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Direct observation of Frank–Read sources in stoichiometric bismuth telluride crystals

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Stoichiometric crystals of bismuth telluride have been grown from the melt by the horizontal zone levelling technique. The multiplication of dislocations and dislocation density was studied by using chemical etching. Dislocation spirals and loops due to Frank–Read sources have been observed on the basal plane.

1. Introduction

In recent years considerable attention has been devoted to the telluride of bismuth, Bi_2Te_3, because of its potential application in the fabrication of thermoelectric devices. Bismuth telluride is a layered semiconductor which crystallizes in rhombohedral lattice structure with the space group D^5_{3d} ($R\bar{3}m$). The atoms are arranged in layers in the order

Bi–Te–Bi–Te–Te–Bi–Te–Bi–Te–Te– – –

and readily cleaves between the weakly bonded Te layers [1].

The multiplication of dislocation is of importance to the plasticity of crystals. Frank and Read [2] proposed the classical multiplication mechanism in which a dislocation, anchored at each end, expands in its slip plane. This was first observed by Dash [3] in silicon samples plastically deformed at 1000 °C, using infrared transmission microscopy. Dislocation studies on the cleavage surfaces of Bi_2Te_3 crystals by etch pit technique have been reported by various groups [4–7]. Only a few results are available regarding the movement and multiplication of dislocations in Bi_2Te_3 crystals. Sagar *et al.* [7] have observed concentric dislocation loops and multiturn spirals on the basal plane in heat treated and quenched Bi_2Te_3 crystals grown by horizontal zone levelling from a non-stoichiometric tellurium-rich melt. They have used a solution of bromine in methanol (the precise concentrations not mentioned) as etchant for studying the dislocation characterization. The exact mechanism responsible for the dislocation loops in Bi_2Te_3 crystals has not, however, been clearly established.

Here we report on the direct observation of regenerative multiplication of dislocations by Frank–Read sources on the basal (0001) cleavage planes of stoichiometric bismuth telluride crystals.

2. Experimental procedure

Bismuth telluride crystals were grown from the melt by the horizontal zone levelling technique. Appropriate quantities of the constituent elements of 99.999% purity were vacuum sealed in thoroughly cleaned quartz ampoules of length 10 cm and diameter 10 mm. The sealed ampoule was kept in a constant temperature furnace at 700 °C for about 24 h. The ampoule was periodically rotated at a speed of 10 to 12 r.p.m. for homogeneous mixing of the constituents. The growth was carried out in a horizontal gradient furnace by keeping the ampoule with a temperature of 700 °C at the hotter end and 600 °C at the cooler end for about 72 h. X-ray diffraction studies were carried out with CuK_α radiation. It has been found that good stoichiometric crystals of bismuth telluride are obtained under the present growth conditions.

The crystals obtained were carefully cleaved at liquid nitrogen temperature and a stock solution of bromine in methanol (10% by volume) was used as the etchant for dislocation studies. The etched surfaces of the crystals were observed in reflection using a Versamet-2 metallographic microscope.

3. Results and discussion

Fig. 1 shows the X-ray diffractogram of a typical bismuth telluride crystal. The standard values of the X-ray powder data [1] along with the data obtained in the present case are given in Table I. From this, it is evident that the present Bi_2Te_3 crystals are stoichiometric in proportion. The results are also in agreement with the value reported for stoichiometric Bi_2Te_3 thin films [8].

When the cleavage faces of the crystals were etched in 5 ml of 10% bromine in methanol by volume for 30 s, small shallow pits of undefined shape and prismatic loops were observed. Further etching of the crystal for a total time of 1 min resulted in the development of spirals and closed loop patterns. Etching for longer times made the crystal surface corroded. So this composition of etchant and etching time was found to be the optimum condition for obtaining visible multiturn dislocation spirals and loops. This can be seen from the optical micrographs 2 to 12. From these figures, it is fairly clear that the multiplication mechanism [2] is responsible for the present observations. According to this slip mechanism, the most suitable explanation for the large

