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Characteristic Etch Patterns on (111) Faces of Diamond

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Octahedral faces of diamonds have been etched in $NaNO_2$ and triangular etch patterns have been produced which have characteristics similar to the trigon pattern reported by other workers on (111) natural faces of diamond. It has been shown that the formation of wings associated with a trigon, fish-shaped structure, formation of a salient in $[11\bar{2}]$ direction and a triangular pit surrounded by three oppositely oriented triangular hillocks is a consequence of the dissolution process. The implications are discussed.

Introduction

The controversy regarding the origin of trigons on (111) faces of diamond, as to whether they are formed by growth or by dissolution, still persists. In this connexion Bedarida & Komatsu (1966) from their studies of some peculiar features such as vicinal faces built up by extremely thin growth layers on (111) faces of diamond have suggested a growth mechanism for their formation. Bedarida (1967) has reported the influence of some particular features on (111) faces of diamond on the evolution of the shapes of trigons, which are sometimes not equilateral, and has suggested that they form by growth. Varma (1967*a*, *b*) has reported optical studies of the trigons in relation to the features surrounding them. Certain inalienable characteristics discovered by him have been explained on a growth hypothesis. He has conjectured a growth mechanism for the formation of trigons and fish-shaped structures observed on the (111) faces of natural diamonds. Since the morphology of the etch patterns produced on crystal faces depends on the nature of the etchant, the method of etching, the crystal to be etched *etc.*, the authors tried to etch (111) faces of different crystals by different methods selecting different etchants with a view to producing in the laboratory features similar to those reported by Bedarida & Komatsu (1966), Bedarida (1967) and Varma (1967). Of the different methods and different crystal faces tried, it was found that when (111) faces of some crystals were etched in the oxidizing melt, the features produced on them were similar to those reported by Bedarida & Komatsu, Bedarida and Varma. The method of producing these features and the studies made on their morphology are discussed in this paper and it is shown that all the microstructures having the same morphology as those observed on natural (111) faces of diamond can be produced by etching (111) faces in the laboratory.

Experimental

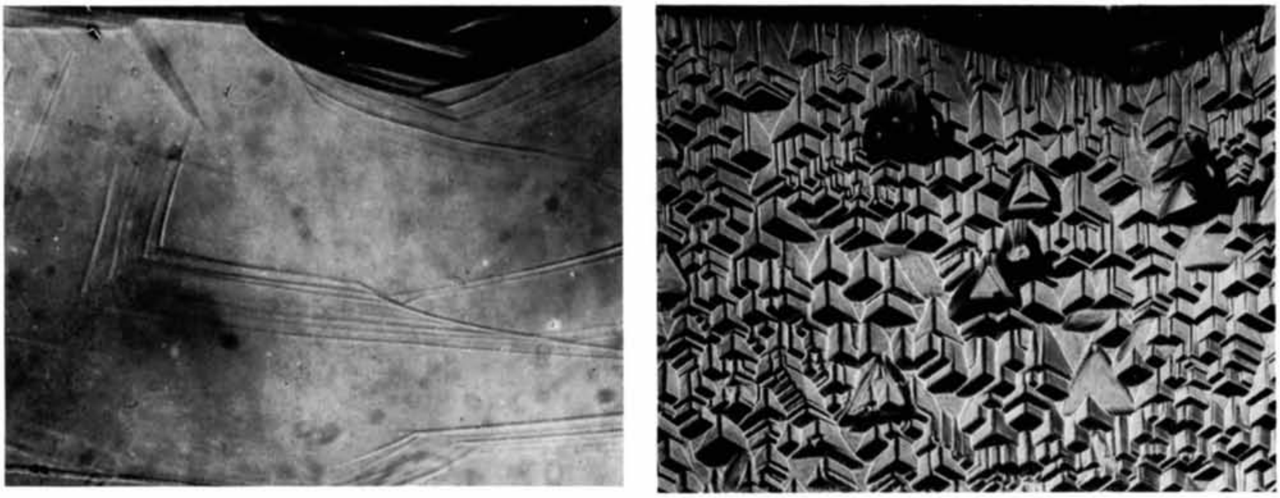
The (111) faces of diamond were etched in $NaNO_2$ at 860 °C for 15 min and the etch patterns were first studied optically. Wherever high resolution was necessary the etch patterns were examined in an electron microscope by preparing a single-stage carbon replica as reported by Patel & Patel (1968). Of the large number of crystals etched and the etch patterns studied on their (111) faces only a few which are of interest are reported here.

