CHAPTER XI

ETCH HILLOCKS ON THE CARBON FACE

11.1 Introduction

During the attempts to obtain 'perpendicular' pits with sides parallel to \langle10\bar{1}0\rangle\ directions using a mixture of NaOH + KNO$_3$ (2 : 1 by weight) it was found that above 630°C some habit basal planes developed certain trigonal (Fig. 73) and circular (Fig. 74) etch figures with a different appearance from the usual etch depressions. The examination with light profile microscopy showed that these features are elevations as shown in Fig. 73.

Etch hillocks have been observed on various crystals, e.g. aluminium (Orem 1957), germanium (Allen and Smith 1955, Batterman 1957), barium titanate (Stadler 1963), diamond (Patel and Agarwal 1965), NaCl (Patel and Chaudhari 1969) and magnesium oxide (Gosh and Clarke 1961, Venables 1961 and Bowen 1963). Of these only MgO has shown any relation between pyramids and the internal structure of the crystal and that they form only at dislocations where impurities have precipitated. The implication of the investigations discussed in this chapter is that a definite correlation of etch hillocks and dislocations could be established in SiC. The studies were mainly developed to three aspects viz.
(i) nucleation and development of hillocks, (ii) the origins of formation and (iii) the cause of formation.

11.2 Nucleation and Development of Hillocks

As mentioned earlier all the features reported here were produced by the mixture at 630°C unless otherwise noted. The etching time varied from 5 mts. onwards as required.

The general pattern of these features is similar to those due to etch pits usually formed on SiC basal planes. Figures 74a and 74b show the development of these hillocks in the subsequent stages of etching for 10 mts. and 20 mts. respectively. Generally no new hillocks are generated during such etchings, but occasionally, on prolonged etching, the faces were found to have a higher density of hillocks of assorted sizes (Fig. 75a). Most of the hillocks were terraced crystallographically, an example of which is shown in the electron micrograph in Fig. 76. During the etching the crystal faces acquired a convexity and it was found that the crystals were 'eaten away' very fastly from their sides.

11.3 Correspondence of Hillocks with Dislocations

To investigate if there exists any correspondence between these hillocks and dislocations, the faces with hillocks were etched in the usual etchants which
produced pits on the (0001) basal planes. Etching them in Na$_2$O$_2$ or Na$_2$CO$_3$ revealed that the hillocks were exclusively produced on the B face i.e. on the carbon face, hence NaOH which could easily produce pits on both (0001) and (0001T) planes had to be used. Figure 77a shows the result of NaOH etch at 630° C for 5 mts. on a face which initially contained hillocks. (Fig. 77b). Except the hillock marked A which has reduced in size, all the hillocks are replaced by pits and no new pit is originated. The hillock A is thought to have originated at screw dislocation. Evidence for this will be provided later. The outer periphery of some of the pits is not perfectly hexagonal which is because of the convexity acquired during the etching in the mixture. However, the bottom parts of the pits have hexagonal terraces. It can be seen in Fig. 75b that even the rows of hillocks in Fig.75a have turned to rows of pits after the NaOH etch.

11.4 The Opposite Sides of a Thin Flake

Figures 78a and 78b show the two sides of a thin flake etched in the mixture. Figure 78b is the habit B face of the flake with hillocks while Fig. 78a is the opposite fractured A face having pits. The perfect correspondence between hillocks and pits in number and position on the two faces is striking.
The exact correspondence between hillocks and pits renders clear evidence that the hillocks are formed at the sites of dislocations and is a crystallographic phenomenon related to the defects in the crystal. However, the hillocks could not distinguish in this case also, between the two types of edge dislocations though characteristic hillocks were produced at screw dislocations like the characteristic etch pits.

11.5 Nucleation of Hillocks at Screw Dislocations

It was indicated earlier that the odd hillocks like A in Fig. 77a might have originated at screw dislocations. This was verified by etching the B faces with spirals of small step height which did not have appreciable depressed centres. An example of this is given in Fig. 79a showing the unetched face and Fig. 79b showing the etched face. The hillocks formed at the origins of spirals are bigger in size.