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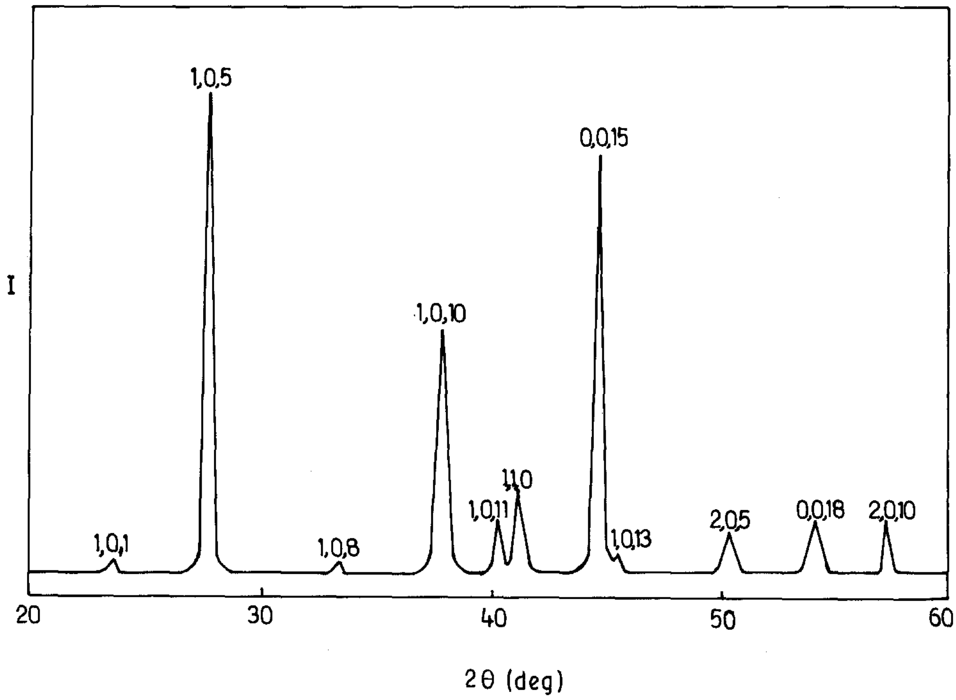

Figure 1 X-ray powder diffraction pattern of Bi_2Te_3 crystal.

amount of slip occurring on a single slip plane can be obtained by a process of expansion and subdivision due to simple motion of dislocation [9].

Although the origin of the loops is not completely understood, the reason for their occurrence has to be sought in the stoichiometry of Bi_2Te_3. This point of view is based on the fact that similar types of closed loops do not occur in the Te-rich Bi_2Te_3 crystals of Sagar *et al.* [7]. They have observed spirals and concentric loops only in the heat treated and quenched Bi_2Te_3 samples grown from the non-stoichiometric Te-rich melt. When these samples were heated at 500 °C for a few days in vacuum, there may be a possibility of the removal of excess Te atoms, thus rendering these samples nearer to stoichiometry. This supports the present observation of ideal Frank–Read dislocation mill on the basal plane of stoichiometric Bi_2Te_3 crystals without any heat treatment. Moreover, the different shaped pyramidal pit formation in the Te-rich samples [6, 7] is not at all found in the present case. Hence this implies that, deviations from the stoichiometric proportions of the constituent elements may have an important effect on the dislocation pattern of Bi_2Te_3.

An example of Frank–Read spiral due to a section of dislocation that lies in the (0 0 0 1) slip plane and leaves that plane at a point in the interior of the crystal is shown in Fig. 2.

The various events in the development of Frank–Read sources are quite clear from Figs 3 to 6. In this case the dislocation line connects two interior points on the two arms of L-shaped dislocation. The pinning of these anchor points may be due to other dislocation intersections. When this dislocation leaves the slip plane at these points under the action of shear stress it will bow out as stress increases and the expanding loops double back on itself. Thus a large

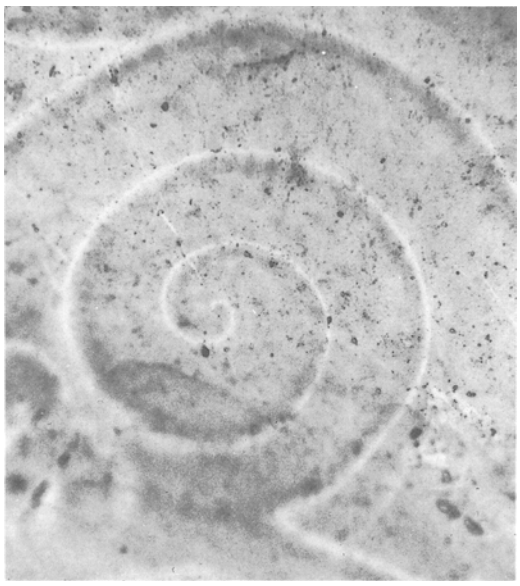

Figure 2 A circular spiral originating from a single dislocation (×470).

