Growth Feature and Characterization of $Bi_{0.75}Sb_{0.25}$ Single Crystal Alloys

Sanketsinh Thakor
Department of physics,
Gujarat University,
Gujarat, India
thakor988@gmail.com

S.M.Vyas
Department of physics,
GujaratUniversity,
Gujarat, India
s_m_vyas_gu@hotmail.com

Vimal Patel
Department of physics,
Gujarat university,
Gujarat, India
Vimalpatel082013@gmail.com

Piyush patel
Department of physics,
Gujarat university,
Gujarat, India
Piyush_patel130@yahoo.com

***Abstract* –Single crystal Bi1-xSbx alloys have been grown with antimony concentration (X=0.25) by zone melting method. Some interesting features were observed on the top free surface of the as-grown Bi1-xSbx (X=0.25) single crystal. Also new dislocation etchant was developed by the successive trial–error method. The dislocation etchant was found to reveled new dislocations on the cleavage surface of the crystals. The results are discussed in details. In depth structural analysis using X-Ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDAX) measurement of grown samples have been performed. XRD data confirmed rhombohedral structure revealed that complete solid solution is formed between bismuth and antimony.**

Keyword: Bi-Sb, Crystal growth, Etching, triangular layer growth features, dendrites growth features, XRD, SEM, EDAX

I. INTRODUCTION

The characteristics of BiSb single crystal alloy have been of interest for decades due to the very narrow band gap, uncommon thermo magnetic, thermo electric and semiconducting properties. Bi and Sb are semimetals with a rhombohedral structure. They have a small energy overlap between the conduction and valence bands, high carrier mobilities, and small effective masses. Because of these properties, Bi and Sb have frequently been used for quantum-size effect studies. The $Bi_{1-x}Sb_x$ alloy system can be either a semiconductor or semimetal depending on the Sb concentration [1–10]. At low Sb concentration Bismuth and antimony have rhombohedral structure often called the A7 structure of point group R3m. They present two atoms per unit cell and similar lattice parameters, and the $Bi_{1-x}Sb_x$ alloy has metallic nature and becomes more and more semimetal with antimony concentration exceeding about x = 0.1.In this paper we do characterization of $Bi_{0.75}Sb_{0.25}$ single crystals which is grown by zone melting method and also discussed growth features which are observed on the top free surface of crystals like triangular layer growth, tiny hillocks and dendritic growth mechanism are also discussed. By using the XRD, SEM, EDAX techniques, we have discussed structure, surface characteristics and proportion of alloy respectively.

II. EXPERIMENTAL DETAIL

Homogeneous single crystals of Bi-Sb alloy were used for growth feature analysis and characterizations which is grown by zone melting technique with a temperature gradient in the molten zone of about 30°C/cm and a growth velocity of 0.5 cm/hr. The degree of homogeneity was determined by etching studied and density measurement. On cleaving the crystal at 0°C by a sharp blade along the (111) plane it was found that the orientation of the crystal was almost parallel to the growth axis. The features observed on the top free surface and on the cleavage plane were studied by optical microscope.

For X-ray diffraction study, several small crystals were finely ground with the help of an agate mortar and filtered through 100 pm sieve to obtain grains of nearly equal size. X-ray diffxactograms were taken with the help of an X-ray diffractometer employing CuKα radiation. Peak behaviour of obtained powder diffxactograms indicates good crystallinity for all compounds. Powder X-ray diffxactograms for compounds were analysed by using Powder-X software for the confirmation of crystal structure and determination of lattice parameters. Surface morphology of crystals and constituent elements were identified by the SEM, EDAX detailed results are discussed.

III. RESULT AND DISCUSSION

A systematic study of the growth features observed on cleavage plane of the crystals is discussed in detail. Typical growth feature in Figue-1 shows the transverse striations; there are two distinct sets of striations intersecting each other at an angle of 120^0. Striations are due to motion of 111 family plane reported; these indicate that crystals probably grow by layer mechanism [11, 12]. The transverse striations were observed in almost all as-grown crystals. The crystals were subjected to successive etching and it was found that there was no change in the appearance of these striations. This indicates that they are not merely surface features but bulk phenomena. The features indicate the surface orientation as to be consistent with symmetry.

