CHAPTER VI
STUDIES ON CHEMICAL ETCHING OF Bi-Sb CRYSTALS

The work reported in this chapter deals with the results from the etching of Bismuth-Antimony crystals. Chemical etching is an extremely complex phenomenon and is often influenced by a large number of factors. Among these are the nature of the individual crystals, crystalline perfection, crystallographic orientation, type and concentration of impurities in the crystals as well as in the etchant, the temperature and the hydrodynamics of the solid-liquid interface. Factors of importance to chemical etching can be distinguished as those predominantly
affecting the overall (macroscopic) rate of etching and those affecting primarily the microscopic nature of etching, that is the resulting microscopic nature of the surface. It is the latter phenomenon which is of interest in the present context.

Etching is often employed for the determination of dislocation densities and thereby assessing the degree of crystal perfection. But it has been pointed out that one-to-one correspondence between etch pits and dislocations has not been established conclusively. It is therefore an accepted fact that etch pits should not be attributed exclusively to dislocations without further verification. Such verification often poses numerous problems. For example, it may not be always possible to observe lineage boundary, long enough to facilitate the measurement of the tilt angle by X-ray diffraction, as has been employed by Vogel et al. Secondly, X-ray topography, if employed, reveals (often) the dislocations lying on the plane under observation, whereas etch pits indicate dislocations running perpendicular to the plane of observation. Further, differential etching being (often) anisotropic,
can not be employed in all planes and the anisotropy of dislocation densities is a major obstacle in the use of this method for verification.

For the formation of etch pits at dislocation sites, it is necessary that the etching rate along the dislocation line be greater than that on the rest of the surface. It has been proposed that the increased etching rate along a dislocation line is due to the strain field associated with the dislocation. Alternatively, the increased activity of dislocation lines is attributed to the presence of the impurities, preferentially segregated near the dislocation. Results of Lacombe et al.\textsuperscript{2,3,4} indicate that dislocations are revealed by etching only if they are decorated by impurities. Similar results have been obtained with certain etchants on Germanium crystals\textsuperscript{5}.

The impurity mechanism for the dislocation pit formation is quite plausible and consistent with electrochemical mechanism of dislocation, i.e. the impurities along the dislocation serve as localized anode, thus leading to the formation of pits. It is not plausible, however, that strain fields of
dislocation constitute a necessary or sufficient pre-requisite for the enhanced attack. There are no strain fields present in an array of dislocations forming a low angle boundary. Yet individual dislocations along such boundaries are as readily revealed by etching as are isolated dislocations. Similarly there are no strain fields at the intersection of screw dislocations with the surface and yet this type of dislocations are readily revealed by etching. Thus it is evident that the etching of dislocation poses quite a number of problems, in theoretical as well as practical aspects.

Nevertheless, etching is a valuable tool in revealing dislocations. Etching methods have been successfully developed for Germanium, Silicon, Silicon-Iron, Aluminium containing critical impurities, Zinc, Lithium fluoride, Silicon carbide, Cu 7.5 at.% Aluminium alloys, Bi$_{(2-y)}$Sb$_y$Te$_x$Se$_{(3-x)}$, Bi$_2$Te$_3$ etc. to mention only a few. In applying this technique various methods have been employed to establish a correspondence between etch pits and dislocations. They are:
(1) Perfect matching of etch pits on matched cleaved surfaces.

(2) Repetition of the pattern on successive grinding and etching which allows the tracing of dislocations to some distance within the lattice.

(3) Introducing various types of plastic deformation and establishing the agreement between theoretically estimated dislocation density and the measured etch pit density.

A brief review of the experimental results on dislocation etch pits in Antimony, Bismuth and Bi-Sb alloy crystals is presented below.

Wernick et al.\textsuperscript{16} 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 observed on Germanium and Silicon were observed. These boundaries were not long enough to permit X-ray
orientation measurements. However, these authors have derived a mathematical relation for the spacing of dislocation along intersecting low angle boundaries. It can be shown from Frank's boundary equation that a model having minimum free energy for dislocation tilt boundary must consist of an array of two kinds of parallel edge dislocations, which utilize two of the three $a/2$ [110] Burgers vector lying in the (111) planes. Thus if the boundary trace makes an angle $\theta$ with the nearest Burgers vector, then the other two Burgers vectors are used and the number of dislocations per unit length of the boundary is given by

$$\gamma = \frac{\theta}{\sqrt{3b}} \cos \phi$$  \hspace{1cm} (1)

Where $\theta$ is the angle of the tilt boundary. Considering the intersection of the three boundaries, in order that the sum of the three tilt angles may be zero, one boundary, say A, must have an opposite sense of tilt from the other two, say B and C, so that

$$\theta_A = \theta_B + \theta_C$$  \hspace{1cm} (2)
Combining equations (1) and (2)

\[ \frac{\gamma_A}{\cos \phi_A} = \frac{\gamma_B}{\cos \phi_B} + \frac{\gamma_C}{\cos \phi_C} \]  \hspace{1cm} (3)

The angle \( \phi \) is defined as that between the boundary trace and the nearest Burgers vector, and hence it can not be greater than 30°, so that \( \cos \phi \) is not very different from unity.

