CHAPTER XI

FAST ETCHING OF DIAMOND SURFACES

11.1 Production of trigon pattern on (111) faces

From the study of the etch patterns on diamond surfaces as carried out by various workers and described in the previous chapter, we see, that according to Tolansky and his school of workers, the fundamental differences between the triangular pits produced in the laboratory and the natural trigons observed on the octahedral faces are that :-

(1) The pits are oriented oppositely to the trigons.

(2) The pits are not having sharp corners and rectilinear sides as the trigons have.

Further, Omar and Kenawi (1957) by etching octahedral faces of diamond in low pressure oxygen produced pits having sharp corners and rectilinear sides. Tolansky and Patel (1957) have reported that the rectilinearity of the pits depends upon the slow rate of the etching of the diamond. If the etching is carried out at a higher temperature the pits get rounded off. Evans and

Sauter (1961) have reported that the orientation of the pits depends on the temperature of etching. They have shown that if octahedral faces of diamond are etched at a temperature of 1000^{o} C, triangular pits of the same orientation as that of trigons are produced. Patel and Ramanathan (1962) have reported that the orientation of the pits depends also on the total energy of the dissociated atoms of the oxygen which are responsible for producing the etching and not only on the temperature of the etchants. They have shown that even by etching diamond octahedral faces at 500^{o} C in potassium chlorate pits of the trigon orientation can be produced. Hence by adjusting the temperature of etching and selecting the proper etchant, pits can be produced on (111) faces of diamond having the same orientation as that of the trigons. Thus when the pits produced are of the same orientation as that of the trigons, their sides are neither rectilinear nor the corners very sharp and when they are produced with rectilinear sides and sharp corners, their orientation is opposite to that of the trigons.

In fact, Frank and Puttick (1958), produced sharp edged triangular pits having trigon orientation by heating diamonds in fused kimberlite at about 1450°C. But the features produced by them do not possess all the characteristics of the trigons observed on the natural octahedral faces of diamonds.

Therefore in the present work, by using fast etching techniques, it has been possible to produce pits of the trigon orientation having sharp corners and rectilinear sides and possessing all other characteristics of the trigons. In fact, the pits produced appear exactly the same as the trigons, and hence it is difficult to distinguish between the two.

Etch pattern produced at a temperature of about 800°C

The cleavages to be etched were heated to about 800° C to 900° C in an atmosphere of oxygen at a pressure of about 2 atmospheres. Figures 82 (X 650) and 83 (X 1000) represent the photomicrographs produced during the experiments. It is very clearly seen that the pits produced have sharp corners and rectilinear sides. It has been verified that they are oriented in the same way as the trigons are on a natural octahedral face. It is clearly seen from the figures that the corner of one pit makes a precise contact with the side of the neighbouring pit as reported by Frank, Puttick and Wilks (1958) in the case of trigons. The importance of this feature is very nicely described in detail in the section on trigons.

Etch pattern at still higher temperatures

Thoroughly cleaned octahedral cleavage faces of diamond were subjected to high temperatures by keeping them in the carbon rod before ignition so that they were appreciably etched within a few seconds.

Figure 84(b) (X 540) represents the etch pattern thus produced on the (111) cleavage face of a diamond, while figure 84(a) (X 540) represents the trigon pattern observed on the natural (111) face of diamond. Similarly figures 85(a) (X 540) and 86 (a) (X 540) represent the natural trigon patterns and figures 85(b) (X 540) and 86(b) (X 540) represent the patterns produced in the laboratory. The natural patterns are given here only for comparison with the patterns produced in the laboratory.

Attention is drawn to the following :-

(1) The etch patterns consist of triangular pits of different sizes.

(2) They are oriented in the same way as the trigons are.

(3) The etch patterns in figures 84(b), 85(b) and 86(b) resemble the natural trigon patterns in figures 84(a), 85(a) and 86(a).

(4) The pits have sharp corners and rectilinear sides like the natural trigons.

(5) Looking at figures 85(a) and 85(b) it is rather difficult to say that they might have been produced by different processes i.e. one due to growth and the other due to etch.

(6) As in the natural trigon pattern, a large triangular pit enclosing a number of smaller triangular pits is also observed in the pattern produced by etch.

It may be pointed out that while it would require several hours to produce pits of the same size as seen in figures 84(b), 85(b) and 86(b) when etching is done in potassium nitrate at 550° C., they have been produced here in a period of even less than 5 seconds. This may be due to the very high temperature at which the etching has taken place.

Figures 87(X 650), 88 (X 650) and 89 (X 650) represent different types of etch patterns produced in these experiments. In figure 87, large number of triangular pits as described above are clearly seen. The line seen at the top of the picture is a cleavage line revealing that the pattern is produced on a cleavage face. In figure 88, a large truncated pit having a number of smaller pits is observed along with other pits arranged in such a manner that they form a straight row in <110> direction. Figure 89 (X 650) reveals some isolated pits along with a complicated etch pattern produced on a cleavage face. In all these etch patterns, the characteristics of the etch pits are the same as described above.

Conclusions

It appears that there is very little difference between the triangular pits produced in the laboratory and the trigons observed on the natural octahedral faces.

However one is produced by etching and the other is observed on the natural octahedral faces of diamond. It is therefore conjectured that the trigons on the natural octahedral faces of diamond might have been formed due to dissolution of the crystals in nature. The failure of earlier workers in producing pits having the exact appearance as trigons was due to the lack of proper etching conditions.

11.2 Formation of etch hillocks on (111) faces.

When the experiments on fast etching, described above were pursued further, it was seen that under certain conditions of temperature and pressure, triangular projections described as etch hillocks, instead of the usual triangular pits were produced. The only difference between the two being that the hillocks were elevations while triangular pits were depressions. The present section has been devoted to the study of such hillocks.