TABLE I X-ray diffraction data for bismuth telluride crystal

$h k l$[a]	Standard pattern		Grown crystal	
	d(nm)	I/I_o	d(nm)	I/I_o
1 0 1	0.3780	8	0.3770	8
1 0 5	0.3220	100	0.3220	100
1 0 8	0.2694	5	0.2690	7
1 0 10	0.2378	55	0.2374	53
1 0 11	0.2237	11	0.2232	15
1 1 0	0.2191	35	0.2191	22
0 0 15	0.2032	40	0.2030	88
1 0 13	0.1995	6	0.1993	9
2 0 5	0.1810	20	0.1810	13
0 0 18	0.1694	5	0.1693	16
2 0 10	0.1610	16	0.1610	16

[a] The $h k l$ indices are referred to the hexagonal structure cell.

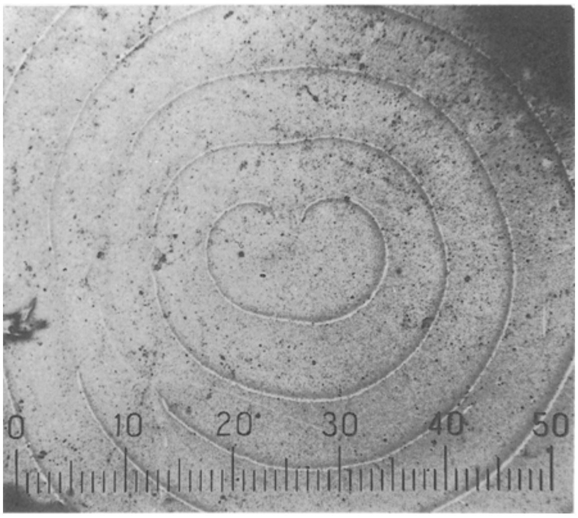

Figure 3 Configuration of dislocations resulting from the operation of a Frank–Read source of the double ended type (× 350). (Marker: 1 div = 5 μm).

Figure 6 Formation of closed loops from a pair of unlike dislocations (× 490).

Figure 4 Formation of an unstable dislocation loop where the two segments have almost joined (× 350).

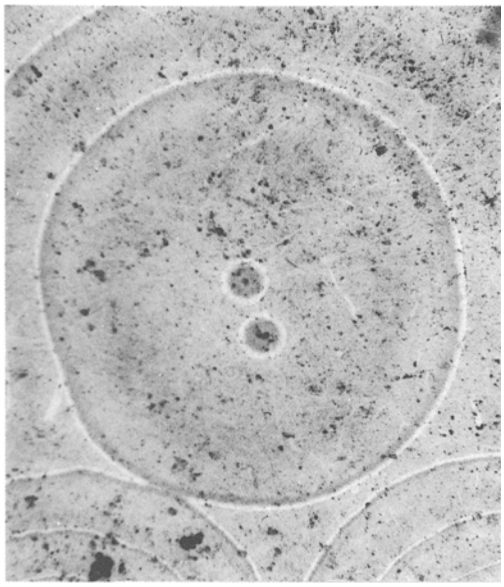

Figure 7 Emergence points of two dislocations inside a single closed loop (× 170).

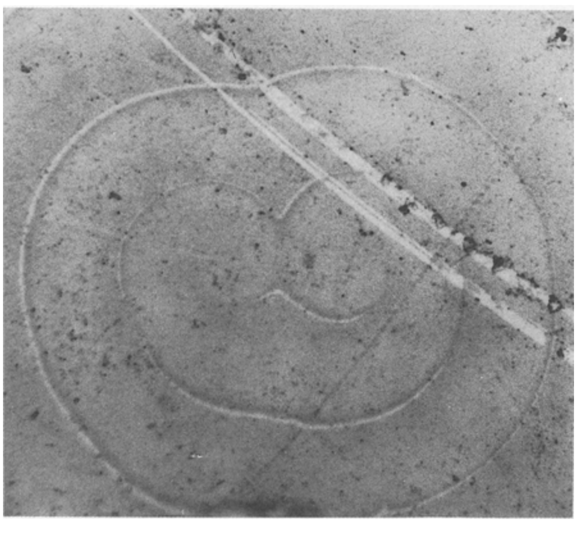

Figure 5 Mutual annihilation of two dislocations of opposite sense (× 320).

kidney shaped loop will be observed (Fig. 3). It is seen that the length of dislocation line is $\simeq 10^{-3}$ cm. This is in agreement with the value ($l \simeq 10^{-3}$ cm) corresponding to the experimental elastic limit, which is the order of magnitude of the Frank network [10]. The very same type of behaviour has been observed in silicon using decoration technique [11]. Fig. 4 shows the two parts of slipped area, which has almost doubled back on itself. Finally the sections of dislocation join and annihilate one another (Fig. 5). This occurs because the two segments moving in opposite directions under the same stress have the same burgers vector but opposite line sense. Further formation of closed loops of dislocation and their expansion is as shown in Fig. 6. Fig. 7 depicts the expansion of a single closed loop with two emerging points of circular dislocation sites. These Frank–Read sources can also

Figure 8 A group of interacting dislocation spirals and loops (× 150).