Observations

Fig. 1(*a*) represents the photomicrograph of a natural (111) face of diamond while Fig. 1(*b*) represents the etch patterns produced by etching the region shown in Fig. 1(*a*) for 8 min. The etch pattern consists of a block pattern of triangular etch pits having stepped sides, the steps being the edges of successive layers deposited on the (111) plane. The electron micrograph of the etch patterns in Fig. 2 shows a fully resolved triangular pit with two wings similar to the trigons having two wings as reported by Bedarida & Komatsu in their Fig. 3; while in Fig. 3 the joining of the opposite wings of two triangular pits, producing a feature similar to the features reported in Fig. 9 of Bedarida & Komatsu, is seen. The optical micrograph of the etch pattern in Fig. 4 shows the fish-shaped structures similar to the one reported by Bedarida in his Fig. 4.

Varma (1967*b*) has suggested a mechanism of formation of trigons around a defect point due to growth and this has been supported by a few illustrative examples. We suggest in this paper a mechanism of formation of a triangular pit around a defect point as a result of dissolution, and illustrate the mechanism producing similar features by etching. Consider some point defects on a (111) face of diamond as shown schematically in Fig. 5(*a*). Etching will produce triangular pits as shown in Fig. 5(*b*). Further etching of the same face will result in Fig. 5(*c*) and (*d*). In Fig. 5(*d*) we have three triangular hillocks surrounding each triangular pit and *vice versa*. It may be noted that the hillocks are oriented in the opposite direction to the triangular pits.

The electron micrograph in Fig. 6 shows a typical etch pattern produced on a (111) face, which consists of a triangular pit and three surrounding triangular hillocks oriented in the opposite direction to the pit,



(a) (b)

Fig. 1. (a) Photomicrograph of a natural (111) face (×200). (b) Block patterns produced on the above face by successive etching (×200).

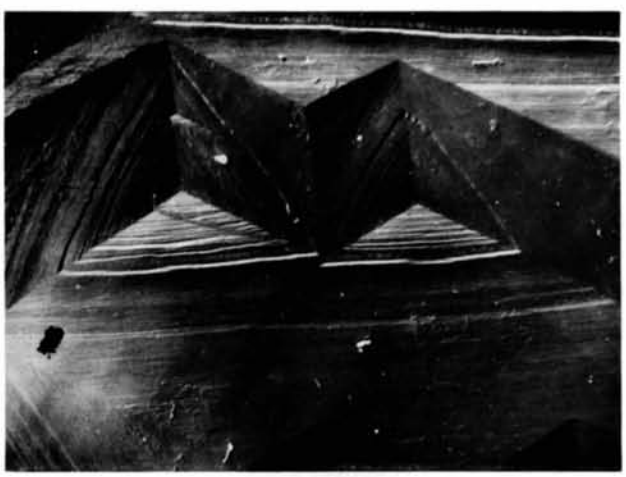


Fig. 2. An etch pit with two wings (×4800).

Fig. 3. Joining of opposite wings of two etch pits (×4800).

