CHAPTER XI

A STUDY OF ETCH PHENOMENA IN ANTIMONY CRYSTALS

The results presented in this chapter deal with the etching of antimony crystals grown from the vapour. These microcrystals after unique advantage of high degree of purity and perfection and low dislocation density. So far there has been no report on etching of vapour grown crystals and hence the present results can be considered as the first available on the subject. The earlier work on melt-grown crystal has been reviewed briefly.

Wernick[1] et.al. has studied the etch pits in crystals grown from melt in a zone refining apparatus at the last pass, without seeding. CP-4 reagent has been used for the purpose. Etch pits are 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, reasoning from Frank's boundary equation and the density counts along three rows, the authors have established that they are pure tilt boundaries consisting of dislocations. This has already been discussed in chapter X. Etch pits were observed along the (111) traces also. The effect of annealing the bent crystals on the distribution of these etch pits have also been studied. A modified form of 'Superoxol' produces spiral terraces and closed-loops on the cleavage plane. The polished specimens do not produce spirals on further etching. Superoxol reveals a fine structure on the body of a twin band. These features have not been explained by the authors. The results of the studies indicates strongly that one-to-one correspondence between etch pits and dislocations exist in this metal.

Kosevich[2] reports that CP-4 fails to produce etch pits on the crystals used by him. These were made from commercial purity metal (99.5%) and the failure to produce etch pits may be due to this. He has modified the reagent and for successful production of etch pits, A reagent consisting of 28 parts glacial acetic acid, 5 parts concentrated nitric acid, 4 parts of HF and 3 parts Bromine has been developed, the etching time being 30 to 90 seconds. Etch figures have been revealed along block boundaries, twin lamellae and slip lines. It has been possible to show that fresh pits are produced after deformation. The etch pattern on a twin lamella has the form of a pointed groove and the width of the etched region exceeds the width of the lamella itself on the cleavage plane. The (110) twinning plane approaches (111) etch plane at an angle of 35°. In the process of etching the crystal the lateral side of the twin lamella is gradually exposed and the etched region widens. Further

Kosevich has observed three different forms of etch pits (1) symmetrical pyramids indicating that the dislocation lines are running perpendicular to the cleavage surface (2) eccentric pyramidal pits corresponding to the slip dislocations lying along the $[112]$ direction with Burger's vector a $[1\bar{1}0]$ and (3) flat bottomed pits indicating that dislocations have moved away from the silt. The author has used the reagent to study the twinnning dislocations. The results indicate strong one-to-one correspondence between etch pits and dislocations.

In a subsequent publication Kosevich[3] reports about the etch grooves on the cleavage surface of the antimony crystals using the above reagent. These are formed of small triangular pits arranged closely. These etch grooves appear at random on a cleavage surface. If the crystal is bent fresh grooves appear, but these are strictly oriented. They extend in the $[1\bar{1}0]$ direction corresponding to the point of emergence of the $(11\bar{1})$ plane on the (111) plane. Both types of etch grooves are etched identically and terminate on a large pits and therefore it is concluded that they are of the same nature. The implication of these grooves is not clearly known. It has been suggested that these appear on a vacancy chain or it is possible that they connect two partial dislocations.

Shigetta and Hirmastu[4] have used a solution containing 10 grms $FeCl_3$, 30 c.c HCl and 120 c.c water to study etch pits in antimony crystal. Pandya and Bhatt[5] have used a solution containing 3 parts HNO_3, 9 parts Tartaric acid and 1 part water for the same purpose. The advantage ofthe new reagent is that the etched surface remains bright and is not tarnished as is the case with other solutions. According to the authors, the etchant behaves like CP-4 in all respects.

Thermal etching in antimony has been studied by Lavrentev[6] et.al. ~~The-cleavage.~~ The cleavage surface of the specimen has been annealed in an atmosphere of dry hydrogen at 600°C and etched thermally. The etch pits were distributed along twin boundaries, cleavage steps and in the initial stages, have the shape of flat triangles. The speed of etching is much greater in the (111) plane than in a perpendicular direction,as a result, the depth of the figure is much smaller than its size in the cleavage plane. The appearance of the etch figures on the twin boundaries is explained by the fact that distortions are concentrated between the twin and the mother crystal which results in strong etching. The development of etch pits on the cleavage lines and in some regions free from twin nucleation is apparently due to local stress which develop during the cleavage. It has also been observed that characteristic etch pits appear in some twin layers during etching which have accentric vertices and has been attributed to the dislocations in the $(11\bar{1})$ plane of the twin layers.

