OPTICAL AND ELECTRON OPTICAL STUDIES
ON NATURAL CUBIC DIAMONDS

A Thesis
submitted to the University of London
by
KARIMA MOHAMED A. RAGAB
for the Degree of Doctor of Philosophy
June 1978

Submitted from:
Department of Physics,
Royal Holloway College,
University of London.
Acknowledgements

I would like to express my gratitude to my supervisor, Dr. Roy Miller, for his encouragement, assistance and his continuous guidance.

I also wish to extend my thanks to Dr. M. Moore for providing me with the diamond crystals.

Many thanks to all the laboratory staff for their considerable help and cooperation.

Sincere thanks must also go to my husband and my children, Ahmed and Tamer, for allowing me to complete my research.

I would also like to thank all my Egyptian friends.

Finally, I am grateful to Ain Shams University for the financial help which enabled me to carry out this work.
ABSTRACT

A detailed experimental study has been made of the surface topography of sixty cubic diamonds from the Congo, by means of optical microscopy, electron microscopy, scanning electron microscopy and cathodoluminescence. Ultra violet absorption studies indicate that all sixty cubic crystals are type I.

A comprehensive review is given, of the general properties of diamond, its crystal growth, and previous work on the topography of cube faces. A detailed description of the general characteristics of tetragons is given, and a classification of tetragons according to their type, as point bottomed and flat bottomed, is given for the first time. The mechanism of the formation of tetragons is also discussed in chapter VIII. The arrangement of some small tetragons over a considerable area in the form of rows running parallel to the $\langle 100 \rangle$ direction has also been studied. It is suggested that such arrangements of pits are produced along grain boundaries on the surface of the crystal by dissolution in nature.

The roughness of the cubic surfaces of natural diamond is largely attributed to the frequent appearance of tetragons, which are very deep and sometimes have complex structures, in addition to the existence of different facets of (111) and (110) on the surface. Of the sixty cubic crystals examined, eight showed different crystallographic facets on their surfaces, in addition to the cubic faces, such as octahedral facets, characterized by trigons. These are observed in different areas on the surface, juxtaposed on the cubic faces with tetragons. Some of the octahedral facets are oriented in opposite directions and show adjacent trigons which sometimes appear as parallelogram shaped
features. Another striking feature is the appearance of trigons on the octahedral facet of the side wall of some tetragons. This phenomenon supports the theory that the cubic crystal grows by layers on the (111) planes. The occurrence of trigons also at the truncated octahedral corners of some cubic crystals has been studied. The presence of many octahedral facets, either at the corners of some crystals or at different places on the surface, suggests that this type of cubic crystal grew by layer deposition on the (111) planes. The square shaped pits produced by laboratory etching in KNO$_3$ on the natural and polished surfaces of cubic diamond have also been studied. It is found that the etch pits are distributed at random or they are crowded together on some areas on the surface, which are the sites of dislocations. Aspects of the internal structure of diamond, as revealed by etching cut surfaces were also studied. The etch patterns showed areas of heavy and light etching which accord with the pattern obtained by X-ray topography and are explained as a combination of the normal facets and the non-faceted hummocky surfaces whose mean orientation was roughly $\langle 100 \rangle$. 
## CONTENTS

<table>
<thead>
<tr>
<th>Acknowledgements</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>3</td>
</tr>
<tr>
<td>Contents</td>
<td>5</td>
</tr>
<tr>
<td>Introduction</td>
<td>8</td>
</tr>
</tbody>
</table>

### Chapter I

**General properties of diamonds**

1.1 Introduction                                                                 | 10   |
1.2 Structure of diamond                                                                 | 13   |
1.3 Physical properties of diamond                                                          | 17   |
1.4 Optical properties of diamond                                                             | 18   |
1.5 Types of diamonds                                                                     | 20   |

### Chapter II

**Crystal growth**

2.1 The crystal state                                                                                | 24   |
2.2 Theories of crystal growth                                                                        | 26   |
2.3 Theories of perfect crystals                                                                    | 28   |
2.4 Theories of imperfect crystals                                                                 | 32   |
    A - edge dislocation                                                                            | 34   |
    B - screw dislocation                                                                          | 36   |
2.5 Layer growth in diamond                                                                         | 40   |

### Chapter III

**Surface topography of diamonds**                                                              | 42   |
3.1 Introduction                                                                                | 43   |
3.2 Characteristic features on natural octahedral faces                                         | 43   |
3.3 Characteristic features on natural dodecahedral faces                                  | 50   |
3.4 Characteristic features on natural cubic faces                                           | 53   |
### Chapter IV

| Experiment methods for examining the surface topography of natural cubic diamond | 54 |
| 4.1 Introduction | 55 |
| 4.2 Vickers projection microscope | 55 |
| 4.3 Method of examination using Vickers optical microscope | 57 |
| 4.4 Topographical studies of surfaces by using the scanning electron microscope | 59 |
| 4.5 Examination of the surface topography of the crystal by transmission electron microscopy | 63 |
| 4.6 The shadow casting technique | 65 |
| 4.7 The technique of two stage replica | 68 |
| 4.8 Classification of the types of diamonds by using Hilger spectrograph | 71 |

### Chapter V

| Experimental work on surface topography of natural cubic diamonds | 73 |
| 5.1 Introduction | 74 |
| 5.2 Previous work on cubic diamond | 74 |
| 5.3 Optical studies on the structure of cubic faces | 77 |
| 5.4 Electron optical studies on natural cubic diamonds | 79 |
| 5.5 Classification of tetragons according to their bases | 93 |
| 5.6 Some other features observed on the surfaces of cubic crystals | 106 |
| 5.7 External structure and defects on cubic faces | 111 |

### Chapter VI

| Examination of octahedral and dodecahedral facets on cubic diamonds | 115 |
| 6.1 Introduction | 116 |
6.2 Octahedral faces at the corners of natural cubic crystals 119
6.3 Dodecahedral faces on the edges of natural cubic crystals 125
6.4 The topography of octahedral facets 134
6.5 Trigons on the side wall of the tetragon 145
6.6 Trigons of opposite orientations 153

Chapter VII

Experiments on the etching of diamond 159
7.1 Introduction 160
7.2 Etching diamond crystals 162
7.3 Experimental work on etching 173
7.4 Etching on polished cubic faces 183
7.5 Etch patterns on cut sections of cubic crystals 188
7.6 The etch patterns on the two halves of the colourless crystal 189
7.7 The etch patterns on cut sections of two other cubic crystals 205

Chapter VIII

General discussion on the results 215
8. General discussion 216

Bibliography 230
INTRODUCTION

The natural cube form of diamond is a relatively neglected crystal in comparison with the octahedron, chiefly because its relative roughness and imperfection make it more difficult to study. In this work sixty natural cubic diamonds have been examined by a variety of techniques and new information and conclusions about this interesting form of diamond are presented.