Honess (1927) considers all hillocks the result of the intersection of etch pits. Buckley (1951) has reported that the residual hillocks cannot possess any symmetry related to the crystal face. He is of the opinion that many of the etch hillocks are really growth hillocks. Batterman (1957) produced etch hillocks on germanium having the symmetry of the crystal and has shown that the etch hillocks are true projections produced during etch and not as a result of intersecting etch pits; nor are they growth hillocks. Wijk and Van Dijk (1956) have given an account of etch hillocks on electrolytically polished iron. Orem (1957) has reported the production of etch hillocks on (100) planes of aluminium when etched with acids and bases. J. W. Faust, Jr. (1959) holds the view that hillocks may be formed from humps on pre-etched surface, protective spots on parts of the surface, or the growing together of etch pits. Recently Joshi and Vagh (1966) have reported etch hillocks on the prism faces of cultured quartz.

The formation of hillocks has been explained on the theory of dissolution by Batterman (1957). He has explained that for the hillocks to be formed on a crystal face certain restrictions must be met by the etch rate of both the planes of the hillock face and the surface upon which it forms. He mentioned that in general when local etching is slower than the general etching of the surface, the hillocks will result. These conditions of differential etching i.e. (1) local etching at a slower rate and (2) fast etching of the general surface, will produce the hillocks. He produced the hillocks on germanium surfaces by etching the surfaces of different indices in order to create the conditions of differential etching necessary for producing the hillocks. In the present work it was thought that probably the hillocks may be produced on the octahedral faces of diamond by varying the conditions in which they are etched and thus creating the conditions of differential etching instead of varying the indices of the surface on which they are produced. The experiments in the present work were arranged keeping this thing in mind.

Good quality octahedral cleavages were selected and were etched in an atmosphere of oxygen at different pressures ranging from 100 lbs/sq. in.to 700 lbs/sq. in.. During these experiments the usual triangular pits were produced on the diamond cleavages. But at a pressure of 20 lbs/sq. in. when the energy supplied to heat the coil of the furnace was 50 watts, instead of usual triangular pits, etch hillocks were produced on the octahedral cleavage faces of diamond.

Figure 90 (X 1000) represents the etch pattern produced on the cleavage face of diamond. The triangular etch pattern is clearly seen in the figure along with other complicated structures produced due to etch. The black parallel lines running vertically downwards and some of them passing over the triangular feature are the multiple light profile. The light profile clearly shows that the triangular feature is an elevation of height 1.6 microns on the surface and not the usual depression. In order to confirm that etch hillocks can be produced when etched under the conditions mentioned above and that the triangular patterns are really hillocks, many more crystal cleavages were etched in the same conditions. Thus figures 92 (X 660) and 94 (X 350) represent the typical etch hillocks produced on a cleavage face of diamond. Figure 91 (X 660) represents the hillocks produced on another crystal. That the triangular patterns observed in figures 92 and 94 really represent the etch hillocks and not the usual triangular depressions was confirmed by re-etching the surfaces successively for two different periods under ordinary conditions of etching i.e. in potassium nitrate at 560° C. Thus figures 93(a) (X 660) and 93(b) (X 660) and figures 95(a) (X 350) and 95(b) (X 350) represent respectively the same regions of figures 92 (X 660) and 94 (X 350) after two hours and four and a half hours of re-etching. It is quite clear from these figures that the triangular features of figures 92 and 94 have reduced in size and even some of them have washed away as the time of etching is increased. This suggests as reported by Patel and Tolansky (1957) that the features are elevations and not depressions. Thus it is confirmed that crystallographically oriented triangular etch hillocks can be produced due to etch. The etch hillocks thus produced have nothing to do with the dislocations in the crystal.

Discussions

It is quite clear from the experiments described above that the production of the hillocks on crystal faces by etching is a matter of creating conditions of etch such that at some isolated places local etching is slower than the general dissolution of the surface. These conditions may be created either by manipulating the indices of the surface on which they appear or by controlling the conditions of etching. It may be pointed, however, that the triangular hillocks produced above do not have perfect triangular shape, it is because of the fact that the diamond cleavage faces, which were true (111) faces acquired a little convexity due to etching. The convexity acquired during the etching experiments may be explained by the movement of the layers from the inside edges of the crystal due to the etching. This is explained schematically in figure 96, in which the horizontal lines represent the layers of the crystal and the ends of these lines are the edges of the layers. The edges of the first layer will be attacked first, and then subsequently the edges of the other layers also will be attacked one after the other. The layer which is attacked first will be shorter than the one attacked a little later. This will thus produce the convexity observed.

11.3 Terraced pits on (100) faces

In order to see, what happened to faces other than octahedral when subjected to fast etching; some polished (100) cubic faces were taken. They were etched for about 2 minutes at 800^o C., in the atmosphere of oxygen, at a pressure of 300 lbs/ in^2. Figures 97 (X 350) and 98 (X660) represent the typical patterns produced due to etch. The etch patterns consist of terraced square shaped pits in which the corners are not sharp and the sides are not rectilinear. It was seen that the sides of the pits make an angle of 45° with respect to the edges of the (100) face suggesting thereby that they have the same orientation as that of the square pits on natural (100) faces.

It is seen that terracing is quite common on the natural faces of cubes as revealed by the electron micrographs of figures 99 (X 8500) and 100 (X 3050) taken on the natural faces of the cubes.

The fact that fast etching produced the terraced pits on (100) faces is used to interpret the terracing of pits observed on the natural (100) faces as due to dissolution and hence all the pits observed along with the terraced pits on (100) faces may also be due to dissolution.