The present work relates to the etching of the vapour grown crystals. It has already been mentioned that these microcrystals grown from vapour offer many advantages to the etch studies. The reagemts used in this work are given in Table XI-1. The results obtained are briefly presented here. Most of the reagents behave alike and hence no detailed discussion on the merits of the reagents is necessary.

(1) The etch pits are triangular in shape with point bottom.

(2) The orientation of all the pits were the same as that of the face of crystal itself.

(3) The mean density of the etch pits ranged from 10^4-$10^5 cm^{-2}$

(4) Pits are aligned along slip lines and low angle tilt boundaries.

(5) The pits on the counterparts were arranged in a mirror-like fashion, provided the surface before etching shows good matching.

(6) When two counterparts of the same crystal are etched with any two different reagents, given in Table XI-1, the pits still show correspondence.

<u>TABLE XI-1</u>

Reagent No.	Author	Composition	Ref. in text
1	Wernick J.H. et.al.	CP-4 3 parts HF 5 parts HNO_3(F) 3 parts CH_3COOH(G) 1 part Bromine	1
2	Kosevich V.M.	Modified CP-4 28 parts CH_3COOH 5 parts HNO_3(F) 4 parts HF 3 parts Br_2	2
3	Shigetta J. et.al.	10 grms $FeCl_3$ 30 c.c. HCl 120 c.c. water	4
4	Pandya N.S. & Bhatt V.P.	3 parts HNO_3 9 parts Tartaric acid 1 part water	5
5	Wernick J.H. et.al.	Superoxol 1 part HF 1 part H_2O_2(30%) 4 parts water	1

Fig. XI -1 X 360

Fig. XI -2 X 360

Fig. XI -3 X 360

Fig. XI -4 X 360

Therefore all the reagents listed in Table XI-1 are capable of revealing dislocations which intersect the (111) plane of the antimony crystal. However, the results obtained with $FeCl_3$ were not very satisfactory. The pits obtained are very small in size and very often the surface is stained with the reagent and insoluble precipitates. Sometimes, the film formation is observed with CP-4 but to much less degree. In this respect, the reagent No.4 is much superior to all other reagents and hence has been used in more frequently throughout this work.

Fig.XI-1 shows a region in the crystal with large etch pits. In general the pits are point bottomed, eventhough flat bottomed pits as well as terraced pits are also observed. Fig.XI-2 shows three intersecting rows of etch pits revealed by etching with reagent No.4. The etch pits are aligned in close-packed arrays and individual pits cannot be resolved. The pits are not regular tetrahedra but the vertices of these tetrahedra are shifted towards the base. These are due to dislocations running at an angle to the surface. These have already been discussed in the works of Kosevich and others. These probably represent the dislocations with Burger's vectors a $[1\bar{1}0]$ lying along the $[112]$ direction. Fig.XI-3 shows another region containing etch pit arrays obtained after etching with CP-4. The etch pit density in