Chapter I describes structure and the physical and optical properties of diamonds and their classification as type I and type II diamond. Chapter II deals with theories of growth of perfect and imperfect crystals in general of particular diamonds.

Diamond has three characteristic forms which are very common. The octahedron, dodecahedron and the cubic form, each one has its characteristic features which are crystallographically oriented. Chapter III discusses the surface topography of each form. Chapter IV presents the experimental methods used in this work for examining the surface topography of sixty cubic crystals.

The results of optical and electron optical examinations of the surfaces gave the most obvious features, called tetragons, which have been classified and their different shapes, sizes and depths are discussed briefly in chapter V.

The cubic surfaces, besides tetragons, showed also some unique features such as areas of octahedral facets characterized by trigons. These are discussed in chapter VI. Etching experiments were also performed on natural and polished faces of cubic diamond and the observations on the etch pits produced are presented in chapter VII. Some cathodoluminescence studies are presented in chapter VII. The most significant results are discussed and some conclusions drawn on the growth of entire diamond in chapter VIII.
1.1 Introduction:

Natural diamonds have been the subject of more intensive scientific study than probably any other crystal found in nature. This is because of its high reflectivity, which is about 18%, compared with 4% for glass. Also it has high dispersion, which makes the light reflected in a given direction change in colour as the stone is moved slightly; and it has a high refractive index, which is 2.42 compared with about 1.5 for glass at wave-length 5890Å. Because of all these characteristics, diamond is considered as a prized gem-stone.

Diamond is the hardest natural material known to mankind. Its hardness is 10 on Moh's scale and it has a Vickers hardness number in excess of 10000, compared with about 800 for hard tool steel. The hardness of diamond varies greatly with direction. To obtain the best from a diamond mounted as a cutting tool, it must be correctly oriented within one degree. This orientation can be carried out by X-rays or Y-rays. The permanence of diamond is due to its resistance to abrasion and also to its extreme resistance to chemical attack, being acted on only by strong oxidising agents at high temperatures in excess of about 525°C.

Because of its hardness and its resistance, it plays an important role in modern industry as a cutting and shaping tool. Nearly six tons of the yearly output of the diamond-mines are used just in industry, while only one ton is used as decorative gems (Tolansky 1968).

Diamond is found in various crystal forms. As with other natural crystals, these forms are in many cases far from ideal: very often,
for example, the faces may be markedly curved. The diamond crystallizes most commonly as octahedra which nearly approximate to the ideal crystal shape. There are also a number of well-known variants of this habit, such as twin plate octahedra or macle. Rhombic dodecahedra also occurs commonly with rounded faces. The cubic form is rarely found, the faces of such crystals appear to be frosted, and are in fact made up of numerous crystallographic facets, many of which may be quite flat. Tetrahexahedra and hexaoctahedra have been reported by Sutton (1928). Tetrahedra are extremely rare. The various common forms of natural diamond are shown in figure (1.1).

Diamond ranges in colour from clear white to yellow, brown, grey and black. The colouration may be the result of impurities. Even the best gem diamonds contain impurities with concentrations of the order of one part in $10^5$. The commonest impurities among a variety of elements, are silicon, aluminium, copper and nitrogen.

Diamond cleaves naturally along the (111) planes. This cleavage is used in dividing large stones during the shaping process (Raal 1957). Diamond is found either in alluvial deposits such as in Brazil and the Congo, or in volcanic pipes as in the Kimberly mines of South Africa, and in Tanganyika. It is believed that diamond was formed deep in the earth under high temperature and pressure and subsequently brought to the surface in the volcanic pipes, in concentrations of about one part in 25 million. The alluvial deposits presumably originated from such pipes by weathering and subsequent transportation by water to their present sites.

The nature of diamond varies from pipe to pipe, and from deposit to deposit.
The octahedron

The dodecahedron

The cube

Figure (1.1)  Forms of diamond
The natural cubic diamonds upon which this thesis is based come from surface alluvial deposits in the Congo, where they are found in small numbers.

1.2 Structure of diamond:

Diamond is one of the crystalline forms of carbon. It crystallizes most commonly in octahedra whose faces are \( \{111\} \) planes, or dodecahedra whose faces are \( \{110\} \), and less commonly as the simple cubic form, with \( \{100\} \) faces. Carbon's other allotrope, graphite, which crystallizes in the hexagonal form and diamond whose structure has been determined by W.H. Bragg and W.L. Bragg (1913).