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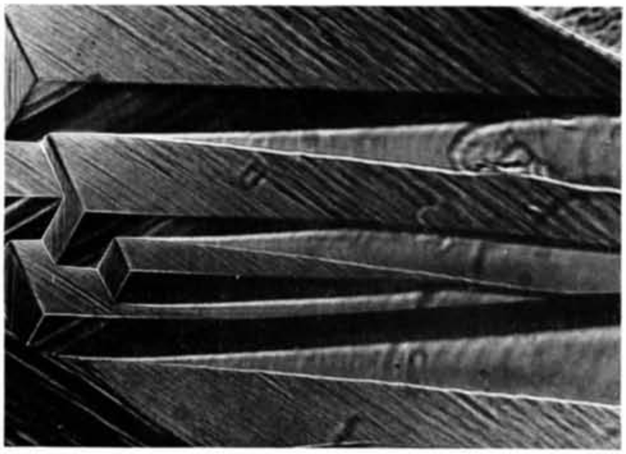

Fig. 4. The fish-shaped structure produced by etching (×200).

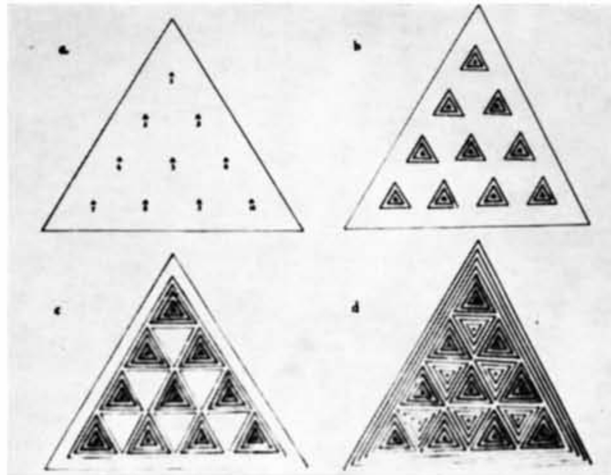

Fig. 5. Schematic diagram showing the formation of the hillocks around defect points due to etching.

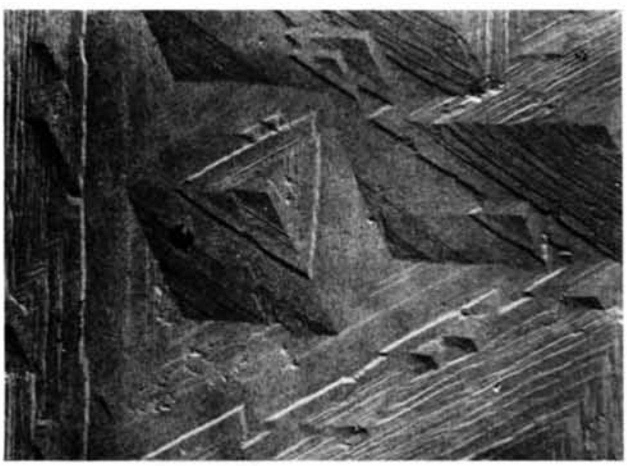

Fig. 6. A pit surrounded by the three oppositely oriented hillocks (×4800).

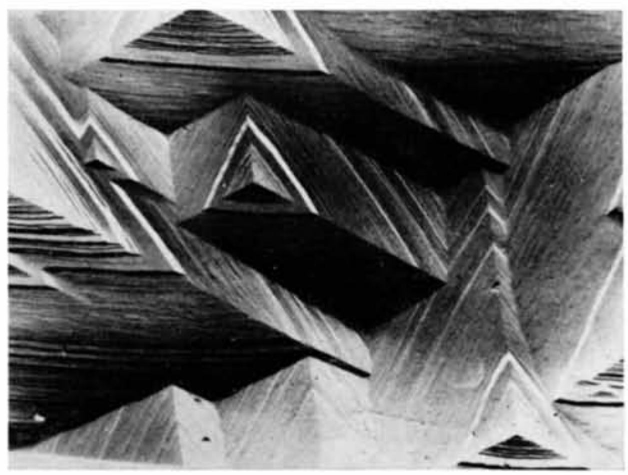

Fig. 7. A pit surrounded by the three oppositely oriented hillocks (×4800).