11.6 Formation of Hillocks

A possible mechanism for the production of a pyramid can be discussed by analogy to the formation of an etch pit at a point where a dislocation intersects a surface. This is explained in terms of an enhanced rate of dissolution along the dislocation core, relative to the rate of removal of material normal to the
surrounding surface. In the case of pyramids, the process is one in which the exposure of the tip of a dislocation to the etchant results in a reduced rate of dissolution in the immediate vicinity of the dislocation relative to more remote regions of the surface.

The convexity acquired by the surface on etching and the appearance of smaller hillocks on prolonged etching suggest that the dissolution of the surface is much faster than that around the dislocations. Because of this, with the increase of time in etching, more emergent sites of dislocations come into contact with the etchant and new hillocks are formed. The pyramids are largest at the ends of the dislocations which have been exposed to the etchant for the greatest time. This may make the identification of hillocks originated at screw dislocations difficult because it is difficult then, to say whether a hillock has resulted from an edge dislocation close to the original surface and therefore etched for a longer time or from a screw dislocation further from the original surface and etched for a smaller time. Nevertheless, examination of large number of faces etched in the mixture has shown that it is possible to distinguish between screw and edge dislocations, if the size distribution of hillocks produced under identical etching conditions is studied (Figs. 77 and 79).
In addition to the enhanced rate of dissolution of the surface and the inhibitive action at the dislocations, it appears that some sort of deposition also takes place on these sites. Let us consider the hillocks A, B, C and D in Fig. 74a. The apices of all the four hillocks have moved in the same direction of their eccentricity on continued etching (Fig. 74b). Assuming that no deposition occurs at the dislocation sites (a) the distance between the apices should remain the same throughout the experiment if there is no dissolution at all at dislocation sites, or (b) the apices should move in the opposite direction of the eccentricity if dissolution takes place at the apices of the hillocks also. Since these are not the case, the possibility of deposition of some material at the sites of dislocations should be conjectured. The eccentric hillocks represent inclined dislocation. The apices of the hillocks B and C in Fig. 77b are in the opposite directions of the point bottoms of the pits in B' and C' in Fig. 77a.

A number of questions arise from the above discussion: (i) what is the role of KNO₃ which affects SiC above 850°C only and that too irregularly; (ii) why does this occur on the B face alone while etch pits develop on the A faces; (iii) what could be the material formed if deposition takes place; and (iv) if this is not so, why then do the tops of hillocks not
develop depressions when etched in NaOH alone? The pits at the original sites of the hillocks are formed only after their complete vanishing. The face always retains its shining also.

Redeposition of SiC on the carbon face is a possible mechanism of the development of hillocks. Silicon carbide crystals are recovered from boron carbide and silicon by dissolving the solid solutions in molten NaOH in the recrystallization process of SiC (Knippenberg 1963). Similarly, addition of KNO$_3$ may help the formation of some materials which ultimately may cause the formation of SiC which then deposits on the B face. However, a positive statement cannot be made without the knowledge of the various reactions that would take place and the products thus produced.

Though these results were obtained on the commercial crystals which contain many impurities in considerable amounts, there is no evidence that these hillocks are produced by the impurity precipitates at dislocations as in MgO (Bowen 1963) because the shallow origins of the spirals are more preferable sites for the nucleation of hillocks. As a result the hillocks formed at these sites are bigger than those at edge dislocations. The hillocks developed should be smaller in size, if the inhibitive action of etching by impurity precipitate should
The occurrence of triangular hillocks in certain cases can be analogous to the trigonal spirals observed on the habit planes of SiC. It should be assumed that these crystals belong to the $\alpha$ type and not to the $\beta$ type as on etching, the pits formed are hexagonal and not trigonal. But the reason why certain faces develop exclusively trigonal hillocks cannot be explained.

The author does not have the explanations now for the questions unanswered, but further investigations on this line are indeed interesting.

11.7 Implications

The results discussed above invalidate in the case of SiC, the suggestions of (1) Hones (1927) that the hillocks are intersection of adjacent etch pits, (2) Buckley (1951) that these residual hillocks cannot posses a symmetry related to the crystal face and that the majority of the etch hillocks produced are really growth hillocks, (3) Batterman (1957) that though they are true projections produced by etching, they are not a result of intersecting etch pits, and (4) Faust (1959) that they may be formed from humps on pre-etched surface or protective spots on parts of the surface or growing together of etch pits. The production of hillocks at sites of dislocations is a matter of choice of the etchant (which is the case here), or of the conditions.