The carbon atoms composing diamond consist of a nucleus and two shells of electrons. The inner shell is complete and has two electrons, while the outer shell is incomplete with only four electrons. In order to complete the outer shell, four electrons are required and the atoms combine together by sharing electrons in such a way that each atom may be considered to have a complete set of eight electrons. Figure (1.2) shows diagrammatically how the atoms are arranged (Custers 1956). The unit cell of the diamond lattice is shown in figure (1.3). It may be considered as a face centred cubic lattice with four additional carbon atoms "B" within the cells sited in such a way that each is equally spaced from the other four carbon atoms "A" (a corner atom and three neighbouring face centred atoms), there being only one carbon atom on each cell diagonal. Although 18 atoms are involved in a unit cell, the cell is composed of only eight atoms, because all but the four atoms "B" in the body of the cell are shared. Those on the faces are shared with neighbouring cells so that only half the atoms may be considered as belonging to each, while those at the
FIGURE 1.2  (Custers, 1956)
Figure (1.3) The unit cell of diamond crystal
corners are shared between eight cells, so that only one eighth may be considered as belonging to each. The length of the edge of the diamond unit cell is 3.566Å. The atoms are located at the positions

(000), (\frac{1}{2}, \frac{1}{2}, 0), (0, \frac{3}{2}, \frac{1}{2}) and (\frac{1}{2}, 0, \frac{1}{2})

(\frac{1}{4}, \frac{1}{4}, 1), (\frac{1}{4}, \frac{1}{4}, 1), (\frac{1}{4}, 1, 1) and (\frac{1}{4}, 1, 1)

Thus the arrangement is such that each carbon atom is situated at one corner of a regular tetrahedron with four nearest neighbours symmetrically placed at equal distances of 1.544Å. The bonds between the atoms make an angle of 109° 18'. The density of diamond is 3.52 gm cm⁻³. This arrangement of atoms in a crystal is known as the diamond structure and it is found also in various other substances like silicon, germanium, zinc sulphide and grey tin.

In graphite the carbon atoms are arranged in nearly plane layers, each of which is a hexagonal network. The atoms in these hexagonal layers are linked by strong homopolar bonding, and are closer even than the carbon atoms in diamond, but the links between the rows are by von der Waals forces, and those are very much weaker.
1.3 Physical properties of diamond:

Diamond is colourless and transparent in the pure and perfect form, but very often the crystal shape is not perfect, e.g. the dodecahedra have rounded faces and the cubic forms have uneven rough surfaces. The best natural diamond contains impurities with concentrations of the order of one part in $10^5$. It appears, however, that a few substances can enter into the diamond lattice substitutionally to more than a few parts in $10^4$.

The 'permanence' of diamond is due to its resistance to abrasion, being abraded only by diamond itself. It is the hardest material known to mankind. Its hardness is due to the close packed crystal structure and the bonds which are extremely strong and very difficult to break. The direction in a crystallographic plane in which abrasion is difficult, is termed the "grain", e.g. the dodecahedral plane has two of such grain directions, the octahedral has three, while the cube form has four of such grain directions. The dodecahedral and the cube faces are appreciably softer than the octahedral faces. Diamond has a cleavage direction along the $\{111\}$ planes and this is used in dividing large stones and in shaping processes. Twins occur in natural diamonds and are a source of difficulty in shaping gem stones.

Most diamonds are extremely good electrical insulators and this property is used as one method of separating them from associated minerals.

Diamonds have been classified as type I and type II in relation to their absorption in the infrared, visible and ultraviolet regions, as we will explain later. Diamond has a much higher thermal conductivity at room temperature than any other material, and this plays an important part in industry. A good gem quality crystal of type IIa, conducts heat five
times better than copper. It has also a low coefficient of expansion, $35 \times 10^{-6}$ per °C compared to $397 \times 10^{-6}$ per °C for steel (Sutton 1928).

1.4 Optical properties of diamond:

The 'fire' of the gem stone depends firstly on the high refractive index, which implies a low angle of total reflection, and secondly on its high dispersion, which makes the light reflected in a given direction change in colour as the stone is moved slightly.

Diamond is isotropic when it is free from strain, but many natural diamonds show strain bands, when examined between a polarizer and analyzer. Strain does not greatly affect the properties of a diamond as a gem, though it may make the shaping more difficult. Nearly all diamonds are birefringent, (Tolansky 1966). Brewster (1815) was the first to recognize the existence of birefringence in diamond. Friedel (1924), concluded that nearly all the crystals he had examined showed birefringence up to some extent. According to Friedel and Riboud (1924) all diamonds are isotropic at formation and they pass through a plastic state at higher temperatures, sufficient to cause permanent deformation, which gives rise to birefringence. Raman and Rendall (1944) observed parallel striations between crossed polarizers. Ramachandran (1946) also observed lamination in diamonds when he used polarized light. These laminae were found to be parallel to {111} planes. He interpreted this as due to alternate compression and tension between two varieties of diamond layers having slightly different lattice spacing.

Harrison and Tolansky (1964) etched sections of octahedral crystal parallel to the cubic plane. The stratigraphic etch pattern so obtained corresponded to the birefringence pattern. They suggested that the
stratigraphic pattern produced is the result of the different types of layers which are differently susceptible to etching. They suggested further that the correlation between the etch pattern and birefringence pattern may be due to the small difference in either the thermal expansion property or the elastic strength or the lattice dimension of the two types of layers. Tolansky did not agree with Friedel's explanation of plastic deformation, which did not account for the crystallographic orientation of the pattern and occurrence of birefringence in chips and cleavages. Seal (1966) suggested that birefringence is partly the result of the stress set up by the slight mismatching of the properties of different layers and might also result from inclusions.

Lang (1967) concluded that birefringence is not necessarily the result of stress between the different layers, but it is the consequence of dislocations and precipitates. He suggested that birefringence is also likely to be due to fracture and plastic deformation of the crystals. This was supported by Frank (1967). Wilks (1971) who tried to correlate the density of point bottomed pyramidal trigons with the degree of birefringence observed in diamonds. She noted that the density of pyramidal trigons is much less on the stones showing a small amount of birefringence than on the birefringence stones. She noted also that the density of flat bottomed trigons is substantially less on all stones, and the density is not much different on the birefringent and the non-birefringent stones.
1.5 Types of diamonds:

