor material with minimum level of defect density. Scanning of the surface by SEM confirm the crystal quality exhibiting large surface area with uniform texture and less defects. Elemental mapping of surface of the substrate also show almost uniform distribution of the In, Sb and Bi composition. SEM scanning of a dent (crystal defect) with the resolution of 500 nm scale indicates presence of nano-structures of size ~150 nm.

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