CHAPTER 6

HILLOCKS AND PITS ON
{OLD FACES}
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Formation of hillocks, both crystallographically oriented and irregular, on the faces of different crystals has been reported by a number of investigators. Some of them have studied hillocks on 'as-grown' faces of the crystals, while some others were able to produce them by selective etch methods.

Daly (1899) reported hillocks on hornblende and interpreted them as etch hillocks. On diamond crystals, hillocks observed by Williams (1938) were described by him as growth hillocks. According to Buckley (loc. cit.) all symmetrical figures that are hillocks are growth hillocks. Contrary to Buckley's view, Batterman (1957) showed that hillocks are produced during etching process and possess the symmetry of the crystal face on which they occur. The faces bounding the hillocks were interpreted by him as limiting etch planes. The idea of Batterman was extended by Irving (1960) to correlate the shape of hillocks and that of etch pits. Augustine and Hale (loc. cit.) reported characteristic hillocks on prism faces of synthetic quartz and attributed them to growth. Joshi and Kotra (1968) observed rows of hillocks on first order prism
faces of synthetic quartz and showed that they were replaced by pits on etching. Sugawara (1968) has discussed preferential crystal growth along tilt and twist boundaries in hematite. He attributed the linear arrays of minute hills to growth at the sites of screw dislocations along twist boundaries. Recently, Yajima and Mathai (1970) showed one to one correspondence of etch hillocks with dislocation etch pits on habit faces of SiC and attributed them to the accumulation of reaction product at the dislocation sites.

To understand the mechanism of formation of hillocks, due to growth or dissolution, on 'as-grown' faces demands a critical study. In this chapter an attempt has been made to explain the formation of hillocks and pits on (021) faces.

6.2 Growth hillocks

Triangular hillocks were observed on (021) faces of some crystals. Figure 49 represents one such case. These triangular hillocks with rounded corners have their bases perpendicular to the c-axis of the crystal. The faces on which they occur are found to be rough and mottled. It is conjectured that after the cessation of growth, these crystals might have come in contact with some etchant which has dissolved some
portions of the structures already present on these faces and has also produced irregular dissolution of the surface. In some regions of these faces densely populated triangular hillocks were also observed. One such case is shown in figure 50. In regions marked A and B of this figure triangular depressions, in addition to triangular hillocks, are seen. These depressions have reasonably sharp pointed corners and their orientation is quite opposite to that of hillocks. It is suggested that these triangular depressions are formed due to the interaction of growth hillocks. The regions inside and outside the triangular depressions have mottled character which justifies the suggested possibility that these crystals have been attacked by the etchant after the cessation of growth.

6.3 **Needle-shaped pits**

It is a well known fact that when a crystal is attacked by a suitable etchant, the initial dissolution often takes place in a manner which is related to underlying structure. After contact with the etchant for a suitable time, the crystal faces show etch pits. The shape of the pits depends on the nature, concentration and temperature of the etchant. In some crystals of topaz (001) faces were seen covered with needle-shaped etch pits. Figure 51 illustrates one such case. All these
pits are shallow and are oppositely oriented with respect to hillocks shown in figure 49. It is conjectured that these etch patterns represent the initial stage of crystal dissolution.

6.4 **Triangular etch pits**

Some of the faces exhibited on these triangular etch pits. Two such cases are illustrated in figures 52 and 53. These etch pits are comparatively bigger in size and depth than the needle-shaped pits shown in figure 51. It is suggested that all these triangular etch pits should have been initially needle-shaped. If the rate of advance of etch fronts along directions perpendicular to the sloping sides of the needle-shaped pits is greater than that along a direction perpendicular to their bases, the needle-shaped pits should become triangular ones. If etching continues, interaction among these triangular depressions is to be expected. Such an interaction can lead to the formation of structures which look like block patterns. In certain regions, block patterns were, in fact, observed on these faces (see figures 54 and 55). Similar patterns have been observed on diamond crystals and mechanism of their formation has been explained by Tolansky (1954, 1962). As observed on diamond crystals, here
also block patterns appear to be consisting of rectangular blocks piled upon one another. The central part, bounded by three triangular depressions, is an elevation. One face of the elevation is observed to extend and combine with one face of the adjacent depression to form a face of the block. The dimensions of the block depend upon the size of hillocks and pits. Hillocks and pits formed by natural etching (see figures 52, 53 and 54) may be compared with those illustrated in figure 50.