Robertson, Fox and Martin (1934) found by chance that one crystal of diamond among a number of 300 crystals was different from the rest in its infrared spectral absorption. They confirmed by various methods that a strong absorption band at 8μ, present in the spectrum of all the diamonds, was absent in this particular one. Robertson et al. divided diamonds into two main classes. Their division depended mainly on the physical properties of diamonds which they studied, and according to the diamond absorption in the ultraviolet, visible and infrared regions. They designated as type I those which were transparent down to about 3000Å, where the absorption increased fairly rapidly at shorter wave-lengths. They considered that this is the most common form of diamond and that it is generally isotropic. Type II diamonds are very rare and are transparent well down to about 2250Å; they are non-fluorescent and are isotropic. A convenient way of identifying diamonds as type I or type II is to observe their transparency with respect to the strong Hg 2536 line, obtained by filtering the light from a suitable mercury lamp. The difference in the absorption spectra indicates that type II diamonds are more nearly perfect crystals than type I diamonds, i.e. that type II are relatively free from some kind of defects or impurity which produces additional absorption in type I diamonds. The chief optical absorption characteristics of type I, both in ultraviolet and infrared regions, indicate the presence of some impurity or crystal defect which lowers the symmetry of structure. Nitrogen is one of the main impurities which occur in natural diamonds. Optical spectrographic analyses have shown the presence of smaller traces of numerous other
elements, the chief of which are silicon, aluminium, iron, magnesium
and calcium.

Much work has been done on the physics of impurity and defect
structure in diamonds. The first extensive work on the study of the
physical properties of diamond was carried out by Robertson, Fox and
Martin (1934). They recognized that the characteristic optical
absorption feature of type I and type II can largely be explained in
terms of the presence or absence of nitrogen platelets. This nitrogen
is in substitutional positions in the diamond lattice which give rise
to electron paramagnetic resonance spectra as a result of the single
unpaired electron at each centre. In most of type II there is a weak
continuous optical absorption which is probably due to the presence
of a minute amount of graphite or amorphous carbon in the structure.

Seal (1966) divided diamonds into four classes on the basis
of ultraviolet and infrared absorption spectra. They are type Ia, Ib
and IIa and IIb. The absorption characteristics depend mainly on the
concentration of nitrogen platelets. It was shown that type Ia con­
tains up to 0.33% of nitrogen, while type Ib also contains nitrogen
but in smaller amounts than type Ia. Raman and Nilakantan (1940)
discovered that type I diamonds show anomalous "spikes" projecting
from certain parts in an X-ray Laue pattern. Hoerni, Wooster (1955)
suggested that these spikes indicated the presence of defects in cube
planes. They assumed that planes of carbon atoms occurred with an
abnormal electron distribution. Again the type II appears to be the
more perfect form. Frank (1956) also suggested that spikes could be
produced by the occurrence of the occasionally abnormal spacing in the
<100> direction and postulated, as a possible origin of such abnormal
spacing, the segregation, in \{100\} planes, of silicon atoms as an impurity. Kaiser and Bond (1959) showed that a considerable amount of nitrogen is present and that the amount of this substance is correlated with the strength of the infrared absorption at 7.8\mu. From their studies they concluded that nitrogen is present in substitutional positions in diamond lattice and it is obviously the cause of spikes.

Evans and Phaal (1962a) were able to obtain transmission electron micrographs of thin plates of diamonds and showed the presence of platelet defects in type I diamonds. They showed that the platelets are present in \{100\} planes and they were able to calculate their numbers and extent.

Sobolev et al. (1968) found that nitrogen is present not only in platelets, but also in other disordered forms. Lang (1969) proposed a structure for the nitrogen impurity platelets. He explained that nitrogen is present in platelet form. Moore and Lang (1972) studied platelet distribution by X-rays, topographical methods, and according to their studies, the platelets are 150\textdegree to 200\textdegree in diameter. Tolansky and Rawle (1970) showed that diamonds are formed by the deposition of layers of type I and type II. Thus nearly all diamonds are the mixture of the two types. The predominant type determines the ultimate classification. Tolansky (1955) suggested also that type II diamonds cleave better than type I diamonds.

Most diamonds are extremely good electrical insulators and this property is used in one method of separating them from associated minerals. Custers (1952, 1955) showed that a small proportion of type II diamonds are semi-conducting. He classified non-conducting diamonds as type IIa and semi-conducting as type IIb.
2.1 **The Crystal state:**

A crystal is defined as a regular polyhedral form, bounded by plane surfaces. Many naturally occurring crystals do not have smooth faces, which is the case with diamonds of cubic form, as will be discussed later. A crystal is recognized as being built up of a large number of identical three dimensional unit cells and by the tendency for it to grow in many cases by the deposition of sheets of layers. In general the theories of crystal growth can be divided into two main groups, one of which stresses the importance of the environment which surrounds the crystal during its growth, while the other lays importance on the structure of the crystal itself. According to crystal growth, the form of a crystal is influenced by three main factors, i) its internal structure; ii) the nature of the solvent and iii) a variety of external factors, such as the crystal's proximity to the walls of the vessel or to other crystals and the effects of diffusion or concentration gradients.

The first quantitative theory of crystal growth was given by Gibbs (1878). If a crystal is in equilibrium with its surroundings at constant temperature and pressure, this implies that for a given volume the Gibbs free energy must be minimum. However, whereas the atoms or molecules in a liquid are randomly arranged, the structural unit in a crystal has a regular arrangements.

Curie (1885) proposed that there was an intimate connection between crystalline form and the surface energy of solids and calculated the shape and the end-form of a crystal. Curie's theory of crystal growth was not based on the actual atomic arrangement of the crystal surfaces, and it was extended further by Wulff (1901), who calculated the velocities of growth of different faces in the direction of their normals. He
suggested that these are proportional to the surface free energies of
the particular faces.

Crystals are generally grown in the laboratory by one of three methods,
using electro-deposition or thermal diffusion:

1 - crystallization from solution.
2 - crystallization from melt.
3 - crystallization from vapour.

