CHAPTER 8

DISLOCATION ETCHING OF Sb_2Te_3 AND Sb_2Te_3 BASED ALLOY CRYSTALS

Although many sophisticated analytical techniques are now available for revealing dislocations, the chemical etching technique enjoys a special status among them because of its simplicity. Moreover, the method is quite rapid as compared to other methods. Chemical etching has a wide range of applications. However, in the present study, this technique has been employed for the determination of dislocation densities and thereby assessing the degree of crystal perfection. The discussion which follows is confined to the use of chemical etching for studying crystalline defects (dislocations in particular) only.

For the formation of etch pits at dislocation sites, the etching rate along the dislocation line is very essential to be greater than that on the rest of the surface. It has been proposed that increase in the etching rate along a dislocation line is due to the strain field associated with the dislocation in comparison with the normal strain-free surface.

There are various methods employed to establish a relation between etch pits and dislocations:

(1) Matching of etch pits on matched cleaved surfaces.

(2) Repetition of the pattern on successive etching or polishing and etching which allow the tracing of dislocations to some depth within the crystal.

(3) Introducing various types of plastic deformation and looking for corresponding increased etch pit density.

A brief review of the experimental results on dislocation etch pits in Antimony, Bismuth, Tellurium, Bi-Sb and Bi_2Te_3 crystals is presented below. Various workers[1-7] have reported etchants for Sb, Bi and Te. Wernick et al.[1] have studied etching of Antimony crystals using CP-4 reagent and superoxol. Etch pits were triangular in shape and randomly distributed over the surface. Closely spaced rows of etch pits suggestive of low angle boundaries similar to those in Germanium and Silicon were observed. Kosevich[2,3] used CP-4 reagent and studied the etch figures on Antimony crystals. He has also observed etch grooves connecting large pits. Shigetta and Hirmastu[4] were able to show that an etchant containing ferric chloride develops etch pits on the cleavage plane of Antimony. The motion of dislocations in Antimony crystals has been studied by Solfer and Startsev[5] by this technique. They observed wedge-shaped tracks which indicated the path of the motion of the dislocations and the point bottomed pits at their termination were interpreted as due to dislocations which were arrested. These traces were thought to be dislocation loops involved in the process of slip. On the cleavage of Bismuth, Lovell and Wernick[6] were able to obtain triangular etch pits which were attributed to dislocations as indicated by the deformation studies. Using 5% aqueous solution of $AgNO_3$, Pandya and Bhatt[7] have also observed the same kind of pits on (111) plane of Bismuth. Lovell et al.[8] were the first to report a chemical etchant composed of 3 parts of HF, 5 parts HNO_3 and 6 parts CH_3COOH which produced dislocation etch pits on cleaved faces of tellurium single crystals. Blakemore et al.[9,10], using concentrated sulphuric acid at about 150°C produced etch pits at dislocation sites on faces of melt grown tellurium crystals. Herrman[11] observed two types of etch pits, which were mirror images of each other; on the cleavage faces of tellurium on etching with hot concentrated sulphuric acid. Brown and Heumann[12] used 50% HNO_3 as an etchant, for revealing cellular boundaries in Bi-Sb single crystals. Various workers have reported etchants for Bi_2Te_3[13-15] . Drabble et al.[13] have used a solution of HCl , HNO_3 and H_2O to etch their iodine-doped Bi_2Te_3 samples. Sagar and Faust[15] have used a stock solution of 10% bromine in methanol + methanol for obtaining well defined dislocation etch-pits on Bi_2Te_3 cleavage planes. Sagar and Faust[16] have studied diffusion of Copper in Bi_2Te_3 crystals in the room temperature range by etching technique. Small etch pits due to Copper particles along dislocations were observed in samples in which Copper was diffused for a few hours at room temperature. It was further reported that such pits were not observed in samples in which Copper diffusion took place for a few days. Zhitinskaya[17] et al. have determined perfection of their Czochralski grown Sb_2Te_3 single crystals by evaluating the density of dislocations. They found that the density of dislocation in Czochralski grown crystals was 10^3 – 10^4 cm^{-2}, i.e., two orders less than the density of dislocations in crystals grown by directional crystallization method.

