# CHAPTER VII

## STUDIES ON THERMAL ETCHING OF ANTIMONY CRYSTALS

This chapter deals with the studies on thermal etching of antimony crystals. Thermal etching is known to be produced at crystal imperfections, thermally etched dislocation pits and thermal grooving at grain boundaries being examples. It may also occur independently at off and on the portions of the surface removed from the locii of terminating imperfection. Two causes commonly postulated in this case are (1) the kinetics of atomic migration on a surface which is experiencing an unbalanced exchange of material with its environment and (2) reduction in free surface energy accompanying the new orientations introduced during etching.

Thermal etching has been studied in detail in silver[1-9]. Divergent views and contradictory results have been reported regarding the utility of this method to reveal dislocation sites. Thermally etched grooved along grain boundaries have been studied by Chalmers et al[1]. Mullins[6] gives a general indication that thermal etching can be employed to study dislocations. Moore and others[3,4] have studied the influence of surface energy on thermal etching without specifically assuming dislocation sites. Studies on individual dislocations in silver crystals have been made by Hendrickson et al[2] and Hirth et al[5]. Hendrickson et al[2] report that there exists a close agreement between the measured pit density and the theoretical estimate of dislocations in bent crystals. Hirth et al[5], on the other hand, report that there is no unequivocal agreement between thermal etch pits since pit densities on $\{100\}$ and $\{110\}$ planes differ largely. A possible explanation for the noncorrespondence may be due to the fact that the formation of etch pits at dislocations is dependent on the component of Burgers' vectors normal to the surface. Danilov[8] studying thermal etch pits on silver crystals at high temperatures explained the existance of pits on the basis of the fact that the evaporation proceeds more intensely than the movement of the atoms over the surface. Patel[9] observed that the number of etch pits on various facets of silver crystals is independent of the time of etching.

Among other metals studied are copper[10-13]; chromium[14], silicon[15], silicon-iron[16], antimony[17] and germanium[18]. Results of these studies indicate that generally, the correspondence between the dislocations and etch pits occurs. Etch spirals indicative of screw dislocations have been observed in some cases[10,12].

The present work has been undertaken to study the correlation between thermal etch pits and chemical etch pits and to assess the merits of thermal etching as a means to study dislocations. In attributing etch pits to dislocations, the same criteria referred to in the previous chapter for chemical etching have been applied.

Etching is carried out in a tube furnace described in Chapter IV, generally under a vacuum of the order of $10^{-3}$ mm.Hg. In some cases an atmosphere of argon is used, especially at high temperatures where metal evaporates under vacuum resulting in very large pits which interact with each other making the study more difficult.

Etching at 325°C is very slow. Fig. 1 is the surface before etching. The following features may be observed on this cleaved surface: (1) a sub-boundary running across the surface as indicated by the contrast (2) a twin band and (3) a number of cleavage lines. Fig. 2 represents the surface after etching for 15 hours. It is seen that pits are formed along the sub-boundary, cleavage lines and along the sides of the twin band. In addition to this a number of pits is distributed at random. Some of them are well defined triangular pits. These etch pits are shallow. On