The techniques of growing crystals by any of these methods were discussed
by Buckley (1951). Crystallization from solution or from vapour may
take place under suitable conditions of supersaturation. The atomic
theories of crystals grown from vapour were laid down by Volmer (1922,
1939), Stranski (1928) and Becker and Doring (1935). They considered
that crystallization is governed by the process of nucleation. Under
certain conditions, the rate of nucleation in solution increases extremely
rapidly with a small increase in super-saturation. Nucleation is induced
by the presence of foreign bodies and by agitation of the system.
By an appropriate annealing process, some crystal lattices may be changed
from one type to another. Crystallization also may be associated with
chemical reaction of association and dissociation. The external form of
many crystals grown from the melt is almost entirely dependent on the
physical shape of the apparatus and the conditions in which they are
grown.

Although the regular internal structure is the essential characteristic
of a crystal, nevertheless, much information about this structure can be
determined from the external form, i.e. from its habit and surface topo-
graphy. It was possible since early days, through the studies of crystal
symmetry and the optical properties of a crystal, to determine the basic
crystal structure, but precise studies of crystal structures only become possible with the development of X-ray techniques (Bragg, 1913). When a substance crystallizes, it always belongs to one of several definite crystal classes according to its atomic or molecular configuration. The angular relationships between the crystal faces of any one of these crystal types are always the same, although some faces may be suppressed and the habit of the crystal may vary. The orientation of the faces may be described by the Miller indices \([hkl]\). Crystallographers have classified crystals into 32 different crystal classes, within seven crystal systems, distinguished by their external symmetry characteristics, e.g. carbon crystallizes in two allotropic forms, which are diamond and graphite.

2.2 Theories of crystal growth:

The theories of crystal growth are divided into two main groups.

1 - theories of ideal "perfect" crystal growth.

2 - theories of imperfect crystal growth.

As regards the growth of the ideal perfect crystals, the main contribution has come from Volmer (1922, 1939), Kossel (1927), Stranski in (1928), Becker and Doring and Frankel (1946). Volmer and Weber (1926), Kossel (1927) and Stranski (1928) and Kaischev and Stranski (1934) have given the kinetic theory of ideal perfect growth, whereas Burton, Cabrera and Frank in (1949, 1951) have discussed the theory of ideal imperfect crystal growth in which dislocations play such an important role. The first theory (of ideal crystal growth) ignores crystal imperfection and introduces a number of simplifying assumptions in analyzing the growth process. In this theory, the crystal surface is supposed to be
undeformed and the growth is assumed to occur at absolute zero of temperature and scarcely any account is taken of the medium at low supersaturation.

The basic atomic theories of crystal growth from vapour were laid down by Volmer (1922). He suggested that crystallization is governed by the process of nucleation and that when a crystallizing particle arrives at a surface, it only loses a part of its energy and binds itself to the surface. Because of the residual energy, the particle can still move laterally. Thus these adsorbed particles, constitute a layer which interposes between the solution and the crystal surface, and it attains equilibrium with the crystal surface immediately. Volmer deduced that the velocity of spread of the layers is approximately proportional to the square of the density of particles in it. Bravais (1866) concluded that the velocities of growth of different faces of a crystal are dependent upon the density of atoms in the planes. Stranski (1928) and Becker and Doring (1935) considered that crystallization is governed by the process of nucleation. It has been shown by Tammann (1898) and others, that the rate of nuclei formation increases with super-cooling. It was concluded that under certain conditions the rate of nucleation in solution increases extremely rapidly with a small increase in supersaturations, and that nucleation is induced by the presence of foreign bodies and by the agitation of the system. Burton and Cabrera (1949) have discussed the influence of surface structure on growing surfaces of crystals.
2.3 Theories of perfect crystals:

Perfect crystals are those in which the atomic arrangement is periodically repeated in three dimensions without any break.

An atomic theory for perfect crystals was given by Kossel (1927) and Stranski (1928). According to them, in the simplest case, molecules can be represented as simple cubes. These cubes are attached face to face, and each cube is attracted equally by all its six neighbours.

The energy required to separate two cubes is called the binding energy, and it is different for different materials. According to their theory, once the layer has been initiated by a single atom, the planes will spread rapidly to completion. Figure (2.1) shows the simple crystal growth process conceived by them near to absolute zero. If the temperature is increased from near absolute zero, the molecules on the layer start vibrating. These vibrations become stronger as the temperature is raised, and some of the molecules have sufficient energy to break away from the surface of the crystal. These are generally the most loosely bound ones. Two processes will occur simultaneously, some molecules will arrive, while others will depart. When the rate of the two opposing processes are equal, equilibrium is attained. Under these conditions the surface will appear as in figure (2.2). If a crystal grows, some kind of steps must exist on the surface. Growth largely depends on the presence of kinks in the step. The number of kinks that will exist in a molecular step at a finite temperature has been calculated on simple thermo-dynamical conditions by Frank (1945), (1946). Burton, Cabrera and Frank (1951) deduced that the concentration of kinks is to be higher than the value suggested by Frank. They suggested that the number of kinks is dependent upon temperature and is practically unchanged by
Figure (2.1) A surface of a perfect crystal

Figure (4.2.2) Crystal surface at higher temperature.
supersaturation of vapour. Thus at temperature "T", the distance between kinks is given by the equation

$$n = \frac{3}{2} a e^{\frac{Q}{kT}}$$

where "a" is the distance between the two molecules in the lattice, and $Q$ is the nearest neighbour interaction energy. If the temperature is nearly 0.5 to 0.8 times the boiling point in K°, $\sqrt{KT} \sim 4$, $n = 4a$, and therefore there are kinks every four molecules on the surface. The rate of arrival is proportional to the vapour concentration, while the rate of departure depends upon the temperature. Experiments by Verma and Krishna (1966) indicated that the arrival of molecules at any particular point is more due to surface migration rather than direct arrival. During the growth of a crystal from the vapour, the molecules arrive at the surface, and then diffuse through a considerable distance before evaporating again. According to Burton, Cabrera and Frank (1951) a molecule diffuses through a considerable distance before re-evaporation. Therefore, the process of growth on a perfect crystal, whose surface has steps, will be the result of these processes:

1 - The arrival of molecules from the vapour phase on the crystal surface.
2 - Surface diffusion of the molecules until they meet a step.
3 - The diffusion of molecules along the edge of the step until they reach a kink.