DEVELOPMENT OF AN ETCHANT

The inhomogeneities in the grown crystals are revealed by etching because reactions take place at inherently different rates at the inhomogeneity sites. The structural defects like point defects, line defects, inclusions, segregation area, etc., are selectively attacked by the etching reagent and as a consequence their precise locations are manifested finally by some visible etching characteristics, such as cavities, striations, local decolouration etc. Before etching, many of the inhomogeneities and defects associated with the section of interest may be small in size and even entirely invisible. But during etching, the area occupied originally by certain of these inhomogeneities will increase in size beyond their original dimensions and eventually reach a size which will be visible and amenable to detailed study with a variety of techniques.

The successful application of etching depends upon several factors. Some important factors are as follows:

1) The condition of the crystal surface that is to be etched.
2) Chemical composition of the etching reagent selected.
3) Temperature of the etching reagent selected.
4) The length of time for which the specimen is etched.

Etching reagent should possess the following characteristics:

1) The reagent should be of such composition that it will give good all round results and reveal the greatest number and variety of structural characteristics, defects and irregularities present. At the same time, it should be able to

distinguish its effect from those produced by any of the etchants which can attack on only definite type of defects. Thus, the selective etching should enable one to study only specific defects.

2) The composition of reagent should be simple and stable so that the concentration of reagent will not change appreciably upon standing or during use at room temperature and also if possible, at moderately higher temperatures.

3) At a particular temperature, the reagent should have constant characteristics, so that the etching condition can be easily reproduced. In the etching process the time of etching and the temperature are also important factors.

   (a) Temperature of etching: The rate at which the etching reagent attacks the specimen depends on the temperature at which etching takes place. The precise influence of temperature, however, varies according to the composition and previous history of the specimen. It is therefore desirable for obtaining reproducible results, to carry out etching experiments only at definite temperatures.

   (b) Time of etching: The etching time is perhaps one of the most important factors contributing to successful etching and attendant appearance of the structure enabling detailed study possible with the help of optical techniques. For example, for short time of etching as compared to that appropriate for a particular material, the etched structure will not be completely developed nor will the sufficient details revealed to permit accurate interpretation of the etched area. However, too long a time of etching is just as unsatisfactory as one too short, owing to details of the surface structure being thereby obscured to varying degrees and frequently some parts of the structure being completely obliterated. The time of etching depends on the conditions of the specimen [i.e. annealed, hardened etc.] and the temperature of the reagent.

4) The reagent, while acting on the specimen should not form products which would precipitate on the surface of the specimen considered, but must have such a composition that reaction products are immediately dissolved chemically or physically in the solution. They must possess closer affinity with the etchant than with the specimen.
5) The reagent should be non-injurious and non-toxic to the person conducting the work.
6) For orientation determination, the etchant should develop etch pits or facets with plane faces accurately parallel to crystallographic planes of low indices.

There is no report found in literature on dislocation etching of Sb_2Te_3 and based pseudobinary alloy crystals under present study. Looking to the requirements, discussed above, of the etchant and the surface to receive it, i.e., in the present case, cleavage planes of $Bi_xSb_{2-x}Te_3$ [x = 0, 0.2, 0.5 and 1], and $In_{0.2}Sb_{1.8}Te_3$ single crystals, numerous trials were taken and it was found that the etchant developed by the present Is well suited for revealing dislocations.

It is well known that for metals, the necessary ingredients of an etchant are generally an oxidant and a complexant which may, respectively, react with the specimen surface and dissolve the products formed. Mineral acids like HNO_3 and HCl and iodine and bromine are well known oxidants for etching of metals, alloys and intermetallics. In the present case also, they were found to work well. In the trials done by the author all the chemicals used were of AR grade and all the etching trials were carried out at room temperature on freshly cleaved surfaces.