Figure-1: The transverse striations; there are two distinct sets of striations intersecting each other at an angle of 120^0.

This parallel and equally spaced indicating crystallographic association. It is possible that some crystallographic plane like {111} may be responsible for these features. The observations indicate that the layer growth mechanism may be effective for the growth of $Bi_{0.75}Sb_{0.25}$ single crystal from the melt.

In figure-2, tiny hillocks observed on the top free surface of the crystals. These are similar to the growth trigons observed in the case of Sb-diamond and Sn-Se single crystal alloy. This can be interpreted in terms of layer growth mechanism by the above workers. [13-15]

An example of the cellular dendrites is shown in figure-3. This feature was observed on the solid – liquid interface of the crystal grown at rate of 1.5 cm/hr. This is due to the phenomenon of very high constitutional super cooling.

After numerous trials it was found that the etchant composed of 4 parts nitric acid (70% AR grade), 7 part citric acid (saturated solution) and 1 part distilled water is capable of producing well defined dislocation pits(I)Starting of the reaction is characterised by the evolution of the bubbles from the surface of the crystal, and (II) the action of the etchant is slow enough for longer times of etching to be tried keeping the surface bright, are the two very important characteristic of this etchant. [16]

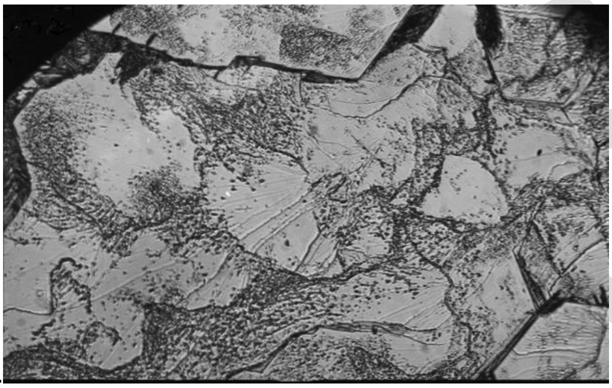

Figure-2: Tiny hillocks observed on the top free surface.

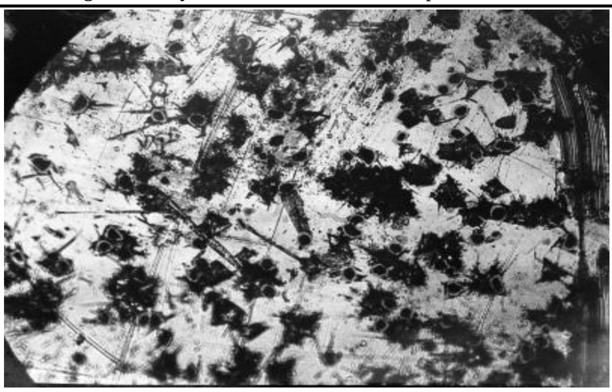

Figure-3: Cellular dendrites growth.

A dislocation etchant would reveal a low angle boundary on a crystal. In the present case a low angle boundary delineated by this etchant is shown in the Figure-4. Some of the etch pit indicate dislocation in <112> direction. Further a specimen was pin indented on the cleavage plane and subsequently etched. Rosettes of etch pits around the indentation mark were observed as an etching result indicating that the etchant can reveal freshly introduced dislocations as well. The average dislocation density of the crystals as measured by the etch pit count method was found to be 3 x 10^4 cm^{-2} on an average. [16]

The XRD characterization studies show that bismuth antimony single crystals have certain preferred orientation respective to the growth mechanism. X-ray diffractograms of $Bi_{0.75}Sb_{0.25}$ are indexed based on a rhombohedral structure system with R3m group with cell parameter a = 4.326 and c = 11.330 Indexed powder X-ray diffraction pattern obtained for the grown crystals are shown in figure-5.All the Bragg's angles of corresponding peaks in XRD pattern matches exactly with the characteristics of reflection peaks of BiSb alloy reported in JCPDS data file. [17]

Single crystals of $Bi_{0.75}Sb_{0.25}$having dimension of 50 mm length and 7 mm diameter were obtained. EDAX As represented in figure- 6 does the compositional analyses of $Bi_{0.75}Sb_{0.25}$ crystal.