Fig. 1 X 170

Fig. 2 X 170

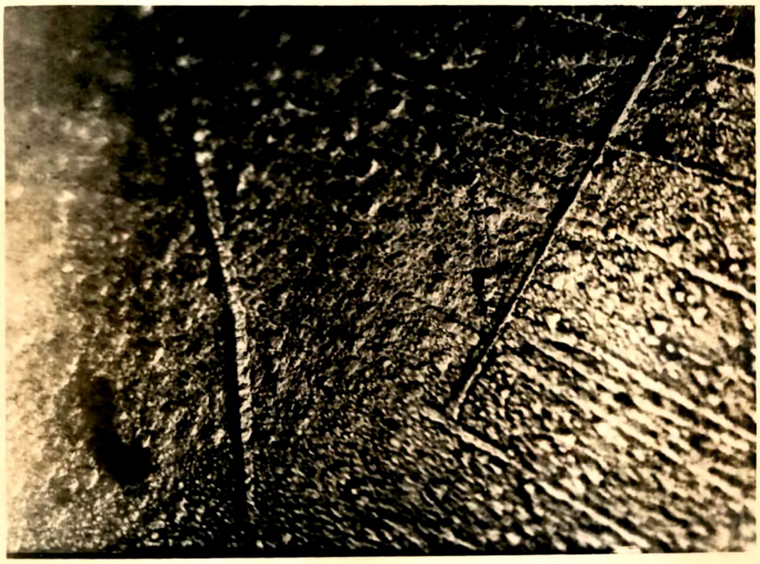

Fig. 3 X 170

further etching for another 15 hours the specimen takes a completely corroded appearance. The sub-boundary takes the form of a continuous etch channel. Pits along cleavage lines also form a continuous row. This can be observed in Fig. 3. A number of specimens has been tried and similar results have been obtained. Average density of pits in Fig. 2 has been estimated to be of the order of $10^7$-$10^8$ $cm^{-2}$. It is difficult to assign such a large dislocation density to the specimen used, which from the results of chemical etching is estimated to contain a dislocation density of the order of $10^5$-$10^6$ $cm^{-2}$. Also it is inconceivable that pits and channels observed along cleavage lines are due to dislocations. Though the earlier work of Lavrente'v et al[17] also shows pits along cleavage steps, they may be due to the preferential evaporation at the steps on cleavage planes. Thus,under the conditions of the experiment the correlation between etch pits and dislocations is rather uncertain.

It was decided to increase the temperature to 380°C. A strikingly different result was obtained. Well defined triangular pits were obtained on the (111) plane and in this case surface remained bright. In order to ascertain whether these are due to dislocations, two cleavage counterparts were etched at this temperature. Figs. 4 and 5 show

Fig. 4 X 90 Fig. 5

the cleavage counterparts. The cleavage is not perfect as is evident from the noncorrespondence of twin bands on both the surfaces which in turn indicates the non-uniform stress distribution during cleavage. The surfaces etched at 380°C for 4 hours and 8 hours are shown in Figs. 6 and 7 respectively. The one-to-one correspondence between pits is not observed. However, the pit density in both the specimens is same and the noncorrespondence may reasonably be attributed to the dislocation rearrangement during the cleavage. Twin bands show a fine structure similar to that obtained by chemical etching with super-oxol. The absence of etch pits along cleavage lines in Figs. 6 and 7 is noteworthy. However, cleavage lines show a fine structure which again is due to the preferential evaporation along these steps and not due to dislocations. Examination of Fig. 7 shows that there are three types of pits, (A) dark pits which are deep and point-bottomed, (B) bright pits which are also point-bottomed but shallow and (C) shallow pits which are stepped showing one triangle inside another. The cause for the difference between these pits is not known at present. The results of Figs. 6 and 7 can be considered to be a fair evidence of dislocations being revealed by thermal etching.