Therefore,

\[ \gamma_A = \gamma_B + \gamma_C \]  \hspace{1cm} (4)

i.e. the dislocation density in one row is the sum of the dislocation densities in the other two. When two boundaries meet at a point, \( \gamma_C = 0 \), and hence

\[ \gamma_A = \gamma_B \]  \hspace{1cm} (5)

Etch pit densities along intersecting boundaries were shown to satisfy the above relations (4) and (5), and hence it is reasonable to conclude that they are formed at the sites of the dislocations. In addition
to this, distribution of the etch pits along slip lines and the distribution in bent and annealed crystals confirm the above results.

Kosevich\textsuperscript{17,18} used CP-4 reagent and studied the etch features on Antimony crystals. He has also observed etch grooves connecting large pits, the origin of which is not completely understood. Shigetta and Hirmastu\textsuperscript{19} were able to show that an etchant containing ferric chloride develops etch pits on the cleavage plane of Antimony. The motion of the dislocation in Antimony crystals has been studied by Soifer and Startsev\textsuperscript{20} by this technique. They observed wedge-shaped tracks which indicated the path of the motion of the dislocations and wedge-shaped tracks having point bottomed pits at their termination which were interpreted as due to dislocations which were arrested. These traces were thought to be dislocation loops involved in the process of slip. They concluded that impurity decoration was not necessary to reveal the dislocations.
On the cleavage of Bismuth, Lovell and Wernick \(^{21}\), were able to obtain triangular etch pits which were attributed to the dislocations as indicated by the density and the deformation studies. Using 5\% aqueous solution of Ag\(\text{NO}_3\), Pandya and Bhatt \(^{22}\) have also observed the same kind of pits on (111) plane of Bismuth. Palatnik et al. \(^{23}\) have studied the formation of etch pits on (111) planes of Bismuth and Antimony, and on (0001) plane of Zinc by subjecting them to spark treatment and etching. They studied the distribution of dislocations in these planes. A three dimensional picture of the dislocation distribution was obtained by them in the vicinity of the point of attack on the crystal by the spark. Kosevich \(^{24}\) has studied the undulatory relief of Bismuth crystals by etching technique. He observed that the dislocation density is a periodic function having maxima coinciding with points of retardation of the movement of crack.

Little information is available on the etching of Bismuth-Antimony alloy crystals. Yim et al. \(^{25}\) used 20\% H\(\text{NO}_3\) as dislocation etchant to reveal
segregation. No detailed informations have been reported by him.

Brown and Heumann\textsuperscript{26} used 50\% HNO\textsubscript{3} as an etchant, for revealing cellular boundaries in Bi-Sb single crystals. He also used the solution containing 1 part HF, 3 parts HNO\textsubscript{3} and 20 parts water for cleaning the etched surfaces.

A systematic study of the development of a new etchant was undertaken and the results are compared with those reported by the earlier workers. In attributing the etch pits to dislocations, the following criteria are adopted.

(1) Matching of pits on cleavage counter parts should be reasonably good.

(2) Pit density should remain constant and should not increase after repeated etching.

(3) Wherever possible the density calculation should show reasonable agreement with theoretical estimate.
The nature and distribution of pits should agree with the earlier results which have been conclusively proved to be the dislocation sites.

Single crystals of Bi-Sb grown by the horizontal zone melting technique were cleaved at 0°C temperature with a sharp blade along (111) plane. Freshly cleaved faces were etched in the etchant for few seconds. They were then cleaned in running water rinsed in acetone and finally air dried. The etch patterns were studied by Vickers Projection Microscope. Most of the work was carried out on Bi$_{88}$Sb$_{12}$ alloy crystals. However, no change in the etch pattern was observed in the alloy range containing 1 at.% to 12 at.% Antimony.

Yim reported 20% HNO$_3$ as an etchant for checking microsegregation arising due to constitutional supercooling. In the present work an attempt is made to study the characteristics of the dislocation etchant.

Fig.VI-1 shows the characteristic random distribution of sharp, point bottomed etch pits produced by the etchant (20% HNO$_3$) in 5 seconds.
All the pits are almost of the same size. A small low angle boundary is also visible in the photomicrograph. The edges of the basal triangles of pyramidal pits are in the \(\langle110\rangle\) direction and their three oblique faces are parallel to the \(\{111\}\) planes as shown schematically in Fig.VI-2.

It is essential to establish the reliability of a particular etch for revealing dislocations on a crystallographic plane, before using that etch for dislocation studies in particular material. This requires some experiments to demonstrate that the characteristic pits produced by the etch on the crystal surface mark the sites where the dislocations intersect the surface. One of the methods of establishing the reliability of the etch for revealing dislocations which is valid for the cleavage plane, is to establish a one to one correspondence between the etch pits on the opposite halves of a cleavage. An experimental verification of such a one to one correspondence on the opposite cleavage plane is generally considered a quite adequate proof that the
pits produced on the cleavage plane do mark the sites of dislocations.