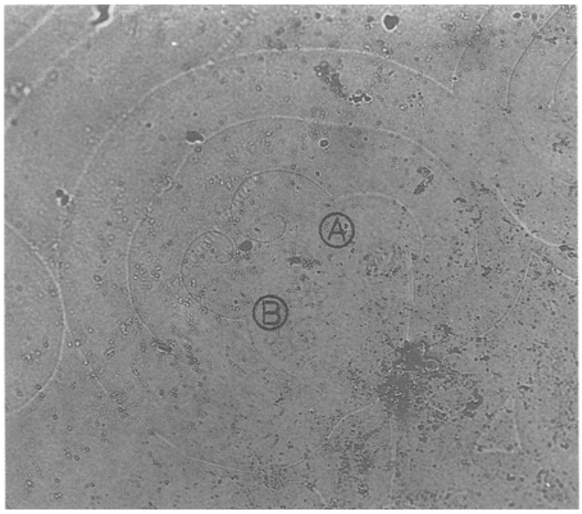

Figure 10 Expanding loops from two Frank–Read sources (A and B) of opposite sign (× 290).

Figure 9 Unequal movement of two dislocations (× 490).

Figure 11 An expanding spiral spreading from multiple sources (× 500).

be considered as two oppositely winding spirals joined together.

Many other interesting observations of dislocation loops were revealed on the basal plane of Bi_2Te_3. Fig. 8 represents the expansion of closed loops from multiple dislocation sources of various orientations lying in the same plane. This implies that the neighbouring parts of the same crystal plane have undergone slip in different directions. Further, it is also observed that the various sections of dislocation have bulged in different proportions. This may be due to the fact that the stress required for the expansion of each pair of unlike dislocation sources is not the same. Fig. 9 illustrates the unequal spiralling of the two pivot points of dislocation. The lack of stable pinning of anchor points and the interference from other dislocations can result in the formation of slightly asymmetric closed loops. Dislocation loops expanding around two Frank–Read sources (A and B) oriented face to face and sweeping out the whole plane are depicted in Fig. 10. Fig. 11 represents a dislocation spiral resulting from the operation of more than one pair of sources. Fig. 12 is an example of a single closed loop formed by the successive interaction between three Frank–Read sources. The individual nature of the central part of the sources could not be resolved in this photograph.

In many cases, the successive arms of the loops originating from different dislocations are observed to join with each other. This can be explained only if the heights of the different series of steps are the same, i.e., the dislocations are of the same strength.

4. Conclusions

The dislocation spirals and loops observed on the basal plane of Bi_2Te_3 are due to Frank–Read dislocation multiplication mechanism and the shape of these are shown to be in accordance with the theory. The internal stresses produced in this sample may be related to the constraining of neighbouring regions due to the thermal gradient. The stoichiometry of Bi_2Te_3 is of primary importance for the occurrence of

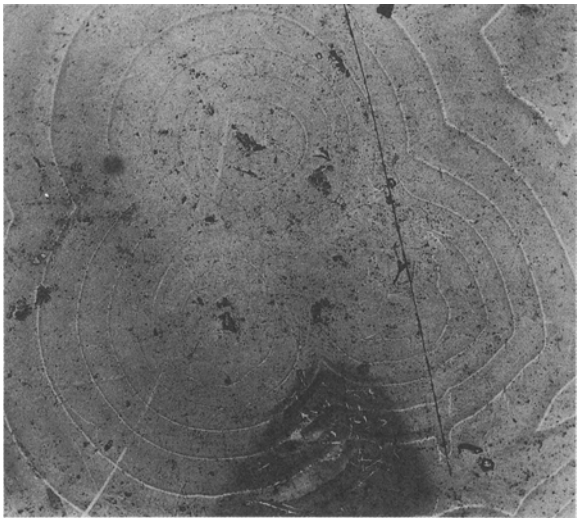

Figure 12 A single closed loop formed by the interaction between three Frank-Read sources ($\times 120$).

dislocation loops. The dislocation density is found to be $\sim 10^3\ cm^{-2}$.

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