CHAPTER - VII

CHEMICAL ETCHING OF SnSe AND SnS SINGLE CRYSTALS
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This chapter deals with the results from the etching of cleavage planes of SnSe and SnS single crystals. No systematic study on chemical etching of SnSe and SnS single crystals has so far been reported in literature, except for an etchant for SnSe cleavage reported by Bhatt et al\(^{(1)}\). The present author has developed chemical etchants for the cleavage faces of these crystals. The results obtained with these etchants are discussed. The etchants developed have been used to assess the perfection of crystals.

Though many sophisticated analytical techniques for revealing dislocations are now available, 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. It is used:

(a) For revealing defects in the crystalline materials and to study the behaviour and mode of formation of dislocations.

(b) For orientation determination in conjunction with optical goniometry.

(c) For preparation of clean surfaces.
(d) To obtain reproducible electrical properties of semiconductors.
(e) To determine impurity distributions.
(f) For controlled removal of material.

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. Therefore it is an accepted fact that chemical etching is a simple, rapid and valid method revealing dislocations which makes it a valuable tool for studying perfection and plasticity of crystalline materials.

Various methods have been employed to establish a relation between etch pits and dislocations:

1) Perfect matching of etch pits on matched cleaved surfaces.
2) Repetition of the pattern on successive etching or polishing and etching which allows 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.
DEVELOPMENT OF A NEW 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 under 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 their 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 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 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.
Looking to the above requirements of the etchant and the surface to receive it [i.e. in the present case, cleavage planes of SnSe and SnS single crystals], numerous trials were taken and it was found that the etchants developed by the present author possess most of the properties discussed above and were 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. It was also observed that the crystal surface in question has a high tendency to corrode and frequently to capture the reaction products, as also evident from the earlier reported results on etching. This fact poses a severe difficulty in developing a successful etchant. 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.

**Etchant For SnSe :-**

For the cleavage plane of SnSe, after a numerous trials with HNO$_3$, H$_2$O, I$_2$ and methanol it was found that an appropriate mixture of I$_2$ in methanol and HNO$_3$ (70%) gives good results of dislocation etching. Some
of the systematic stages of trials are presented in Table (1). Thus, the etchant consisting of 25 parts of saturated solution of I$_2$ in methanol, 50 parts of methanol and 1 part of concentrated HNO$_3$ (70 %) is capable of producing well defined etchpits. For testing the etchant, the tests like matching of etchpits on cleavage counter pants, successive etching of the surface etc. were conducted. Fig. 2(a) and 2(b) show the etch patterns on the oppositely matched cleaved faces. Some mismatch of pits may be due to high dislocation mobility (2) resulting into rearrangement of dislocations due to uneven stresses developed at the time of cleaving the specimen. Branching and bending of dislocations may also be responsible for this (3). Nevertheless, there is a quite good general correspondence between the etch pits on the matched faces indicating the etchant to be a dislocation etchant.

The test of successive etching is based on the fact that a dislocation line cannot terminate within the crystal. Fig. 3 (a) and (b) show the etch pit patterns obtained on the same region on the same cleavage surface etched for 15 sec. and 30 sec, respectively, using this etchant. It can be seen that the pits have to some extent increased in size with the etching time, whereas, their number has remained the same, indicating thereby that the pits are at the sites of emergence of dislocations.

Fig. 4 shows a typical configuration of etch pit distribution. There are seen distinct rows of closely spaced etch pits as well as branching of
TABLE - 1

EFFECT OF ETCHANT COMPOSITION ON ETCHING CHARACTERISTICS

<table>
<thead>
<tr>
<th>ETCHANT</th>
<th>TIME</th>
<th>OBSERVATIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Saturated solution of I$_2$ in methanol</td>
<td>10 sec</td>
<td>Over etched, corroded surface.</td>
</tr>
<tr>
<td>2. 1 part saturated solution of I$_2$ in methanol + 1 part methanol</td>
<td>20 sec</td>
<td>Etch pits observed, over etching, but surface less corroded.</td>
</tr>
<tr>
<td>3. 1 part saturated solution of I$_2$ in methanol + 2 part methanol</td>
<td>20 sec</td>
<td>No corrosion, ill shaped etch pits.</td>
</tr>
<tr>
<td>4. 20 part saturated solution of I$_2$ in methanol + 50 part methanol</td>
<td>30 sec</td>
<td>As above but pits tending to shape.</td>
</tr>
<tr>
<td>5. 25 part saturated solution of I$_2$ in methanol + 50 part methanol + 0.2 part HNO$_3$</td>
<td>30 sec</td>
<td>Rectangular etch pits with clear surface.</td>
</tr>
<tr>
<td>6. 25 part saturated solution of I$_2$ in methanol + 50 part methanol + 1 part HNO$_3$</td>
<td>15 sec</td>
<td>Well defined rectangular etch pits with fairly discernible point bottoms (fig.1).</td>
</tr>
</tbody>
</table>
Fig. 1 × 400
Fig. 2

Fig. 3
rows. These rows resemble the low angle boundaries commonly observed in metallic and intermetallic crystals\(^{(3-9)}\). Three rows of dislocations meeting at a point are known as triaxial boundaries. A model based on minimum free energy\(^{(10)}\) for dislocation tilt boundary gives the relation.

\[
    n_a = n_b + n_c
\]

where, \(n_a\), \(n_b\) and \(n_c\) are average density of pits along A, B and C branches, respectively. This relation is satisfied with A, B and C designations indicated on the photograph in the figure above.