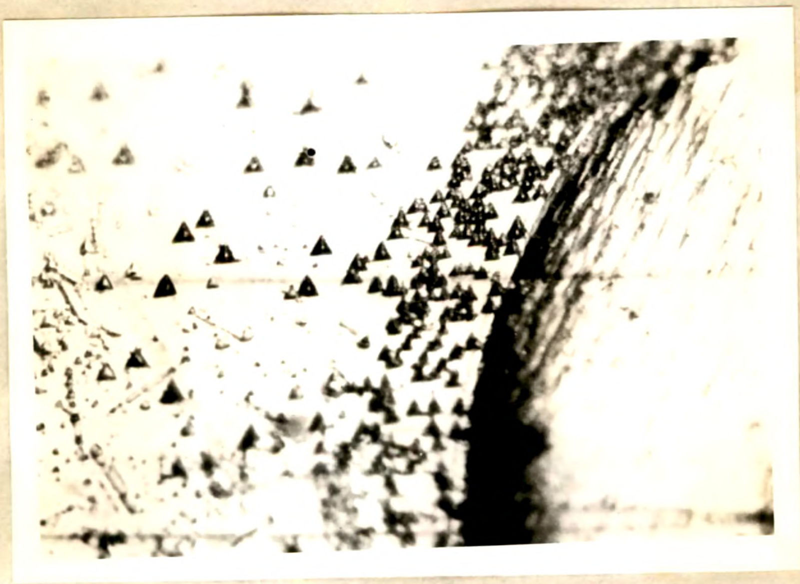

Fig. XI -5   X 360

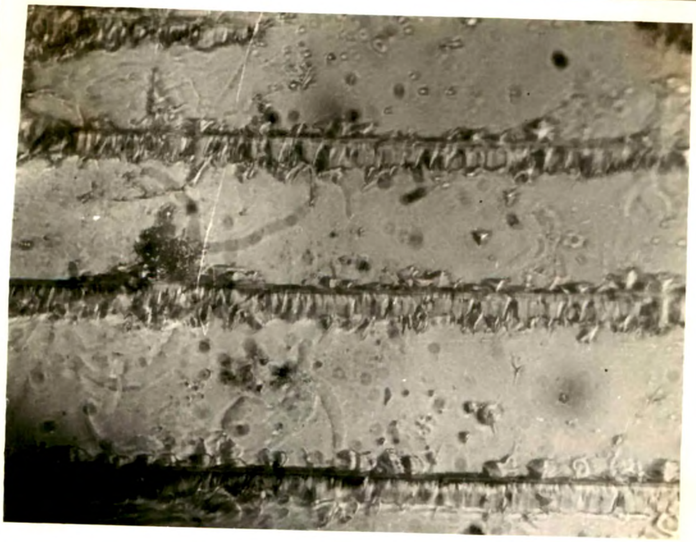

Fig. XI -6 X 360

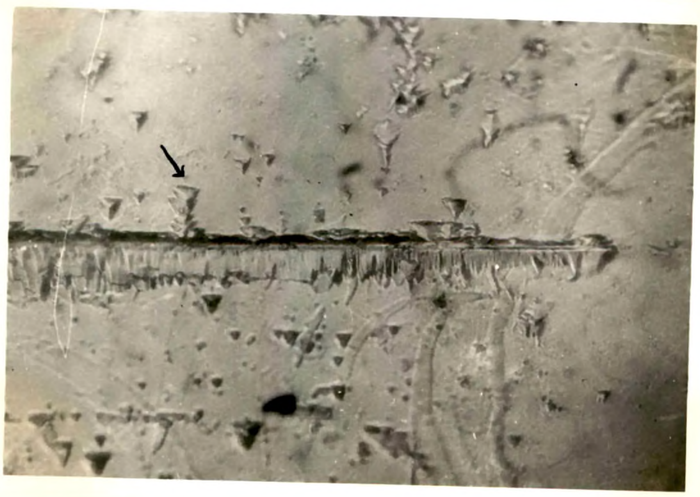

Fig. XI -7 X 360

this region is much higher than those observed in Fig.XI-2 and the relatively smaller size of the pits can be attributed to this. Fig.XI-4 is the result of etching with the modified CP-4 shown under oblique illumination. The four heavily etched lines seen are the twin traces. Triangular etch pits are also seen in the figure.

A very interesting observation is shown in fig.XI-5. The face consists of two planes one (111) and the other probably (100). The region after etching with reagent 4 develops pits only on (111) plane. This observation shows that the reagent is useful only on the (111) plane and cannot be used in other planes. Similar observations have been obtained with other reagents also.