The etchant gives well defined pits on a clear background. Sometimes flat bottomed pits are observed, showing absence of dislocations. Fig. VI-3(a) is a photomicrograph of an etched surface by the etchant 20% HNO₃. All the etch pits are sharp and point bottomed triangular in shape. The cleavage counterpart of this surface etched by the same etchant [Fig. VI-3(b)] shows pyramidal pits with a few terraced pits. In regard to the formation of the terraced etch pits, there are two possible mechanisms. In the first case (Gilman²⁷) terraces are formed as a result of variation in concentration of impurities segregated at dislocations. Terraced pits can also be found if the dislocations are inclined to the surface (Faust²⁸). However, Figures VI-3(a) and 3(b) show exact one to one correspondence of the etch pits.

The orientation of the pits on the two opposite halves does not possess the mirror image
character pointing to the fact that the cleavage plane in Bi-Sb is not a reflection plane, and the etch pits would not in general possess the reflection symmetry about this plane. As a result the pits on the opposite cleavages are inverted with respect to each other about any of the binary axis [Figs. VI-3(a) and 3(b)].

Minor deviation from a perfect match between the etch pits on the two opposite halves of a cleavage are frequently observed. Figures VI-4(a) and 4(b) are the examples, where the etch patterns on the two halves show small deviation from identical mirror images. The photographs show a spot (surrounded by a rectangle) with deviation between the two patterns. The spot surrounded by rectangle shows a situation where one pit on one halve of the cleavage corresponds to a large flat bottomed pit with the small point bottomed pit at the centre, on the other halve. The situation can be explained by the hypothesis that the flat bottomed pit is the result of bending of the dislocation at the cleavage in a direction parallel to the cleavage plane, so that only one side of the
cleavage will have dislocations intersecting the cleavage surface and would thus form etch pits. Mismatch due to bending of dislocations at the cleavage plane has been reported by Sagar and Faust in Bi₂Te₃ and Bhatt et al. in Bi-Sb crystals.

In addition to the randomly distributed etch pits, rows of closely spaced etch pits on cleavage surface and sometimes branching of rows were also observed as shown in Fig. VI-5. These rows resemble the low angle boundary observed in Antimony by Lovell and Wernick. The linear density of etch pits along these boundaries satisfies equation (4) and are thus due to dislocations.

A freshly cleaved surface of the crystal was indented by microhardness tester attached to Vickers Projection Microscope (load 100 gm) at room temperature. The etching of this surface is done and etch pits along the glide bands are shown in Fig. VI-6. High pit density is observed around the indentation mark. This may represent the production of new dislocations during indentation.
From these observations it seems that the etchant reported by Yim is capable of revealing the sites of emergence of fresh and aged dislocations inclined to the (111) plane of Bi-Sb crystals.

Kosevich\textsuperscript{31} reported the etchant composed of 1 part nitric acid and 5 parts acetic acid to reveal dislocations in Bismuth crystals. An attempt was made to study the capability of this etchant to reveal dislocations in Bi-Sb crystals. Nitric and acetic acid used are of A.R. Quality. Fig.VI-7 shows random distribution of sharp point bottomed and terraced etch pits obtained after etching the specimen for one or two seconds.

The indices of the planes of the etch pits are determined stereographically. The edges of the triangular etch pits are in \langle110\rangle direction and three planes of the point bottomed etch pits developed on etching are parallel to \{111\} slip planes as shown in Fig.VI-2.

Figures VI-8(a) and 8(b) represent a pair of matched cleavages etched in the above etchant. One
face was intentionally etched for a longer time than its counterpart. Photomicrographs show a general correspondence of etch pits on the two opposite halves of a cleavage. The discrepancy may be due to the branching and bending of dislocations at or near the cleavage plane during the act of cleavage.

A low angle boundary consisting of closely spaced triangular pits obtained after two seconds etching is shown in Fig. VI-9(a). Almost all the pits are triangular in shape. The same area of Fig. VI-9(a) after the second etch is shown in Fig. VI-9(b). Almost all the pits have increased in size but the number of etch pits have remained the same. This is also true for the pits lying along the low angle boundary.

In addition to the randomly distributed etch pits found on the cleaved surfaces, rows of closely spaced pits and branching of the rows were observed as shown in Fig. VI-10. These rows resemble the low angle boundaries observed in other materials by various workers, and they are found to obey equation (4).
With a view to find whether fresh dislocations produced by deformation can be revealed by the etchant, etching of indented crystal surface was undertaken. 'Rosettes' of dislocations are clearly visible around the indentation mark in Fig.VI-11. Pit density is maximum around the indentation mark. Arrangement of etch pits in three \( \langle 110 \rangle \) directions indicates that the slip planes of \( \{111\} \) family are responsible for such glide deformation. This shows the capability of the dislocation etchant, reported by Kosevich, for revealing fresh dislocations in Bi-Sb crystals. Results are again similar to those observed on Bismuth and Antimony crystals.