To test capability of the etchant to reveal fresh dislocations, the specimen was pin indented and etched. The resulting etch pattern near the pin indentation mark consists of well defined rows of etch pits as shown in Fig. 5. The rows are in two mutually perpendicular directions indicating the deformation to have been produced by slip mechanism. The cleavage plane is (001). Therefore the most probable directions of these rows are [100] and [010].Likewise, these correspond to (100) and (010) to be primary slip planes. Fig. 6 shows another pin indented surface etched by the etchant. The cluster of pits arranged near the indentation mark corresponds with the fact that at the sites of severe deformation the local dislocation density also increases severely.

For further test, a specimen was scratched by a pin and etched. The resulting etch pits are seen to be arranged near the scratched mark (Fig. 7).
While the horizontally running etch pit rows delineate the scratch mark itself, the rows flanking this mark are mutually perpendicular. This observation confirms such rows of pits to be due to slip mode of deformation. The indentation and scratch tests thus show that the etchant is a dislocation etchant and it is also capable of revealing fresh dislocations.

Fig. 8 shows an etch pattern observed on the surface which was not deliberately deformed. The systematic arrangement of etch pits along rows may be due to unintentional deformation caused by thermal stresses in crystal growth process or by general mechanical stresses produced while cleaving or handling the specimen.

Thus, it may be conclusively said that the etchant consisting of 25 parts of saturated solution of I₂ in methanol, 50 parts of methanol and 1 part of concentrated HNO₃ (70%) can successfully reveal dislocations intersecting the cleavage plane of this crystal.

**Etchant For SnS:**

There is no report on etching of SnS single crystal. The author has developed an etchant after a number of trials. Some major trials are shown in Table-2. The cleavage plane of SnS is (001) and all trials were carried out on fresh cleavage surfaces obtained at 0°C.

The last composition mentioned in the table was tested for dislocation etching. These tests were as discussed below.
TABLE - 2

EFFECT OF ETCHANT COMPOSITION ON ETCHING CHARACTERISTICS

<table>
<thead>
<tr>
<th>ETCHANT</th>
<th>ETCHING TIME</th>
<th>OBSERVATIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Conc. HCl</td>
<td>30 sec</td>
<td>No observable reaction features</td>
</tr>
<tr>
<td>2. 1 part conc. HCl + 0.5 part CH$_3$COOH</td>
<td>30 sec</td>
<td>Etch pits of irregular shape</td>
</tr>
<tr>
<td>3. 1 part conc. HCl + 0.5 part CH$_3$COOH</td>
<td>30 sec</td>
<td>Nearly rhomb shaped pits, ill-defined.</td>
</tr>
<tr>
<td>4. 1 part conc. HCl + 0.5 part CH$_3$COOH</td>
<td>15 sec</td>
<td>Small sized rhomb-shaped etch-pits.</td>
</tr>
<tr>
<td>5. 1 part conc. HCl + 0.5 part CH$_3$COOH</td>
<td>30 sec</td>
<td>Well defined rhomb-shaped etchpits of good size, reaction evolves bubbles (Fig. 9)</td>
</tr>
</tbody>
</table>
Oppositely matched pair of cleavage surfaces were etched for the same etching time. The etch patterns on the two counter parts are shown matched in Fig. 10(a) and 10(b). It can be seen that there is a good correspondence between etch pits on the two counter parts. Some mismatch observed may be due to branching and bending of dislocations, as well as the cleaving action inducing non-uniform creation and movement of dislocations on the two halves. The etch-pit rosettes obtained by etching of a pin indented cleavage surface is shown in Fig. 11. The etch pit rows are in two distinct directions normal to each other. Like SnSe, these directions must also correspond to [100] and [010] directions. Similarly, the active slip planes may be (100) and (010). Fig. 12 shows an etch pattern on and around a scratch produced on the surface, with etch grooves in mutually perpendicular directions. These tests indicate that the etchant is capable of revealing freshly introduced dislocations also. Since dislocations do not terminate inside the crystal, successive etching should not produce new etch pits and the existing pits should grow in size. This is illustrated in Fig. 13 (a) and 13(b). The sample shown in Fig. 13 (a) was etched for 30 sec and the same sample was further etched for 10 sec. The pattern obtained is shown in Fig. 13 (b). As can be seen that the etch pits have increased in size with the increased etching time.

Thus the etchant consisting of 1 part concentrated HCl, 2 parts glacial CH₃COOH can be said to reliably reveal both grown in and fresh dislocations.
intersecting the cleavage plane.

Fig. 14 shows an intersecting etch figure. There are etch grooves along with the etch pits on a surface etched with this etchant. Such etch grooves were also observed in the case of Bi-Sb crystals\(^{(3)}\) and are believed to be associated with dislocations lying in the surface.

**CONCLUSIONS:**

1. The etchant consisting of 25 parts saturated I\(_2\) in methanol + 50 parts methanol + 1 part conc. HNO\(_3\) (70\% AR) is capable of revealing dislocations intersecting the cleavage surface of SnSe crystal.

2. The etchant consisting of 1 part conc. HCl + 2 part glacial CH\(_3\)COOH is capable of revealing dislocations intersecting the cleavage surface of SnS single crystals.
REFERENCES:


6. Amelinckx S., Phil. Mag., 1 (1956) 269