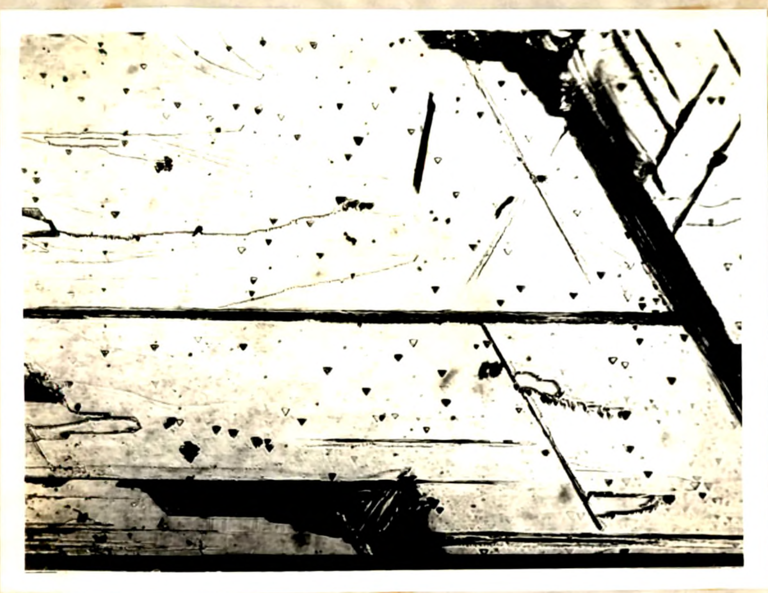

Fig. 6

X 90

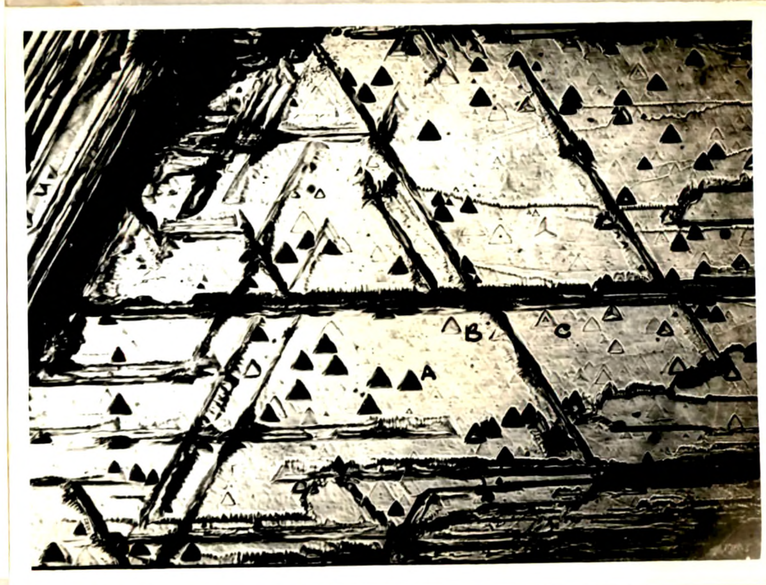


Fig. 7

Successive etching of the cleaved surface at 425°C for equal periods of $1\frac{1}{2}$ hours each results in the topography shown in Figs. 8, 9 and 10. It is seen that the number of etch pits remains constant, whereas the size of the pits increases. One interesting observation in this case is that the point-bottomed shape of the pits in Fig. 8 is gradually transformed into a stepped structure, showing one triangle inside another. Thus terraced pits of Fig. 7 are only the later phase of etching and are not different from the other pits.

Etching at 480°C gives a surface shown in Fig. 11. The sizes of the pits have considerably increased and pits have encroached into each other's space. Such a topography again is not useful for studying dislocation density in crystals, since correct count becomes impossible. There again the depth of the pits is small compared to their lateral dimensions. A light profile running across one such pit shown in Fig. 12, proves this point. It is seen further that in addition to the symmetrical point-bottomed pits and terraced pits obtained, there are pits (shown by arrows) which are not symmetrical. Such pits have been reported in diamond[19] as due to dislocation lines

Fig. 8 X 90

Fig. 9 X 90

Fig. 10 X 90

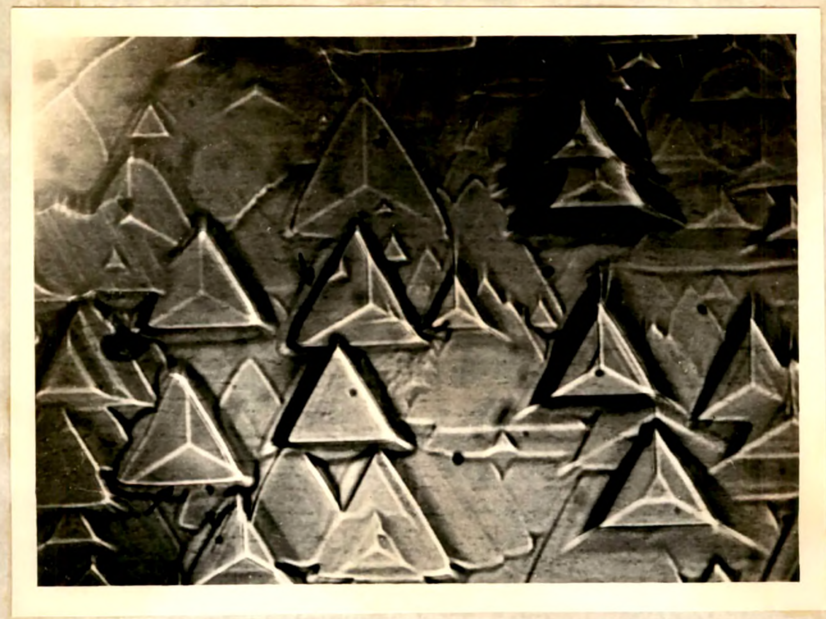

Fig. 11 X 170

Fig. 12 X 360

running at an angle to the surface.