It can be concluded from the above observations that the etchant reported by Kosevich only reveals dislocations inclined to the cleavage plane by producing point bottomed, terraced and flat bottomed etch pits. Addition of acetic acid has increased the rate of attack in comparison to the etchant reported by Yim. Etching time for developing well defined etch pits is one to two seconds. However, deep etching of the crystal surface is associated with the formation of white film on the surface, which irregulates the rate of attack.
This results in the formation of uneven surface.

Longer etching time is advantageous for studying dislocation motion, and the dislocation structure in depth on successive etching. An attempt was therefore made to develop an etchant which can be used for longer times without destroying the reflectivity of the surface and which can be used to study the dislocations in the cleavage plane. The results of the systematic study of the development of a new chemical etchant is presented below.

**Development of an etchant**

The inhomogeneities in a crystal are revealed by etching only because they react at inherently different rates with the usual etching reagents. The structural defects (e.g. point defects, line defects etc.), inclusions segregated area etc. are selectively attacked by the etching reagent and as a consequence their precise locations are manifested finally by some visible etching characteristic, such as cavities, striations, local discolouration etc. Before etching many of the inhomogeneities and defects associated with the section of interest may be extremely small in size even entirely invisible. However, during
etching, the areas 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 under a variety of optical techniques.

The successful application of etching depends upon several factors. Among them important factors are as follows:-

(i) Condition of the metal surface that is to be etched.

(ii) Chemical composition of the etching reagent selected.

(iii) Temperature of the etching reagent selected.

(iv) The length of the time, the specimen is etched.

As far as the etching reagent is concerned, it 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, this selective etching should enable one to study only specific defects.

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

(3) The reagent should have constant characteristics at a particular temperature so that the conditions of etching can be easily reproduced.

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

(ii) Time of etching:—The time of etching is perhaps one of the most important factors contributing to successful etching and attendant appearance of the structure enabling their detailed study possible with the help of optical techniques. For example, if the time of etching is short as compared to that appropriate for a particular material, the etched structure will not be completely developed nor will there be 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 upon the conditions of the specimen (normalized, hardened, etc.) and the temperature of the reagent.
(4) The reagent, while acting on the specimen should not form products which will 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 the crystallographic planes of low index.

Looking to the above requirements of the etchant and the surface to receive it (in the present case cleavage plane of Bismuth-Antimony single crystals), it was found after several trials that the etchant developed by the present author possessed most of the properties discussed above and was well suited for revealing dislocations.
The etchant is composed of (i) nitric acid, (ii) tartaric acid, and (iii) water. Different concentrations of the constituents were tried by varying one and keeping other two constant for getting sharp point bottomed etch pits. Results are tabulated in Table VI-1. It is found that the dislocation etchant composed of 4 parts nitric acid (A.R. Quality, 70%), 7 parts tartaric acid (saturated solution) and, one part water, reveals good, sharp and point bottomed etch pits. Fig. VI-12 shows the random distribution of sharp and point bottomed etch pits. Profile shift shows that they are pits and not hillocks (Fig. VI-13). The planes of the triangular etch pits developed on etching in the above reagent are parallel to the \( \{111\} \) planes and the edges of the pits are in \( \langle 110 \rangle \) directions.

The author has studied the chemistry of the etchant and it is found that the shape of the pit is controlled by the composition of the nitric acid, which works as an oxidizing agent. Some typical triangular pits developed by changing the concentration of nitric acid are shown in Fig. VI-14. It is the mixture of etch pits of different shapes and size.
### TABLE VI-1

**EFFECT OF THE ETCHANT COMPOSITION ON THE MORPHOLOGY OF ETCH PITS (AT ROOM TEMPERATURE)**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Etchant composition in parts by volume</th>
<th>Etching time in seconds</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nitric acid (70%, A.R. Quality)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tartaric acid (saturated solution)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>9</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>9</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>9</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>10</td>
<td>3</td>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td>11</td>
<td>3</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td>12</td>
<td>3</td>
<td>10</td>
<td>1</td>
</tr>
</tbody>
</table>