The reagent consisting of 3 part iodine saturated in methanol, 0.4 part HCl (conc.) and 0.2 part HNO_3 (conc.) was found to be the most suitable for the etching experiments on the single crystals of $Bi_xSb_{2-x}Te_3$ (x = 0, 0.2, 0.5) and $In_{0.2}Sb_{1.8}Te_3$ grown by the Bridgman technique. The crystals were cleaved at room temperature with a sharp blade along (111) plane. The constant orientation of the cleaved plane along the entire length of the ingot indicated the sample to be necessarily a single crystal. No misorientation on the cleavage plane was observed under optical microscope. Always freshly cleaved surfaces were used for the etching experiments. These were etched in the above solution, rinsed in methanol and air-dried. The etching time may be varied from few seconds to 25 sec without corroding the surface to any objectionable extent. The etch patterns were studied by Vickers projection microscope. A typical etch pattern of Sb_2Te_3 to illustrate the etch pits is shown in Fig. 1. The figure shows the characteristic random distribution of sharp, point bottomed etch pits produced by the etchant in 20 seconds. The etch pits are triangular in shape indicating the 3 fold symmetry of the crystals under study. All the pits are almost of the same size, equilateral and having the same orientation. The etchant produces the triangular etch-pits reproducibly. This indicates the pits are likely to be dislocation etch pits. No change in the etch pattern was observed for $Bi_xSb_{2-x}Te_3$ (x = 0.2, 0.5) and $In_{0.2}Sb_{1.8}Te_3$ crystals. To test the etchant, the surface was scratched with a needle and etched. Fig. 2 shows a typical result obtained. It is observed that the etch-pits around the scratch are aligned into rows implying fresh dislocations generated by the deformation produced by the scratch. These rows have been observed always to be parallel to one or other of the edges of the triangular etch-pits. It is quite known that the slip mechanism of plastic deformation is responsible for giving rise to such dislocation rosettes. The tests like etching and matching of opposite counterparts of cleavage and successive etching have been carried out successfully. Thus the chemical etchant of composition mentioned above can be reliably used to reveal dislocations intersecting the cleavage plane.

The same etchant with a change in concentration has been used as an etchant for revealing dislocation in the case of $BiSbTe_3$ crystals.

A mixture of 5 parts saturated iodine methanol solution + 2 parts HCl + 1 part HNO_3 was found capable of revealing dislocations intersecting the cleavage surface of this crystal. The reliability of the etchant was confirmed by tests like etching and matching of counter cleavage surfaces, sequential etching, etc.

Fig.1

Fig.2

Fig.3 shows the etch patterns obtained on oppositely matched cleavage surfaces which were etched in the said etchant under identical conditions. The general matching of the etch-pits indicates that the etch-pits are necessarily at the dislocation sites. The occasional deviations in matching may be due to branching and bending of dislocations[15,18]. Sequential etching test, i.e., etching and observing the etch-pit site and size after different etching time intervals, was also carried out. The etch-pits retain their sites but grow in size with etching time, providing further evidence that the etch-pits are at dislocation sites.

Although the etch-pits are all triangular in shape, there are a few noteworthy differences in the etching characteristics of the cleaved counterparts (Fig. 3):

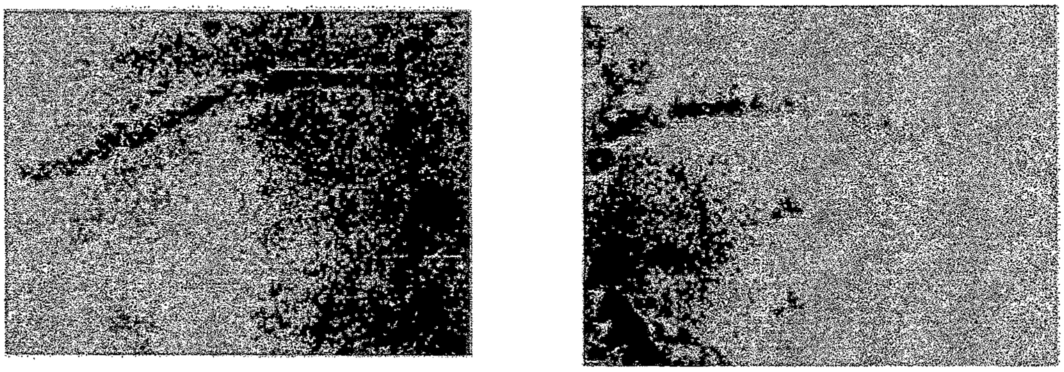
(1) The etch pit sizes are different.