Etching of a twin lamella reveals a fine structure as observed by Wernick et.al. In the initial stages a very irregular array of triangles are formed all along one side of the twin band. On the other edge regularly spaced in complete triangles similar to those obtained in zinc are observed. The tip of the twin always terminates in a large etch pit. These are shown in fig.XI-6 and XI-7. The etched region is much wider than the twin itself. These closely spaced etch pits observed on the surface are probably those lying along the [112] directions with Burger's vectors a[110] ~~directions with Burger's vector~~ as observed by Kosevich. The pits at the other end are those connected with the sharp

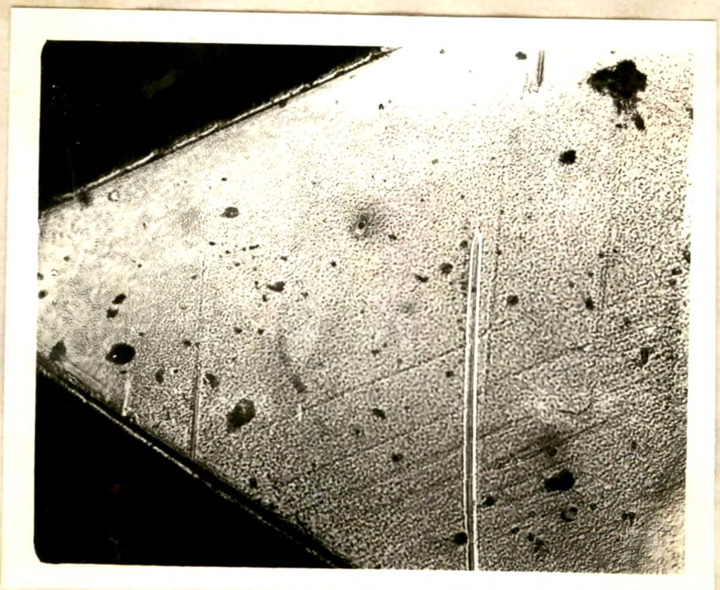

Fig. XI -8   X 55

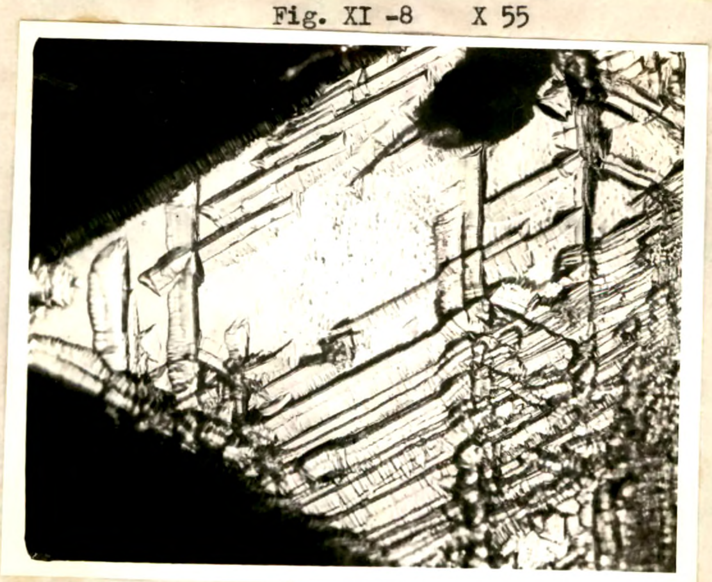

Fig. XI -9   X 55

bending of the plane and are similar to the half hexagonal pits observed in the case of zinc. These pits, as in case of zinc, tend to group in pairs and hence probably are the intersections of the dislocation loops on the surface. In addition to these pits sometimes it is possible to observe the pile up of the etch pits at these boundaries as indicated by the arrows in the fig.XI-7. These are due to the dislocation pile up at these boundaries.

The results of prologned etching of an as-grown face containing twin bands (fig.XI-8) is shown in fig.XI-9. The etched boundary presents a block like appearance and all the etch pits and fine structure have disappeared. The width of this etched region increases on prolonged etching. This is due to the fact that the etchant dissolves the (111) plane more rapidly than the (110) twinnning plane which is gradually exposed to the surface. Among the large number of twin bands all show the same etch pattern. These structures are not dissolved away even when Dash reagent is used for chemical polish. The only way is to polish the surface on various grades of emery paper and finally polish the smooth surface in chemical polish. It has already been reported that the chemical polishing in chromic acid do not remove the twin bands in zinc. The present results on antimony crystals also are similar.