contd...
<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Etchant composition (Nitric acid + Tartaric acid in parts by volume)</th>
<th>Etching time in seconds</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>0 Nitric acid + 7 Tartaric acid (saturated solution)</td>
<td>60</td>
<td>No pits</td>
</tr>
<tr>
<td>14</td>
<td>2 Nitric acid + 7 Tartaric acid (saturated solution)</td>
<td>30</td>
<td>Mixture of different shaped etch pits (Fig. VI-14).</td>
</tr>
<tr>
<td>15</td>
<td>4 Nitric acid + 7 Tartaric acid (saturated solution)</td>
<td>10</td>
<td>All the pits are sharp and triangular in shape (Fig. VI-12). Reveal dislocations.</td>
</tr>
<tr>
<td>16</td>
<td>5 Nitric acid + 7 Tartaric acid (saturated solution)</td>
<td>8</td>
<td>Elongated triangular pits.</td>
</tr>
<tr>
<td>17</td>
<td>7 Nitric acid + 7 Tartaric acid (saturated solution)</td>
<td>5</td>
<td>Surface corroded.</td>
</tr>
<tr>
<td>18</td>
<td>4 Nitric acid + 7 Tartaric acid (saturated solution)</td>
<td>10</td>
<td>Triangular pyramidal pits.</td>
</tr>
<tr>
<td>19</td>
<td>4 Nitric acid + 7 Tartaric acid (saturated solution)</td>
<td>10</td>
<td>All the pits are triangular pyramidal in shape. Reveal dislocation.</td>
</tr>
<tr>
<td>20</td>
<td>4 Nitric acid + 7 Tartaric acid (saturated solution)</td>
<td>20</td>
<td>No pits.</td>
</tr>
</tbody>
</table>
The stereographic method suggested by Reed-Hill was employed to detect the planes of the etch pits developed on etching. The existence of high index planes like (214), (212), (421), (212) and (412) are observed.

It seems that nitric acid reacts with Bi-Sb crystal forming oxidized products. These products are either soluble in tartaric acid directly or after forming complexes. Probably tartaric acid works as a complexing agent. It is clear from the data presented in Table VI-1 that the time of etching for developing well defined sharp triangular etch pits depends upon the amount of tartaric acid. This suggests that the complexing agent controls the rate of attack. Presence of water regulates the necessary dilution required for good etch pits.

In addition to this, the etchant has two more important characteristics:

1) Starting of the reaction is characterized by the evolution of bubbles from the surface.

2) With the progressive etching of the specimen the surface is not tarnished and does not become too coarse to be unsuitable for studies in depth and extension.
The energy which must be supplied to the reacting substances to make them capable of chemical transformation into the products is called the activation energy. Arrhenius suggested that the specific rate of a chemical reaction must be a linear function of the reciprocal of the absolute temperature. Mathematically, \( K = A \cdot e^{-\frac{E}{RT}} \), where \( K \) = reaction rate constant, \( A \) = a constant and \( T \) = absolute temperature.

The activation energy can be calculated from the slope of the curve of \( \log K \) vs \( 1/T \). In the present case the activation energy of the new etchant is found to be \( \sim 5 \text{ K.Cal/mole} \).

One to one correspondence of etch pits on the opposite matched cleavage face is shown in the photomicrographs Fig.VI-15(a) and 15(b). Almost all the pits are sharp and perfectly pyramidal in nature. Few terraced pits are also visible in the photomicrograph. Some discrepancy from the perfect match is due to branching of dislocations at the cleavage plane.

Figures VI-16(a) and 16(b) represent the etch pattern on the matched cleavage faces. One face of the crystal was intentionally etched for a longer time.
to get better contrast. The general correspondence of etch pits is visible. In Figures VI-16(a) and 16(b) a point bottomed pit represented by 'A' on one cleavage face corresponds to three point bottomed pits on the opposite cleavage face. This may be due to the branching of the dislocations at the cleavage plane as shown schematically in Fig.VI-16(c). Pits represented by 'B' are isolated pits on one face corresponding to none at all on the opposite cleavage face. This may be due to bending of dislocation line very near to the cleavage as shown schematically in Fig.VI-16(c). Pits represented by 'C' are point bottomed pits on one cleavage face corresponding to flat bottomed pits on its counterpart. This discrepancy may be due to the bending of the dislocation line deep to the cleavage plane, as shown schematically in Fig.VI-16(c).

Figures VI-17(a) and 17(b) show the etch pattern of the same area after etching for 10 seconds and 15 seconds respectively. Point bottomed and flat bottomed pits are clearly visible in the photomicrographs. Almost all the pits have increased in size and the number of pits are practically constant. This shows that the pits are at the specific defects like dislocations.
Fig. VI-18 shows the intersecting rows of etch pits. These rows resemble to the low angle boundary observed by Wernick et al., in Antimony single crystals. During further investigation on one of the cleavage faces investigated, a large number of rows of pits were found intersecting and forming a number of junctions with three boundaries each. Thus Fig. VI-19 shows five rows of pits intersecting to form two triple junctions. In this figure the rows of pits are numbered for two junctions. The results are tabulated in Table VI-2.

It is interesting to find that for a particular junction, the density of pits in one row equals the sum of the densities in the other two rows at each junction, even though both junctions are interlocked with a common row. Patel and Desai have observed large number of rows of etch pits intersecting and forming a number of junctions with three boundaries each in chemically etched synthetic Calcium Fluoride single crystals.