(2) The relative orientation of the etch-pits is 180° instead of being mirror imaged.

(3) On one counterpart, the etch-pits are point-bottomed whereas on the other they are flat bottomed. (This may not be clear on the photograph but a close scrutiny in the microscope showed this).

These differences ought to indicate different structures of the cleaved surface pair. An attempt has been made here to invoke the structure and bonding differences between these surfaces.

Crystals of Sb_2Te_3 and Bi_2Te_3 belonging to the $R\bar{3}m$ (D_{3d}^5) space group are formed by layers normal to the c- axis and consist of stacks of five atomic planes arranged in the sequence: Te^1 - M - Te^2 - M - Te^1 (M= Sb, Bi)[19]. According to Drabble and Goodman[20], the two Te sites are not equivalent. Te^2 atoms have six M atoms as next neighbours and are coupled by covalent bonds with these M atoms. Te^1 atoms have only three next M neighbours in the same five-fold sandwich, but the M - Te^1 bonds are somewhat stronger than the pure covalent M - Te^2 bonds because of additional ionic contributions. According to Horak et al.[21], the V - VI^1 bonds are shorter than the V - VI^2 bonds in the case of Sb_2Te_3 and Bi_2Te_3. Further, the Sb -Te^2 bond is shorter than the Bi - Te^2 bond. The bond



x 800 x 800

Fig.3

lengths are given in Table 1. The structure can be assumed to be the same in the present case, which is a solid solution of Sb_2Te_3 and Bi_2Te_3 with equal atomic concentrations of Bi and Sb. Of the two M layers one would be Sb and the other Bi. Hence in view of the relative bond strength, it can be concluded that the crystals cleave across Bi - Te^2 layers. Thus while one cleavage surface consists of Bi atoms, its neighbouring cleavage counterpart must consist of Te^2 atoms. Owing to these chemical and structural differences between the cleavage counterparts, the etching rates and their anisotropies are expected to be different. This probably explains the difference in size and morphology of the etch-pits.

As for the relative 180° orientation of the pits on the cleavage counterparts, it should be noted that the space group of the crystal is $R\bar{3}m$, which implied the presence of 3-fold roto-reflection axis (instead of simple 3 fold axis) with the reflection plane normal to the 3 fold [111] axis. The effect of this roto-reflection axis on the etch-pits is to rotate the etch-pit by 120° about [111] axis and simultaneously to reflect it across the (111) plane which is the orientation of the cleavage plane. Since both types of crystals studied belong to the same space group, this particular etch-pit orientation effect is observed in all these crystals.

To determine the average dislocation densities of the crystals, the method of etch-pit count was used. The cleaved samples were etched as described above. The etch surfaces were observed under optical microscope at a magnification of 100. The etch pits in the observed surface area were counted. The surface area under the field of view was evaluated using a micrometer eyepiece with the least count 0.19 μ. The count was divided by the surface area. This process was repeated across the whole cleavage cross section and the dislocation density was averaged. Such averages were obtained for sections from the useful portions of the crystal ingots. The average dislocation density of the crystals grown by the Bridgman technique is given in Table 2. It can be observed that there is no systematic variation of dislocation density with the increase in Bi concentration in Sb_2Te_3 but addition of In in Sb_2Te_3 shows a tendency of reducing it. This may be

TABLE 1

Bond Lengths in Sb_2Te_3 and Bi_2Te_3

Distance between layers, Å		
$Sb-Te^1$	$Sb-Te^2$	Te^1-Te^1
3.06	3.16	3.64
$Bi-Te^1$	$Bi-Te^2$	Te^1-Te^1
3.04	3.24	3.72