The etch pit densities of the vapour grown crystals ~~of~~ are smaller than those of melt-grown crystals

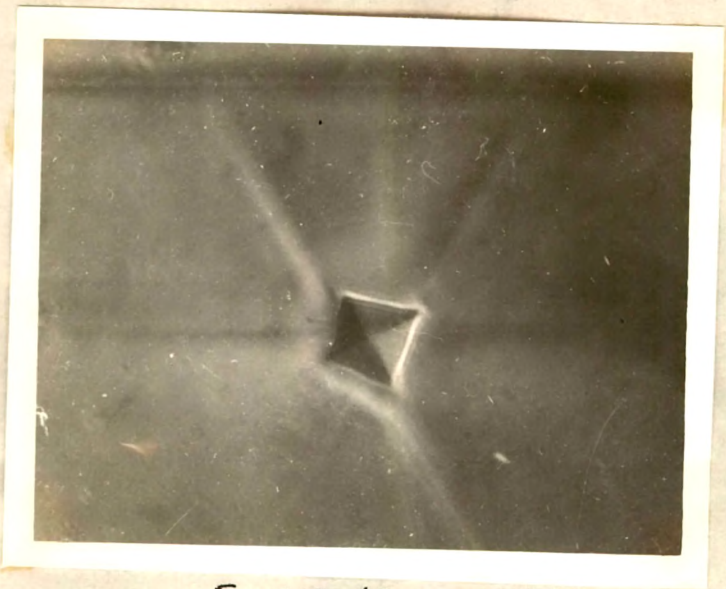

Fig XI-10 ×360

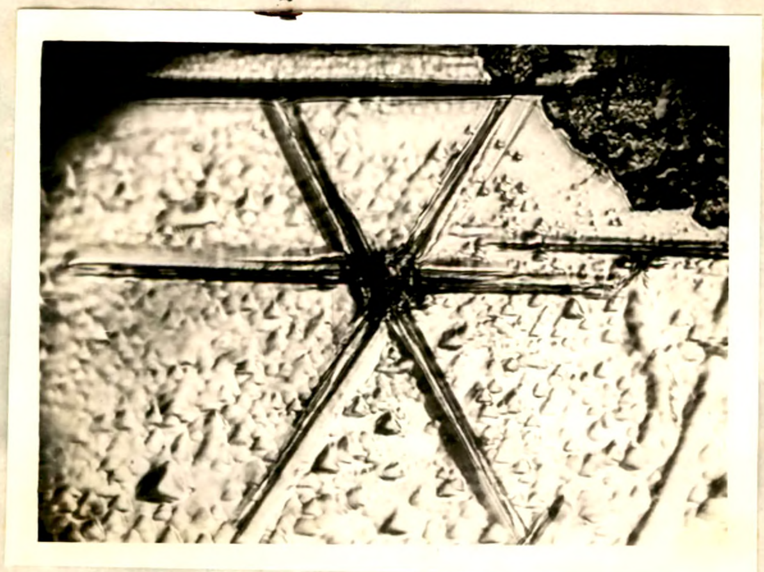

Fig XI-11 ×360

reported by the earlier workers by a factor of 10^2. In the present work the studies have been restricted to the vapour-grown crystals. In view of the small size of the crystal and their brittleness the conventional experiments on the plastically deformed crystals cannot be performed to study whether fresh dislocations are revealed by the etch pits or not. However to study whether the dislocation resulting from the deformation can be revealed or not, a melt grown crystal has been indented in a microhardness tester mentioned in chapter IX. The indentation produces the streak like pattern of twin band around it. This is shown in fig.XI-10. The subsequent etching in reagent 4 results in a pattern shown in fig.XI-11. It can be concluded in general, that etch pits can be identified as dislocation sites and one-to-one correspondence generally exists between them. No etch spirals have been recorded in the present studies.

SUMMARY AND CONCLUSIONS:

(1) The results of etching antimony crystals by various reagents yield similar results.

(2) In general one-to-one correspondence between etch pits and dislocations exist.

(3) All the reagents used are capable of revealing dislocations. only on the (111) plane of the crystals.

(4) No etch spirals have been recorded.

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