Fig. VI-20 represents two sets of two parallel rows of pyramidal etch pits produced by etching the freshly cleaved surface with the above etchant. These rows are surrounded by point bottomed and terraced etch pits. Fig. VI-21 shows etch pits along intersecting
# TABLE VI-2

**ETCH PIT DENSITY/UNIT DISTANCE ALONG LOW ANGLE BOUNDARIES**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Number of Node</th>
<th>Row of etch pits</th>
<th>Number of pits per unit distance</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>A</td>
<td>2</td>
<td>$\gamma_A + \gamma_B = \gamma_C$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>C'</td>
<td>2</td>
<td>$\gamma_{C'} + \gamma_{D'} = \gamma_{E'}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D'</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>E'</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>
glide bands. The above observations indicate that the new etchant is capable of revealing some finer details.

The (111) plane is a plane of easy glide. This plane happens to be also the cleavage plane in this material. When the crystal is cleaved at 0°C it is likely that the edge dislocations may move and if there is some hindrance to the motion, like dislocation net or an impurity atom, the moving dislocation will pile up against this obstacle. The dislocation pile up in [011] direction is shown in Fig. VI-22(a) which shows rows of triangular etch pits. These pile ups are probably ideal ones since the relation \( i \propto \sqrt{x_i} \) (Tables VI-3, 4 and 5) is found to be satisfied by them. Here \( x_i \) are the successive distance of individual dislocations from a selective origin and \( i \), the index of dislocation. Figs. VI-22(b), 22(c) and 22(d) show the plot of \( i \) vs \( \sqrt{x_i} \) for three boundaries A, B and C of Fig. VI-22(a).

Similar results have been reported by Amelinckx et al.\(^{36,37}\) in Silicon Carbide, and Sagar et al.\(^{38}\) in \( \text{Bi}_2\text{Te}_3 \) crystals.
### TABLE VI-3

<table>
<thead>
<tr>
<th>Row of etch pit</th>
<th>Index of dislocation (i)</th>
<th>( \sqrt{x_1} ) in cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.19 \times 10^{-1}</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.69 \times 10^{-1}</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2.11 \times 10^{-1}</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2.39 \times 10^{-1}</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.56 \times 10^{-1}</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>2.84 \times 10^{-1}</td>
</tr>
</tbody>
</table>

### TABLE VI-4

<table>
<thead>
<tr>
<th>Row of etch pit</th>
<th>Index of dislocation (i)</th>
<th>( \sqrt{x_1} ) in cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.15 \times 10^{-1}</td>
</tr>
<tr>
<td></td>
<td>2</td>
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<td></td>
<td>3</td>
<td>2.23 \times 10^{-1}</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2.45 \times 10^{-1}</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.78 \times 10^{-1}</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>2.98 \times 10^{-1}</td>
</tr>
<tr>
<td>Row of etch pit</td>
<td>Index of dislocation (i)</td>
<td>$\sqrt{x_i}$ in cm</td>
</tr>
<tr>
<td>----------------</td>
<td>--------------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>C</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>$1.38 \times 10^{-1}$</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>$2.12 \times 10^{-1}$</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>$2.44 \times 10^{-1}$</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>$2.70 \times 10^{-1}$</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>$2.83 \times 10^{-1}$</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>$2.93 \times 10^{-1}$</td>
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<tr>
<td></td>
<td>21</td>
<td>$3.19 \times 10^{-1}$</td>
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<tr>
<td></td>
<td>23</td>
<td>$3.38 \times 10^{-1}$</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>$3.77 \times 10^{-1}$</td>
</tr>
</tbody>
</table>
Dislocation net work in cleavage plane

The etchant is also capable of revealing the dislocations lying in the cleavage plane as etch grooves. A typical example is shown in Fig. VI-23. The etch grooves in the figure end at the points marked by small triangular pits. These small pits at the ends of the grooves have pointed bottoms.

The cleavage plane being a plane of easy glide in Bi-Sb crystals, the dislocation net will spread in this plane over long distances. Fig. VI-24 shows such dislocation net revealed after etching the cleavage plane for 10 seconds in the above etchant. The salient features are the twisting due to interaction between them and branching of dislocation in the (111) plane. Such dislocation nets were reported by Sagar and Faust in Bi$_2$Te$_3$, and Williams in GaSe crystals.

Fig. VI-25 shows etch grooves revealed due to the dislocations in the cleavage plane intersected by dislocations inclined to the cleavage plane as revealed by triangular etch pits. The triangular etch pits are observed at the nodes of the etch grooves and also at the ends of the etch grooves. Fig. VI-26 is
a typical photomicrograph showing the presence of the triangular etch pits on the network of etch grooves.

Figures VI-27(a) and 27(b) show the effect of successive etching of the etch grooves and pyramidal pits on the cleavage plane. Fig.VI-27(a) shows the etch pits and grooves after first etching. On further deep etching the grooves disappeared as shown in Fig.VI-27(b). Polishing effect of the etchant is clearly visible in the photomicrograph.

The above experiments suggest that the dislocations in the cleavage plane are revealed as etch grooves in the cleavage plane, while the triangular pits are at the sites of inclined dislocations.