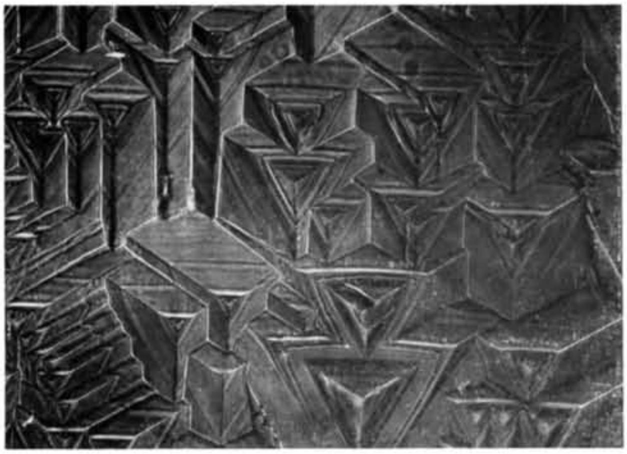

Fig. 8. Etch pits having salients in the [11$\bar{2}$] direction ($\times$ 200).

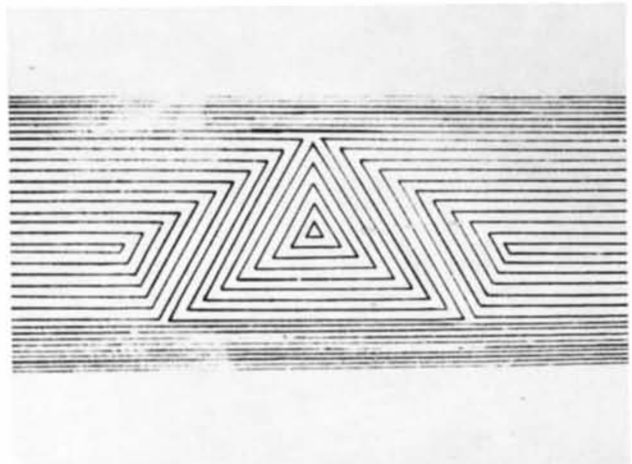

Fig. 9. The line diagram showing the formation of [11$\bar{2}$ salients.

Fig. 10. Pits having salients in the [11$\bar{2}$] direction without the contact of neighbouring pits ($\times$ 200).

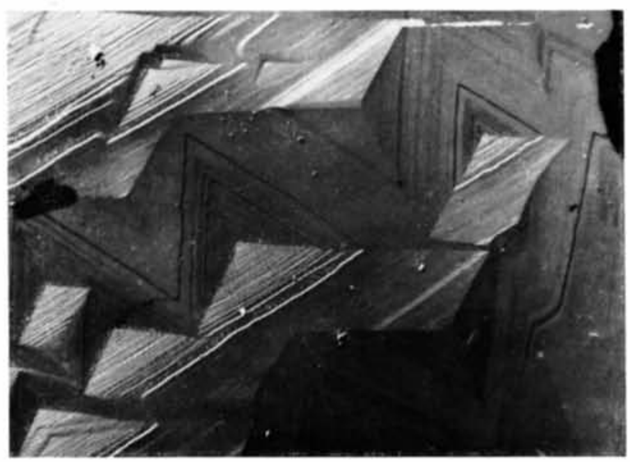

Fig. 11. The salient in the [11$\bar{2}$] direction being formed by pits making contact ($\times$ 2000).

which is exactly the same as shown in the schematic diagram [Fig. 5(*d*)].

Fig. 7 shows another example of a pit formation surrounded by the oppositely oriented hillocks. It may be noted that the triangular pit and the surrounding hillocks are all stepped.

Fig. 8 represents an optical micrograph of an etch pattern produced on an octahedral face which is very interesting from the point of view of certain features which are similar to those reported by Varma (1967*a*).

