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Crystal Growth and Etching of Bi_2Te_3 Alloys

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Abstract *– Anisotropic phenomena in the layered Bi_2Te_3 crystal were investigated. Bismuth is a semimetal with high electron and whole mobility. Interest in Bi_2Te_3 material system has recently been stimulated by promise of a new generation of thermoelectric materials based on this alloy. Single crystals of Bi_2Te_3 were prepared by a modified Bridgman method with 1.5-cm/hour growth velocity and temperature gradient 65^0C/cm. Some interesting features were observed on the top free surface of the as-grown Bi_2Te_3 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 dislocation density calculated by the etchpit count method. The results are discussed in details.*

Keywords*: Bi_2Te_3, crystal growth, dislocation enchant, Single crystals, semi metal and top free surface.*

I. Introduction

The V_2-VI_3 (Bi, Te) binary compounds and their pseudo binary solid solutions are highly anisotropic and crystallize into homologous layered structure parallel to c-axis and are known to find applications ranging from photoconductive targets in TV cameras to IR spectroscopy [1], [2].

Bi_2Te_3 is the most important material for the thermoelectric devices like thermocouples, generators, coolers and IR sensors, good figure merit near to the room temperature [3] - [7]. Bi_2Te_3 finds application also in electronics, microelectronics, optoelectronic and electromechanically devices.

Thermoelectric materials are attracting renewed interest because of the promise that low dimensional or quantum confined, systems will have greater efficiencies compared with bulk materials [8], [9].

A good thermoelectric material should have high σ, like a crystalline material, and a low κ, like a glass, as suggested by Slack et.al. with the concept of "Phonon-glass/electron crystal" model [10].

The concept of Functionally Graded Materials (FGM) is well introduced. There are a lot of especially Japanese activities in Functionally Graded thermoelectric with the main focus on energy conversion [11], [12].

A locally maximized figure of merit for the working conditions, i. e. the temperature profile for the thermoelectric application of the material, should result in a higher efficiency of thermoelectric generators, for instance [13], [14]. The aim of our work is to prove the FGM concept in the case of PELTIER cooling. In this note we report on a crystal growth technique based on zone melting of bismuth antimony telluride mixed crystals for FGM thermoelectric materials.

These materials are generally grown by means of zone melting, Bridgman and Czochralski techniques. Zone melting method is common and economical. The unidirectional solidified ingots exhibit the most excellent thermoelectric performance along the crystal growth direction [15] – [17].

The figure of merit (Z), which determines the utility of materials for thermoelectric applications, is very sensitive to variations in composition. There have been several reports on the influence of chemical composition on thermoelectric properties of Bi_2Te_3 – Sb_2Te_3 solid solutions, which showed that Z could be improved by decreasing the lattice thermal conductivity with enhanced phonon scattering due to the lattice distortion, whereas there are many discrepancies in the published work. For instance [18]. prepared p-type $(Bi_2Te_3)_x(Sb_2Te_3)_{1-x}$ in the composition range x = 0.2 – 0.3 and found that the figure of merit is less composition sensitive when $x < 0.25$, while it decreased rapidly with increasing Bi_2Te_3 content when $x > 0.25$. A similar result was also reported by [19]. Because, bismuth–telluride system has a maximum performance at ~350 K, most of the previous studies have only focused on the study of thermoelectric properties at room temperature. However, though the measurements on temperature dependence of thermoelectric properties is essential not only for understanding the basic transport mechanism involved but also for providing necessary data to construct thermoelectric devices for applications in PELTIER cooling or power generation at different temperatures [20].

Bismuth and antimony tellurides are generally used in thermoelectric devices due to their superior thermoelectric performance at room temperature [21]. After Hicks and Dresselhaus have introduced new concept to improve the ZT, research into the fabrication of low dimensional structures with conventional thermoelectric materials has received much attention [22], [23].

II. Experimental Techniques

Elemental materials Bismuth and Tellurium, both of 99.999 % purity, used for the preparation of the alloy. These were weighted to stoichiometric proportion and sealed in a quartz ampoule (25 cm in length and 1 cm in diameter) under the vacuum of the order of 10^{-5} torr. The ampoule containing charges were placed in a horizontal alloy mixing furnace at the temperature 730 ^{0}C for 48 hour, during which it was continuously rocked and rotated for proper mixing and reaction. The ingot was then cooled to room temperature over a period of 24 hour.