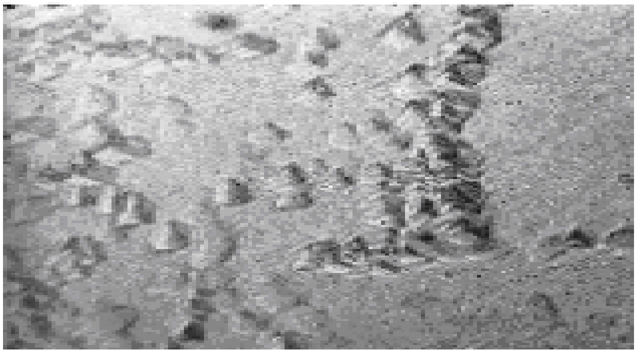

Figure-4: A low angle boundary delineated by etchant.

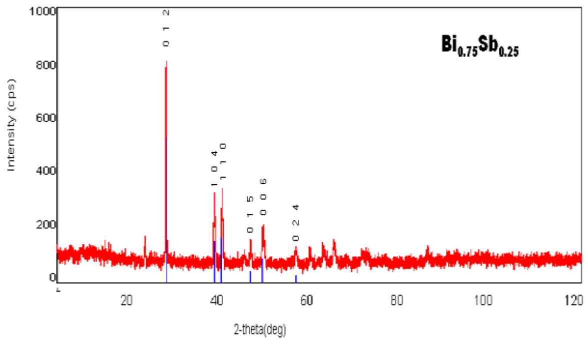

Figure-5: X-Ray diffraction pattern of $Bi_{0.75}Sb_{0.25}$

The EDAX analysis shows the presence of constituent elements. EDAX spectrum gives the percentage of BiSb components in the crystal which is 74.20% and25.80% respectively. EDAX spectrum reveals that these crystals are perfectly stoichiometric and also free from foreign contaminants.

Freshly cleaved $Bi_{0.75}Sb_{0.25}$ crystals were used for SEM characterization. Fig.-7 indicate that the grown crystal are crystalline, shows that the number of cleavage line is very less so perfection of the crystal is more and also indicate the layer growth mechanism in $Bi_{0.75}Sb_{0.25}$ single crystal is predominant.