Thus at a particular temperature, the step will go on receiving more molecules at the kinks than they lose from the kinks, so long as the super-saturation of the vapour persists. Again Burton, Cabrera and Frank (1951) have suggested that the rate of advance of an incomplete layer is proportional to the super-saturation. This means that all steps initially
present, will travel during the growth process, towards the edges of the crystal, leaving few vacancies and adsorbed molecules. Thus all the high index stepped planes will be eliminated during the process of growth and only the low index surfaces will be left. Therefore the further growth of the crystal depends on the formation of steps. The energy yield when an ion is added to an incomplete layer is greater than that of starting off a new layer, therefore there is a tendency for a layer once started to be completed rapidly, the inception of the next layer being delayed.

It is of evident importance to know the origin, rate of spreading and the thickness of these layers on different crystals and the effect on them of the presence of dissolved impurities and of different solvents. Bunn and Emmett (1949) made a careful study of the phenomenon of layer formation on a variety of crystals. The main generalization from their results and many other experimental observations can be summarized as follows:

1 - Layers very often start from the centres of the faces, spreading outwards towards the edges.

2 - Thickness of a layer increases as it approaches the edges of the crystal faces.

3 - In the case of rapid growth of crystals, the boundaries of the layers are often irregular, but as growth slows down, there is tendency to regularity of the shape and conformity to the symmetry of the crystal face.

4 - Impurities strongly influence the thickness and shape of the layers.

5 - Thick layers are often seen on polar crystals. Thinner layers have higher velocity because of the high energy at the step.
Seager (1953) examined crystals of several species. He suggested that the velocity of spread for the layers not only depends on the super-saturation of the vapour, but it also depends on the form of the face and its structure. After studying the structures on large numbers of crystals, he has arrived at the following conclusions:

1 - The growth velocity is a function of super-saturation, but it also depends on the index of the surface. The increase in super-saturation increases the growth velocity and high index faces grow rapidly.

2 - Each form has a critical value of super-saturation below which the growth will not take place on the perfect face.

3 - The value of super-saturation bears an inverse relation to the index of the form, entirely or almost entirely.

4 - Deposition is confined to high index faces, forming the edges of the surface.

2.4 Theories of imperfect crystals:

Imperfect crystals are those with breaks in the regular pattern so that some atoms in the crystal are not properly surrounded by their neighbours. There are a few physical properties of the crystals which are independent of the crystal perfection, such as thermal conductivity, electrical conductivity, whereas the mechanical properties of crystals are sensitive to crystal imperfection such as dislocations.

Burgers (1939), Kohler and Loss (1941) worked out a mathematical theory of growth of imperfect crystals. This theory was further extended by Mott and Nabarro (1948) and Frank (1949). As mentioned earlier, the growth of a perfect crystal from the vapour by the process of nucleation mainly depends on the super-saturation. New deposition will not start
at an observable rate, on a completed habit face of a crystal, unless the super-saturation exceeds a substantial critical amount. This is of the order of 50% for a typical crystal growing from the vapour. Experimental observations are published in which crystals were grown at super-saturation as low as 1%. This type of growth can be explained by the presence of screw dislocations in growing crystals. Gibbs (1928) first realized that continuous crystal growth requires the initiation of new layers, i.e. step formation. Also Burton et al. (1949) and (1951) considered the influence on the nucleation of the presence of dislocations in growing crystals. Smekal (1933) classified the properties of crystals into two distinct groups, a) structure-insensitive properties which are essentially independent of crystal defects and b) structure-sensitive which depend upon the presence of defects. Elasticity, thermal expansion and compressibility, specific heat, paramagnetism, etc. are properties of the first kind, while the ionic and electric conductivity, the internal photo-effect, crystal strength are of the second kind. Imperfections are in general of three different types:

a. Crystal defect which consists of lattice flaws where foreign atoms have taken up the normal positions of the atoms in the crystal lattice, a vacant site may be said to be a special case of this.

b. Crystal defect which consists of either foreign atoms or atoms of the crystal material, outside the regular geometrical arrangement of the crystal lattice and known as interstitial atoms.

c. Flaw which is called a dislocation, it consists of purely geometrical faults in the crystal lattice.

There are two basic forms of dislocation, which are (a) edge dislocation
and (b) the screw dislocation, with a series of intermediate cases which consist of various combinations of these two standard types. According to Frank (1949), imperfections are sometimes trapped in during the rapid growth of crystals at high super-saturation. Also the nucleation of layers in the correct and incorrect orientation gives rise to dislocations. The presence of some impurities causes the layer to grow in abnormal orientation, thereby producing dislocation. Sometimes, aggregation of molecular vacancies gives rise to dislocations. They can also be produced by mechanical stresses which sometimes arise due to the pressure of the neighbouring crystals.

A. Edge dislocation:

This type of dislocation was introduced by Orowan (1934), Polanyi (1934) and Taylor (1934). In this type of dislocation, the slip vector is at right angle to the dislocation. A dislocation here is a line imperfection forming the boundary of the slipped area within the crystal. Figure (2.3) shows a diagram of an edge dislocation. It is clear that the lattice in edge dislocation as shown in figure (2.4) is under compression above the slip plane, and under tension below it, or in other words, this type of dislocation could be regarded as being formed by the removal of a plane of atoms below the slip plane or by the addition of an extra plane on the upper half of the crystal in such a way that the edge of this plane coincides with the dislocation line.

An edge dislocation can move in the slip plane along the direction parallel to the slip vector, under the action of a stress, since no
Figure (2.3) The edge dislocation.

Figure (2.4) The structure of an edge dislocation.
transference of material is needed. Taylor (1934) showed that the motion of a dislocation line of the edge type across the slip plane, produces a shear displacement of an amount equal to the Burgers vector on the part of the crystal above the slip plane relative to that below that plane (Mott 1951). This is its main property which characterizes it when introduced into the theory of plastic flow.