The single crystals of Bi_2Te_3 were grown by the Bridgeman method with the growth velocity was 1.5 cm / hr and freezing interface temperature gradient was 65 ^{0}C / cm.

Some interesting features on the top free surface of the as grown crystals were observed using an optical microscope.

A new dislocation etchant was developed by using AR grade chemicals, as discussed below.

III. Result and Discussion

Typical growth features are shown in Figure 1 and Figure 2.

Figure 1 shows the transverse striations observed on the top free surface of the crystal (Bi_2Te_3). An array parallel striation is running normal to the growth direction and parallel to the solid-liquid interface. The mean distance of separation of striations was found to be 15μ.

Figure 2 shows the triangular layer features indicate the surface orientation as to be consistent with symmetry. 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_2Te_3 single crystal from the melt.

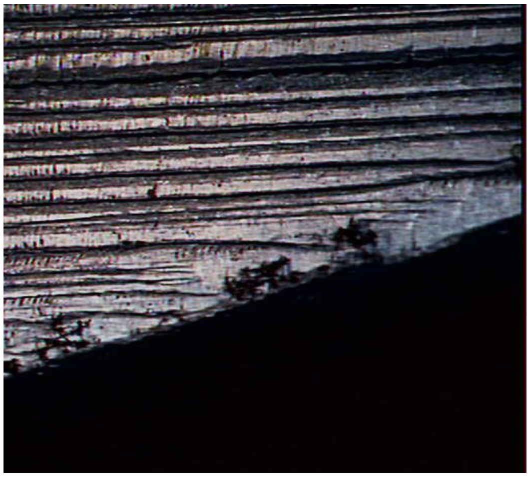

Fig. 1. Parallel Striation with equidistance observed on the top free surface of the crystals

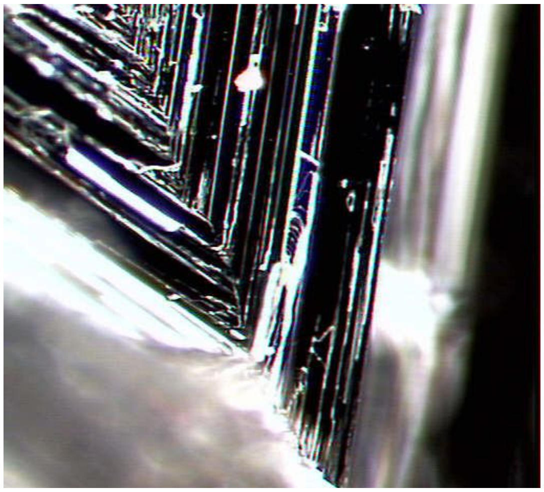

Fig. 2. Triangular layer feature observed on the top free surface of the crystals

The perfection of the grown crystals in terms of dislocation content was estimated by the using dislocation etchant developed by the present authors after numerous trials. The characteristics of the etchant are shown below.

ETCHANT PROPORTIONS: 3 part of concentrated HNO_3 + 6 part of Citric acid (saturated Solution) + 1part of Distilled water.

This mixture is capable of producing well defined triangular etchpits. The etching time is 12 second to yield the etchpits. Figure 3 shows the etchpits, etchant to be capable of revealing dislocations intersecting the cleavage plane.

Fig. 3. Low angle boundary and etchpits on the crystals.

Figure 3 shows the rows of etchpit originating from point are clearly visible. In the upper part of the photograph, scattered etch pits are seen and the rows of etchpits may be due to the deformation introduced during the act of cleavage. The distribution of etch pits and low angle boundary obtained after etching the specimen by the etchant [24].

Fig. 4. Etchpit rows along the Pin indentation mark

To test capability of the etchant to reveal fresh dislocation, the specimen was pin indented and followed by etching shown in the figure 4. The increased density and the arrangement of etch pattern consist of well defined rows of etch pits along the slip-traces near the pin indentation implied that etchant is capable of revealing fresh dislocations also. The average density of dislocations intersecting the cleavage plane of the crystal as measured by the etchpit count method was found to be about 10^4 cm^{-2}.

IV. Conclusion

To summarize the observation on growth features indicate the layer growth mechanism of crystal growth is predominant. The reported etchant successfully reveals dislocations inclined to the (111) plane of the crystals.

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