Variation of orientation of the pits with temperature has been reported in diamond[20,21]. It has been shown that the orientation of the etch pits changes gradually from positive to negative when etching temperature is increased from 350°C. It will be of interest to see whether any similar orientation changes occur in antimony crystals also. Figs. 13, 14 and 15 show a crystal surface etched successively at 325, 380 and 480°C. No change in orientation is observed. The etch pattern is similar to those on specimens etched separately at these temperatures. It is seen again that the density of the pits remains same, whereas its size increases and finally the point-bottomed pit takes a terraced appearance. The appearance of the terraced structure of pits in Figs. 15 and 10 may be due to the fact that the lateral growth of pits becomes more pronounced as compared to its depth.

Since pit size became enormously large even at 480°C, it was decided to etch the crystal at 580°C in an atmosphere of hydrogen gas. The appearance of the surface after etching for four hours is shown in Fig. 16. It is observed that pits are very small as compared to pits produced under

Fig. 13 X 90

Fig. 14 X 90

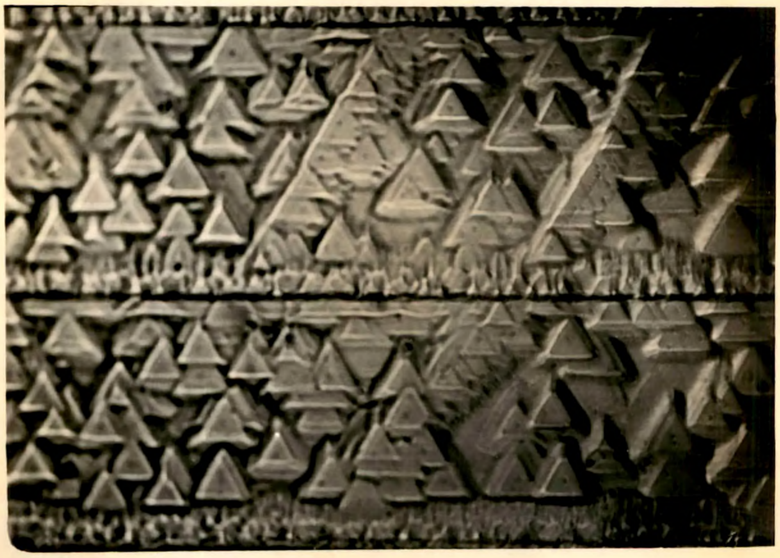

Fig. 15 X 90

Fig. 16 X 540

vacuum and the surface presents a corroded appearance. The observed difference is attributable to the higher rates of evaporation under vacuum as compared to the rate of evaporation in a hydrogen atmosphere. Another conclusion to be drawn from the study of Figs. 16 and 2 is that in order to obtain well defined pits attributable to dislocation, rate of evaporation of the metal should be relatively high.

In order to compare the results of thermal etching with those of chemical etching, a surface etched thermally at 320°C for 2 hours, was etched chemically using reagent E reported in the previous chapter. Results are shown in Figs. 17 and 18. An analysis of these photomicrographs shows that additional pits have been produced after chemical etching. Thus there is an increase in the etch pit density due to chemical etching. It is not known whether the additional pits produced by chemical etching are due to dislocations or not. If they are, then the results indicate that while dislocations are revealed by thermal etching, all the dislocations are not revealed. It should be noted, however, that the difference in pit desnity in chemical and thermal etching is not very different from the difference observed when different reagents are used. It has also been