Single crystal specimens of Bi-Sb were kept at a temperature of about 250°C in vacuum (of the order of $10^{-4}$ mm of mercury) for a few days and quenched by cooling them to room temperature in a few minutes. Samples were then cleaved and subsequently etched in the above etchant for
10 seconds. Sets of curved dislocation lines presumably originating from some unidentified sources were often observed in almost all samples.

Some typical curved dislocation lines are shown in Figures VI-28 to VI-33.

Fig. VI-28 shows a dislocation spiral intersected with small pyramidal pits. The pyramidal pits are at the sites of the emergence of inclined dislocations to the cleavage plane. The background of the photomicrograph is very clear. Fig. VI-29 shows another example of two spiral dislocations of the same sign originating from a single point 'A', and meeting at the point 'B'. The black and white contrast of the spiral is due to the oblique illumination. Fig. VI-30 shows an interesting example of interaction between dislocation loops originating from two different sources. The outer loop is formed due to the annihilation of the inner expanding loops. Small dislocation loops of various size are also visible in the background. Three closely spaced loops of different sizes encircled by a large loop is visible in Fig. VI-31. This may be due to the expansion of the outermost loop from three
closely spaced sources. The near-lying portions of the three loops annihilate each other during interaction, which might have resulted in the formation of a single outermost loop. Fig.VI-32 shows the example where the expanding loops from a source encircles a point bottomed etch pit. A typical example of interaction between two dislocation loops originating from two different sources are shown by 'A' in Fig.VI-33(a). Fig.VI-33(b) represents a dislocation spiral touching an etch groove at the point 'B'.

On deep etching the loops and spirals were completely disappeared. This may be due to the fact that the loops and spirals are in the cleavage plane.

These loops and spirals were observed only on quenched specimens. Spirals and loops were never observed on the specimens which were not subjected to heat treatment, and quenching. The exact origin of spirals and loops is not completely understood at present.

However, it seems that the dislocations are formed during growth by some mechanism and the
presence of vacancy aggregates which is only possible on quenching may be responsible for the existence of dislocation loops in quenched specimens.

Some of the quenching experiments resulted in decoration of the dislocations by some unidentified impurity. The impurity could have been introduced by the contamination of the sample surface or from the surface of the pyrex tube. This impurity diffused in the lattice at high temperature, but precipitated along the dislocation due to decreasing solubility in the lattice on cooling. Fig.VI-34 shows such an example. The sample was cleaved after quenching and then etched. The etch pits in Fig.VI-34 are seen to line up all along the loop, as the impurity precipitates. It may be further pointed out here that when the samples were kept for a few weeks at room temperature and again etched the freshly cleaved surface still revealed pits due to this unidentified impurity decorating the dislocation grooves. The phenomena can be explained as under:-
It is already pointed out (Fig.VI-29) that the dislocations are formed during growth by some mechanism and the presence of vacancy aggregates which is only possible on quenching may be responsible for the existence of dislocation loops. In the present case (Fig.VI-34) it seems that unknown impurities have precipitated along the dislocation loop, formed by vacancy aggregates on cooling the specimen rapidly. These impurity precipitates are revealed on etching.

Above results show the capability of the etchant, developed by the author, for revealing dislocations in the cleavage plane and inclined to the cleavage plane. Such etch grooves, dislocation spirals and loops were never observed on etching the specimens in the etchants reported by the previous workers.

Sagar and Faust have studied diffusion of Copper in Bi$_2$Te$_3$ crystals in the room temperature range by etching technique. Small etch pits due to Copper particles along the 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 along the dislocations in
samples in which Copper diffusion took place for a few days. These authors suggested that pits observed for short diffusion time represent Copper diffusion along the dislocations and no such evidence was found for Copper diffusion along dislocations at high temperature range.

The present author therefore thought that the diffusion of Copper in Bi-Sb crystals may be employed to study the dislocations in the cleavage plane by etching technique although no detailed information about the diffusion of Copper in Bismuth-Antimony crystals is available in the literature.

Bi$_{88}$Sb$_{12}$ crystals were cut in rectangular shapes, with the cut side perpendicular to the cleavage plane. The samples were washed in distilled water, rinsed in acetone and then etched to remove some of the damaged surface resulting from cutting. The samples were then rinsed in high purity methanol. A thick film of Copper was uniformly deposited on one of the cut sides of the samples, using Edward Coating Unit. The samples
were kept at 65°C temperature for 45 minutes to allow the Copper to diffuse into the samples. The samples were then freshly cleaved and etched by the newly developed etchant for 10 seconds. The etched cleavage surfaces were then examined by the Vickers Projection Microscope to observe penetration of Copper in the samples.