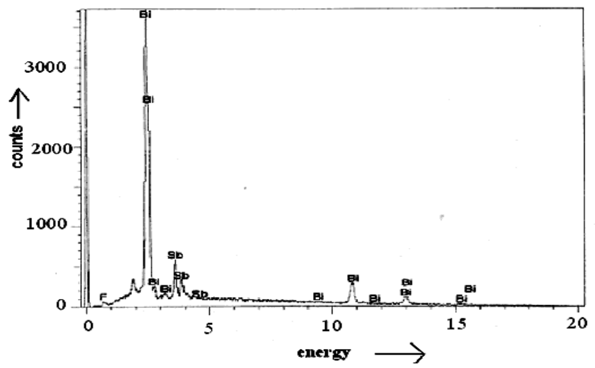

Fig.-6. Compositional analysis's of Bi $_{0.75}$ Sb $_{0.25}$ crystal, by EDAX

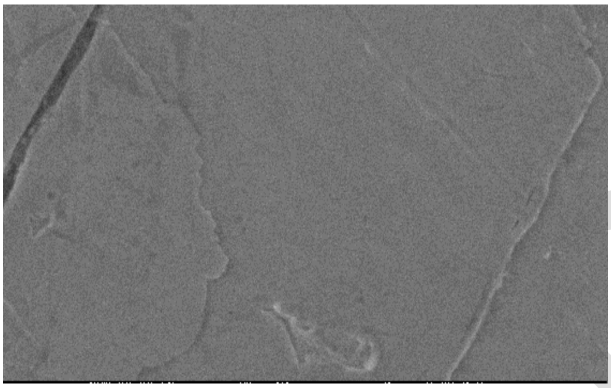

Fig.-7. The SEM image of $Bi_{0.75}Sb_{0.25}$

IV. CONCLUSION

Crystal growth mechanism is predominant by the layer growth mechanism. An etchant developed by the authors is capable of revealing the dislocations intersecting the cleavage plane. X-ray diffractograms of $Bi_{0.75}Sb_{0.25}$ are indexed based on a rhombohedral structure system with R3m group. EDAX spectrum gives the percentage of BiSb components in the crystal which is 74.20% and25.80% respectively. EDAX spectrum reveals that these crystals are perfectly stoichiometric and also free from foreign contaminants.

V. ACKNOWLEDGMENT

Authors are thankful to DST and DRS –SAP for providing necessary facilities and also thankful to Prof. P.N.Gajjar, head of physics department for providing laboratory facilities.

REFERENCES

[1]. A.L.Jain, Phys. Rev., Temperature Dependence of the Electrical Properties of Bismuth-Antimony Alloys, 114, 1518 (1959).
[2]. S.Golin, Band model for Bismuth - Antimony alloys, Phys. Rev. 176, 830 (1968).
[3]. E. J. Tichovolski and J. G. Mavroides, Magnatoreflaction study on band structure of bismuth antimony alloys., Solid State Commun., 7, 927 (1969).
[4]. G. A. Mironova, M.V. Sudakaova and Ta. G. Ponomarev, Fiz. Tverd. Tela, 22, 3628 (1980).
[5]. G. Oelfart, G. Schneider, W. Kraak, and R. Hermann, Phys. Status Solidi (b), 74-75 (1976).
[6]. W. M. Yim and Amith,, thermoelectric property of Bismuth telluride antimony selenite pseudo ternary alloy., Solid-State Electronic. 15, 1141 (1972).
[7]. B. Lenoir, M. Cassart, J. -P. Michenaud, H. Scherrer, and S. Scherrer,Mechanism of thermo power maximum of Bi-Sb semiconducting alloys, J. Phys. Chem. solids 57, 89 (1996).
[8]. D. M. Brown and S. J. Silverman, Phys. Rev. 136, A290 (1964).
[9]. V. G. Alekseeva, N. F. Zaets, A. A. Kudryashov, and A. B. Ormount, Fiz. Tekh. Poluprovodn,Composition controlled synthesis of Bi rich Bi1xSbx alloy nanocrystals by a low temperature polyolprocess., 10, 2243 (1976).
[10]. N. B. Brandt and E. A. Svistova, J. Low Temp. Phys. 2, 1 (1970).
[11]. K. R. Shah, G.R.Pandya, C. F. Desai,Growth and Dislocation Etching of InBi0.8Sb0.2 Single Crystal,Cyst.Res, Technology 33, 5, 733-736 (1998)
[12]. V. P. Bhatt, G. R. Pandya, Dislocation studies in bismuth-antimony alloy single crystals by etch pit technique, J. Phys.C: Solid State Phys., Vol.6, (1973).
[13]. Bhatt V.P.,talati M.C. and Shah H.M.,Ind.J.Pure and Appl. Phy. 8, 236 (1970),
[14]. Bhatt V.P.,Pandya G.R. and Vyas A.R., Ind.J.Pure and Appl. Phy. 18 658 (1970)
[15]. Tolanski S. and Wilcock W.L., Nature London, 157, 583(1946)
[16]. Yim, Y. M. and dismukes, J. P., J.Phys. Chem. Solid, suppl., 187, (1967)
[17]. Lahti, S.Bull., Geol., Surv.Finl. " JCPDS card no. 35-0517,314,66(1981)