Fig. 17 X 225

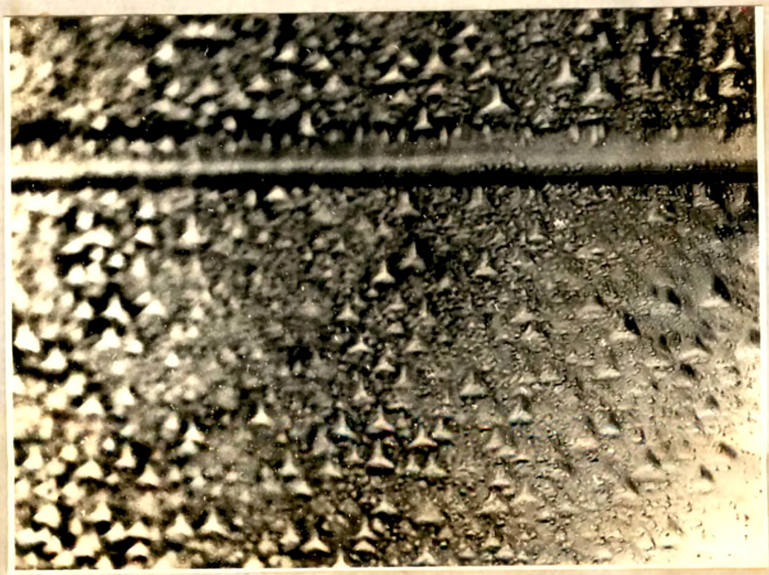

Fig. 18 X 225

pointed out that chemical etching produces pits at impurity sites and other defects also.

Thus the general conclusion that can be arrived at is that thermal etching can be used to reveal dislocations by the proper choice of temperature and vacuum. The phenomenon appears to be basically the evaporation of the metal preferentially at defect sites. It is worth mentioning that as in the case of chemical etching, etch spirals have not been observed during this work. Here again the absence of spirals need not necessarily mean the absence of screw dislocations, but that the formation of etch spiral is quite sensitive to mode of etching and the conditions have not been met with during the studies.

## CONCLUSIONS:

The following general conclusions can be drawn:

(1) Thermal etching can be used to study the dislocations by proper choice of temperature and etching time.

(2) At low temperatures pits not attributable to dislocations have been observed and the surface is not bright.

(3) At temperature between 380°C and 480°C well defined pits have been observed.

(4) In these cases, the pit density remains constant, irrespective of etching time and temperature.

(5) Pits are initially triangular with point bottom, but takes a stepped form on etching for a longer time.

(6) Pit size increases with temperature and time.

(7) No change in orientation of pits with temperature has been observed.

(8) No etch spirals have been observed.

(9) Matching of pits on cleavage counterparts is reasonably good.

(10) Pit densities on thermal and chemical etching show some differences.

## REFERENCES


1. Chalmers, B.,King,R. and Shuttleworth — Proc. Roy. Soc., A 193,(1948), 465.
2. Hendrickson, A.A. and Machlin, E.S. — Acta Met., 3, (1955), 64.
3. Moore, A.J.W. — Acta Met.,6, (1958), 293.
4. Hendros, E.D. and Moore, A.J.W. — Acta Met., 7, (1959), 521.
5. Hirth, J.P. and Vassamllet, L. — J. Appl. Phys.,9, (1958),595.
6. Mullins, W.W. — J. Appl. Phys.,28, (1957),333.
7. Lowe, R.M. — Acta Met., 12, (1964), 1111.
8. Danilov, V.N. — Sov. Phys. Crys., 1, (1962), 127.
9. Patel, H.B. — Current Sci., 20, (1965), 689.
10. Votava, E. and Bregheza, A. — Acta Met., 7, (1959), 392.
11. Ponelet, E. and Bariany, D. — Acta Met., 12, (1964), 593.
12. Young, F.W. Jr. — J. Appl. Phys., 27, (1956),559.
13. Young, F.W. and Gwathmey, A.T. — J. Appl. Phys., 31, (1960),225.
14. Fraser, M.A., Caplan, D. and Burr, A.A. — Acta Met., 4, (1956), 186.

15. Booker, G.R. and Valdre, V. — Phil. Mag., 13, (1966), 421.

16. Dunn, C.G. and Walter, J.L. — Acta Met., 7, (1959), 648.

17. Larventev, F.F., Soifer, L.M. and Startser, V.I. — Sov. Phys. Crys., 5,(1960), 449.

18. Ellis, S.G. — J. Appl. Phys., 26, (1955), 1140.

19. Patel, A.R. — Physica, 27, (1961), 789.

20. Evans, T. and Saunter, D.A. — Phil. Mag., 6, (1961), 429.

21. Patel, A.R. and Ramanathan, S. — Phil. Mag., 7, (1962), 1305.