The etched surfaces of the samples in which Copper was allowed to diffuse were found to be full of small etch pits. These etch pits seemed to line up along the etch grooves which mark the dislocations in the cleavage plane. Density of the etch pits was found to decrease with the increasing distance from the Copper coated end of the sample. Figures VI-35 to VI-38 show the results from a sample which was kept at about 65°C for 45 minutes after Copper plating. Figures VI-35 and VI-36 show a situation where it is difficult to judge whether a pit is due to some precipitate or a dislocation. Figures VI-37 and VI-38 show etch grooves and etch pits in different area of the same specimen as one moves progressively away from the Copper coated end.
Pit density along the etch grooves is found to decrease with increasing distance from the Copper coated end.

On deep etching the pits due to precipitates do not grow much in size.

Crystals showing Copper diffusion profiles, similar to that in Fig. VI-35, were kept at room temperature for about five days. The samples were then freshly cleaved and etched. No etch pits, suggestive of Copper precipitates were found on these samples.

For further study, a Copper coated sample was kept at 250°C for about few minutes in vacuum in a sealed pyrex tube, and then quenched to room temperature. An examination of a freshly cleaved surface by etching failed to reveal any decoration of dislocation. These observations suggest that Copper diffusion at high temperature and for longer times is dominated by lattice diffusion of Copper which results in the formation of an alloy, rather than to precipitate out of the lattice on cooling.
It seems that the phenomenon of diffusion of Copper in Bi-Sb crystals can be employed to study the dislocations in the cleavage plane.

To study the characteristic of a new etchant it is very instructive to compare the etch pits produced by different etchants on the same area. Fig.VI-39 shows characteristic random distribution of etch pits and low angle boundary obtained after etching the specimen by the etchant reported by Yim et al. (20% HNO₃) for five seconds. Slight shift in the position of the centroid is visible in the photomicrograph. Background of the photomicrograph is very clear. The sample was polished electrolytically and etched again by the etchant reported by Kosevich. A careful examination of the photograph reveals that the low angle boundary appears faithfully (Fig.VI-40). Some discrepancies in the randomly distributed point bottomed pits are observed. All pits are small in size with a slight shift in the position of the centroid. Then the specimen was electropolished and re-etched by the new etchant (4 parts nitric acid + 7 parts tartaric
acid + 1 part water) for ten seconds. Fig.VI-41 shows the same region of Fig.VI-39. The new reagent has the advantage that the surface remains bright and etching rate is slow. The dislocations revealed by the above etchants (Figs.VI-39,40 and 41) are inclined to the cleavage plane, which is responsible for the slight shift in the position of the centroid observed in the above photomicrographs.

The fact that the etch pit structure is similar after repeated polishing and etching is also suggestive of etch pit association with dislocations revealed by all the three etchants.

Results obtained by the above mentioned etchants are given in tabular form (Table VI-6).

**Conclusions**

The following conclusions can be drawn from the results presented above.

(1) Dislocations can be revealed by etching of the various reagents mentioned above.

(2) The etchants reported by Yim and Kosevich reveal only dislocations inclined to the cleavage plane.
(3) Deep etching with Kosevich etchant results in the formation of uneven crystal surface.

(4) The etchant developed by the author has two more important characteristics:
   (i) Starting of the reaction is characterized by the evolution of bubbles from the surface.
   (ii) With the progressive etching of the specimen, the surface is not tarnished and does not become too coarse to be unsuitable for studies in depth and extension.

(5) The etchant developed by the author is capable of revealing dislocations in the cleavage plane, dislocations inclined to the cleavage plane, dislocation spirals and loops in the cleavage plane.

(6) The etchant is very sensitive to reveal surface damage.

(7) The diffusion of Copper can be employed to study the dislocation in the cleavage plane by etching technique.
RESULTS OF ETCHING WITH THREE DIFFERENT ETCHANTS

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Etchant Description</th>
<th>Minimum etching time in seconds</th>
<th>Pit shape</th>
<th>Planes and direction of the etch pits</th>
<th>Pit density</th>
<th>Remarks</th>
<th>Reference in text</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20% HNO₃ (W.M. Yim et al.)</td>
<td>5</td>
<td>Triangular pyramidal</td>
<td>Planes: {111} family, Directions of the edges: {110} directions</td>
<td>$10^5$/cm²</td>
<td>Reveals only dislocations inclined to the cleavage plane.</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>1 part nitric acid + 5 parts acetic acid (V.M. Kosevich)</td>
<td>1-2</td>
<td>Triangular pyramidal</td>
<td>&quot;</td>
<td>$10^5$/cm²</td>
<td>Reveals dislocations inclined to the cleavage plane. Etching time is very short.</td>
<td>31</td>
</tr>
<tr>
<td>3</td>
<td>4 parts nitric acid (70%) + 7 parts tartaric acid (saturated solution) + 1 part water</td>
<td>10</td>
<td>Triangular pyramidal</td>
<td>&quot;</td>
<td>$10^5$/cm²</td>
<td>Reveals dislocations in the cleavage plane, dislocation loops, spirals and inclined dislocations. Surface remains bright. This etchant has some polishing effect. Etching time is long and hence the etchant can be employed for the study of dislocation motion.</td>
<td>30</td>
</tr>
</tbody>
</table>
REFERENCES