Varma (1967*a*) from his studies of the salients in the $[11\bar{2}]$ direction which, as reported by Frank, Puttick & Wilks (1958), form when two neighbouring trigons pass from contact to overlapping, has reported an example (Fig. 4 of his paper) in which the two salients are formed without any neighbouring trigons. He has also reported (Fig. 5 of his paper) a situation in which four neighbouring trigons, the corners of which do not touch the sides of their neighbours, have all the salients in the prescribed direction, touching the corners of the trigons to which they belong. The etch pattern in Fig. 8 clearly reveals that a number of neighbouring pits do not make contact although the salients are produced in the prescribed direction. The salients touch the corners of the pit to which they belong. It may be mentioned that irrespective of the period for which the crystal is etched the pattern produced has the same characteristics. In another example Varma (1967*a*) (in Fig. 5 of his paper) has shown three hillocks surrounding a trigon oriented in the opposite direction to the trigon he mentions that the hill tops are the intersections of $[11\bar{2}]$ lines having definite coordinates with respect to the trigon. He has argued that if the trigons are etch pits, they will enlarge on further etching and thus involve a migration of hill tops which he thinks lead to insurmountable difficulties in explaining the mechanism of dissolution. He has therefore concluded that the formation of trigons is not due to dissolution. The etch pattern in Fig. 6 shows a similar case of three hillocks formed around a triangular pit produced by etching. The hill tops have definite coordinates with respect to the triangular pit and they are formed by the intersection of $[11\bar{2}]$ lines as can be clearly seen in the figure.

Discussion

The formation of $[11\bar{2}]$ salients associated with an isolated etch pit can be schematically explained as shown in Fig. 9. Trigons with salients in the $[11\bar{2}]$ direction without neighbouring trigons and trigons with wings are observed when they are situated on a stepped surface (Fig. 3 of Bedarida & Komatsu). Thus the schematic diagram in Fig. 9 represents a triangular pit developed on a step around a dislocation on a (111) face. The central dot represents the dislocation which is etched, and in this process of dissolution etch fronts will start from the edges of the step as well as from the dislocation. These are shown by drawing lines. The etch fronts from the edges are drawn parallel to the edges while those from the centre of the triangular pit are parallel to the triangular boundary. How the two etch fronts advance and interfere and form the salient in the $[11\bar{2}]$ direction as well as forming the wing of the pit is clearly seen in the Figure.

The formation of salients in the case of trigons which do not appear to touch each other can be clearly seen from similar features produced by etching. Fig. 10 represents the optical photomicrograph of the etch pattern on the (111) face in which, the pit marked *A*, a composite pit made up of three pits, does not touch the neighbouring pits. However, the salients in the $[11\bar{2}]$ direction are formed and the intersections of these salients form the three oppositely oriented hillocks surrounding the pit *A*. Fig. 11 shows an electron micrograph of part of Fig. 10, in which the pits are seen not touching each other, even though the salient in the $[11\bar{2}]$ direction is formed. A careful study of these pits reveals that the boundaries of the etch pits do not extend only up to the boundary of the pit but until they meet each other and form the salient. This is clearly seen in Fig. 11. In the optical photomicrograph of Fig. 10, the edges of the intermediate etched layers are not resolved and hence it appears that the pits do not meet, but in fact they do meet and form a salient as reported by Frank *et al.* (1958). In the optical micrograph, the stepped layers are not fully resolved where they are very shallow and crowded and only the deeper portion in which the steps are deeper and not so crowded is seen. Thus the neighbouring pits, even though they give rise to salients, appear as if they do not make contact.

It is now quite clear that the characteristic microstructures which have been observed on (111) natural faces and reported to have been formed by growth, can all be formed by dissolution as well. The authors are therefore of the view that the trigons and the associated microstructures on natural octahedral faces are the result of dissolution and not of growth.

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