Dislocations can also exist which are the inverse of the type shown in figure (2.4), where there is an extra plane coming from below and terminating on the dislocation line. These two types are called positive and negative edge dislocations. By inverting the crystal, a positive dislocation can be transformed into a negative one. However, this distinction is necessary since two like dislocations repel each other, while conversely two unlike attract each other.

B. Screw dislocation:

This type of dislocation was first described by Burgers (1939), and it is considered to occur in the earlier stage of growth, giving rise to steps on the crystal faces. Figure (2.5) shows the screw dislocation and how it forms by slip. In this type of dislocation, the dislocation line is parallel to the slip vector, where a step has been created on the surface of the crystal, as in figure (2.6) for a simple cubic crystal.

Growth can then take place without the necessity for two dimensional nucleation. If a single screw dislocation emerges normally at a crystal face, and growth takes place there, the step persists and then growth may continue without interruption, such that on the left hand side, the plane of the crystal surface is higher and on the right hand side it is
lower. The step does not extend throughout the surface of the crystal but extends only from the point 'F' to the edge of the crystal. This line AF is the boundary line between the right and left parts of the crystal which have slipped by unequal amounts, and hence is the dislocation line. In the case of a dislocation line meeting the surface of the crystal at right angle, the arrangement of molecules is illustrated by the model of figure (2.7). There are two types of screw dislocation, right and left handed. So if there are a pair of dislocations right and left handed together, a family of outward growing closed loops results. But for random distributions of dislocations, more complicated interactions occur. In the case of screw dislocation there is always a step on the uppermost surface. This is shown in figure (2.6). Thus the presence of a screw dislocation means the existence of a step on the final surface. In general, the emergence of screw dislocation on a crystal face eliminates the need of a surface nucleation on that face, provided only that the distance between pairs of dislocations, or between a dislocation and the boundary exceeds the diameter of the critical nucleus of the surface nucleation theory for the degree of super-saturation concerned. Suitably dislocated crystals are thus able to grow at almost arbitrarily low values of the super-saturation.

The theory of growth for dislocated crystals has been developed by Burton, Cabrera and Frank (1949, 1951). They suggested that steps provided by the emergence of screw dislocations terminate at the dislocation point, which remains fixed. Hence when growth takes place, the step can advance only by rotating around the dislocation point. During the growth process, the addition of atoms to a screw dislocation
Figure (2.5) Structure of a screw dislocation.
Figure (2.6) The formation of a screw dislocation.

Figure (2.7) The end of a screw dislocation.
results in a spiral growth. Spirals are of two types, circular and polygonal. The circular spiral is the simplest. The exact shape of the spiral depends on the rate of advance of the growth front in different crystallographic directions. Recently growth spirals have been observed on various crystals. Patel (1967) has reported the presence of spiral on natural cubic diamond. Verma (1951) has obtained phase contrast photo micrographs of spirals originating from various single and multiple dislocations on silicon carbide crystal grown from vapour. Tolansky and Sunagawa (1959, 1960b) observed spirals on cubic faces of synthetic diamonds. Patel and Ramachandran (1968) have reported spirals on octahedral faces of synthetic diamond. Frank and Lang (1959) have tried to correlate the dislocation pattern in diamonds with trigon formations. Lang (1964) performed X-ray topographical studies on diamonds, and observed that all pyramidal trigons are situated where the dislocations outcrop on the surface.

2.5 Layered growth in diamond:

Tolansky made an extensive study using precision optical techniques on various crystals, and showed clearly that many crystals grow by layer deposition. Pandya and Tolansky (1954), during their etch studies on sections of octahedral and dodecahedral diamonds, concluded that diamond grows by layer deposition on \( \{111\} \) faces. This was confirmed later on natural diamond by etch and ultra violet studies by Harrison and Tolansky (1964). By sectioning the octahedra and dodecahedra and slightly etching them, laminations were observed inside the body of the crystals. They suggested that diamond can be formed by deposition of type I and type II
layers which etched at different rates. Similar growth laminae were observed by Seal (1962). Seal (1965) extended this method to natural as well as synthetic diamonds. He suggested that natural diamond grows by layer deposition on octahedral planes, while in synthetic diamonds the growth takes place on other planes as well. During his investigation strong evidence of layered growth on various planes in the case of synthetic diamond has been observed.

Ramachandran (1946) suggested that the birefringence in diamond is caused by juxtaposition of layers of diamond whose lattice spacing is slightly different.

Tolansky and Rowle-Cope (1968) studied micro-diamonds from Premier and Finch Mine. Micro crystals were type II but as they grow bigger, they incorporate/few ultra violet absorbing layers and become type I. This confirms the layered growth of diamonds.

Further evidence for layered growth was obtained by Varma (1962), who showed that diamond grows by the deposition of layers in the [111] plane. The layers pile up one over another, each succeeding layer getting progressively smaller in extent.

Punglia (1972) supported the growth mechanism of tetragons on cubic crystals and suggested that crystals grow by layer deposition on all the faces and when these advancing layers meet obstructions, the tetragons are formed by the incompleteness of the layers in the region of obstruction.
CHAPTER III

SURFACE TOPOGRAPHY OF DIAMONDS
3.1 **Introduction:**

Natural diamonds commonly occur in three forms, namely, octahedral, dodecahedral and cubic. Some other types such as tetra-hexahedra and hex-octahedra have been reported by Sutton (1928). Tetrahedra are extremely rare.

The crystal shapes are often not perfect. Many diamond crystals occur with rough, uneven and curved faces e.g. dodecahedral faces are strongly curved, while the cubic faces are extremely rough and pitted. Most diamond crystals show a variety of surface detail which varies considerably from type to type. According to Tolansky (1955), the surface topography which can be seen on any diamond crystal is a frozen picture of the last stage of growth.