TABLE 2

Dislocation Densities of Bridgman grown crystals

CRYSTAL	AVERAGE DISLOCATION DENSITY cm^{-2}
Sb_2Te_3	1.3×10^5
$Bi_{0.2}Sb_{1.8}Te_3$	1.4×10^5
$Bi_{0.5}Sb_{1.5}Te_3$	1.5×10^5
$BiSbTe_3$	1.4×10^5
$In_{0.2}Sb_{1.8}Te_3$	1.1×10^5

attributed to the increase in the ionicity of the bonds and hence bond strength since In is less electronegative as compared to Bi. However, it has been observed that over all the dislocation density for all the crystals grown by the Bridgman technique was of the order of 10^5 /cm^2 indicating no variation in crystallinity with Bi or In incorporation in Sb_2Te_3.

CONCLUSION

1) The reagent: 3 parts saturated solution of iodine in methanol + 0.4 parts HCl (conc.) + 0.2 part HNO_3 (conc.) works as dislocation etchant on the cleavage plane of the $Bi_xSb_{2-x}Te_3$ (x = 0, 0.2, 0.5) and $In_{0.2}Sb_{1.8}Te_3$ crystal while a reagent consisting of 5 parts saturated solution of iodine in methanol + 2 parts HCl + 1 part HNO_3, works as dislocation etchant on the cleavage plane of the $BiSbTe_3$ crystal.

2) The atomic configurations on the (111) and $(\bar{1}\,\bar{1}\,\bar{1})$ planes of $BiSbTe_3$ crystals have been used to explain the differences in the etch-pit morphologies on the cleaved couterparts.

REFERENCE

[1] Wernick, J. H. , Hobstetter, J. N. , Lovell, L. C. and Dorsi, D. (1958) J. Appl. Phys. 29, 1101.

[2] Kosevich, V. M. (1961) Sov. Phys. Cryst., 5, 715.

[3] Kosevich, V. M. (1961) Sov. Phys. Cryst., 6, 379.

[4] Shigetta, J. and Hirmastu, M. (1958) J. Phys. Japan, 13, 1404.

[5] Solfer, L. M. and Startsev, V. I. (1961) Sov. Phys. Cryst., 6, 457.

[6] Lovell, L. C. and Wernick, J. H.(1959) J. Appl. Phys., 30, 234.

[7] Pandya, N. S. and Bhatt, V.P. (1960) J. Sci. Ind. Res. 19B, 363.

[8] Lovell, L. L., Wernick, J. H. and Benson, K. S. (1958) Acta Met. 6, 716.

[9] Blakemore, J. S., Schultz, J. W. and Nomurn, K. C. (1960) J. Appl. Phys. 31, 226.

[10] Blakemore, J. S., Heaps, J. D., Nomura, K. C. amd Beardsley, L. P. (1960) Phys. Rev. 117, 687.

[11] Herrman, K. (1961) Phys. Status Solidi. 1, 254.

[12] Brown, D. M. and Heumann, F. K. (1964) J. Appl. Phys. 35, 1947.

[13] Drabble, J. R., Groves, R. D., Wolfe, R. (1958) Proc. Phys (London) 71, 430.

[14] Stickler, R. (1964) Acta Phys. Austriaca, 19, 5.

[15] Sagar, A., Faust, Jr. J. W. (1967) J. of Appl. Phys. 38, 482.

[16] Sagar, A. and Faust, J. W. (1967) J. Appl. Phys. 38, 3479.

[17] Zhitinskaya, M. K., Nemov, S. A., Rykov, S. A. and Ivanova, L. D. (1995) Proc. of 14th International Conference on Thermoelectrics, St. Petersburg, 60.

[18] Amelinckx, S. (1956) Phil. Mag. 1, 269.

[19] Wiese, J. R. and Muldawer, L. (1960) J. Phys. Chem. Solids, 15, 13.

[20] Drabble, J. R. and Goodman, C. H. L. (1958) J. Phys. Chem. Solids, **5**, 142.

[21] Horak, J., Stary, Z. and Klikorka, J. (1988) Phys. Stat. Sol. (b), 147, 501.