6.5 Dendritic growth forms

Dendritic growth forms were observed on a couple of faces when examined under an electronmicroscope. Figure 56, an electronmicrograph, shows one such growth form. As in the case of (001) habit faces, here also, these growth features could not be removed with acids. However, by etching them with KOH vapour these features are completely dissolved indicating thereby that they are truly dendrites of topaz. In some cases, triangular elevations formed inside a triangular depression were also seen (see figure 57). These observations show that after etching, the conditions have become favourable for growth.

6.6 Etch hillocks

Etch hillocks are observed to form on
(021) faces, when such faces are etched in KOH at 510°C for 25 seconds. In order to study, in details, their formation on these faces, successive etching experiments on some of these faces were carried out. Figures 58(a) and 59(a) illustrate two stages of successive etching. The etch hillocks shown in figure 58(a) were obtained by etching a crystal face for 25 seconds. A magnified picture of these hillocks is shown in an electron micrograph in figure 58(b). The region of figure 58(a) after etching for 25 seconds more is illustrated in figure 59(a). The structure of hillocks seen in this figure is revealed in an electron micrograph, in figure 59(b). The orientation of etch hillocks reported here is same as that of growth hillocks shown in figures 49 and 50. Comparison of etch hillocks in figures 58(a) and 59(a) reveals that:

1. The hillocks are strictly crystallographically oriented.

2. Some hillocks produced in first etching increase in their size, while others are either reduced in size or are completely wiped off during second etching.

6.7 Discussion

All the etch pits formed due to natural etching are, to begin with, needle-shaped. It is suggested
that on progressive etching these needle-shaped pits become triangular. If the conditions are reverse, one can expect a needle-shaped growth hillock which with the progress of growth should become triangular. Under these conditions, the rate of advance of growth fronts along directions perpendicular to the sloping sides of a needle-shaped growth hillock would be greater than that along the direction perpendicular to its base. The observed pits on \(\{021\}\) faces substantiate this explanation for the formation of growth hillocks on these faces.

Etch hillocks of different sizes are formed at different sites on these faces. Patel et al. (1969) have reported similar results in case of KCl crystals. They have explained the formation of etch hillocks on Betterman's (1957) except. According to Betterman (loc. cit.) the hillocks should continue to grow bigger in size so long as the rate of local dissolution is less than the general dissolution. If, however, during etch the conditions are reversed, the hillocks will be reduced in size and will ultimately be washed off. This explanation, although is quite convincing, does not explain as to why the conditions favourable for the formation of etch hillocks should get reversed during the process of etching. The only
explanation which can be thought of about it is that the impurities may be present at the sites which are favourable for the formation of hillocks. During the process of etching, impurities can retard the rate of local dissolution and give rise to the etch hillocks. In case the concentration of the impurity is different at different sites, hillocks of different sizes should grow at different sites. Observation of such hillocks in the present investigation leads one to believe that their formation should be attributed to the presence of impurities in these crystals. Some of the etch hillocks, reported here, grow bigger in size on successive etching which indicates that they are formed at the sites of dislocations. It is suggested that such hillocks should have been formed due to the segregation of impurities at dislocation sites.

From figures 56(b) and 57(b) it is seen that the shape of etch hillocks changes on progressive etching. In case of (100) faces of synthetic diamond crystals Patel and Patel (1970) have reported that impurities segregated at dislocation sites play a significant role in changing the shape of etch pits. The change in the shape of etch hillocks observed here can also be explained on similar lines. These arguments
further support the author's view that impurities present in topaz crystals are responsible for the production of etch hillocks reported here.

6.8 Conclusions

1. Both growth hillocks and etch pits develop in a sequential order viz., needle-shaped and then triangular.

2. The observed growth hillocks on \{021\} faces are all of nearly equal size whereas etch hillocks produced by laboratory etching on such faces have different sizes.

3. Impurities play a significant role in the growth of etch hillocks.