3.2 **Characteristic features on natural octahedral faces:**

The octahedron is a very common form. The faces are characterized by equilateral triangular depressions called "trigons" (Sutton 1928). They are always oriented in one direction on untwinned faces of natural crystals, having their corners pointing towards the edges of the octahedron (termed negative orientation). The sides of trigons are perfectly straight. Most of trigons are shallow with their bottoms flat, especially on nearly perfect crystals. However some trigons are much deeper and sometimes their sides are extended down and inward to meet in a point like an inverted pyramid, (point bottomed trigons). On the faces of many crystals, the trigons are distributed at random and there is a variety of sizes. Figure (3.1) shows an octahedral face of natural crystal which reveals some typical trigons. They are all oriented in one direction with negative orientation and most of them have flat bases.
Figure (3.1) Octahedral face

optical micrograph X 60
The origin of the trigons on natural octahedral faces has not yet been conclusively proven to be generally due either to growth or to dissolution in nature.

The trigons have been studied and discussed by various workers. Crookes (1907), Sutton (1928), Williams (1932), Tolansky and Wilcock (1947), Wilcock (1951), Halperin (1954), Tolansky (1955, 1960, 1962 and 1965), Bedarida (1967) and Varma (1967a) conceived trigons to have originated by growth.

Van der Veen (1913) assumed that trigons have been formed by three growth sheets approaching from their three sides at an angle 60°. When the growth fronts touch each other they stop and leave a triangular depression or 'trigon'. Tolansky, Wilcock (1946) proposed similarly that trigons can be formed as a result of arresting three advancing plane growth fronts inclined at 60° to each other.

Wilcock (1951) offered an alternative explanation. He imagined the possibility of an advancing growth layer stopping due to some disturbance to form a stationary front over a limited length. A similar hypothesis was put forward by Halperin (1954). He proposed that trigon formation would take place when the advancing layer is disturbed by some surface defects like an imperfect step or an accumulation of interstitial faults in the lattice. This layer proceeds round the corners leaving the triangular cavity. He also studied the shape of trigons. He observed that they are mostly shallow with flat bottoms on certain crystals which are perfect. Some crystal faces have trigons which are deeper and are distributed at random. With crystals having rough faces, the trigons are more complicated. They are very deep and consist usually of a large number of equilateral trigons. Most trigons with a flat bottom are
covered with large numbers of tiny trigons.

Varma (1967a) has studied trigons in relation to the surrounding features. He interpreted trigons as arising from defects and supposed that trigons affect the growth of diamond in the same way as defects do. He pointed out that diamond grows by the deposition of layers in the \{111\} plane where layers pile up one over another, each succeeding layer getting progressively smaller in extent. But according to him, when piling up occurs around a point defect, the orientation of the defect would be negative, i.e. its corners point to the sides of the octahedral face. He conjectured a growth mechanism for the formation of trigons, and also the 'fish-shaped' structure which he had observed on the \{111\} faces of natural diamonds confirmed his point of view of growth phenomenon. Bedarida and Komatsu (1966) from their studies on some particular features such as vicinal faces built up by extremely thin growth layers on \{111\} faces of diamonds, have suggested that growth is responsible 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 he has suggested that they form by growth. Tolansky (1955, 1960, 1962 and 1965) argued that the trigon formation is the key mechanism of growth of octahedral diamond and that the trigons are formed, filled and formed again in the growing crystal. He also observed a case in which the base of a flat bottomed trigon was at the same level as the neighbouring flat area with an intervening plateau which supported his view of growth phenomenon. Sutton (1928) considered also that trigons are a result of growth at different rates. Growth at accelerated rate forming hills and at retarded rate forming trigons.
Wilks (1961) observed that the majority of trigons on the \{111\} faces of natural diamond are low angle pyramids, and there is another variety which are steep sided with a flat base. She suggested that the low angle pyramidal trigons may have been formed due to etching of dislocation lines, but the steep sided flat bottomed trigons arise from some different mechanism. This assumption was supported by Seal (1962).

Seal (1962) reported that most diamonds show surface detail which varies from diamond to diamond. These structures represent the final stage of growth or they may have been produced by chemical attack in nature. He suggested that growth had started at certain centres on the face and continued through sheets of material spreading outwards.

According to the other school of thought, trigons are attributed to etching or dissolution in nature. Miers (1910), Omar and Kenawi (1957), Frank et al. (1958), Frank and Puttick (1958), Patel, Ramanathan (1962), Lang (1964) and Patel (1967, 1968) have tried to explain trigons on natural \{111\} faces of diamond as due to dissolution.

Omar and Kenawi (1957) etched diamond by heating it on a molybdenum filament in oxygen at low pressure. They found that the etch pits obtained are in fact similar in all respects to the natural trigons, except for the inverted orientation, i.e. their etch pits have positive orientations, so they concluded that trigons are probably etch figures produced by an unknown natural etching process. Frank and Puttick (1958) observed the precise contact of a corner of one trigon with a side of another. They tried to explain how the trigons seen in contact have approached this contact either by enlargement from non-contact or by shrinking from overlapping. Also they observed clusters of trigons which appeared to be associated with centres of strain in the interior of the
stone. This indicated that trigons are formed as a result of surface dissolution.

Patel, Goswami and Desai (1964) supported Frank and Puttick's hypothesis. Patel and Patel (1969) agreed again with the view of Frank and Puttick that, it is possible to maintain precise contact of the corners of the pits with the sides of their neighbours, and that such features are produced due to dissolution and not due to growth.

Patel (1964) studied trigons on a twin boundary of natural octahedral face. He observed that the trigons on the two sides of the twin boundary are oppositely oriented. He concluded that these trigon pairs might have been formed due to etching of dislocations on the twin boundary.

Patel and Agarwal (1965) from their studies on the microstructures of the surfaces of Panna diamond, found that trigons on the faces of these crystals could have been produced by dissolution. There is only one important feature of trigons on the octahedral faces of diamond which goes against the dissolution argument: trigons on the same face are of different size, while etch pits produced by etching are usually all more or less of the same size on a particular face. Patel and Patel (1967) explained the formation of trigons during the process of etching on the basis that the crystal surfaces are dissolved layer by layer. The trigons will be nucleated at the site of the termination of dislocations on these layers. Trigons nucleated initially will be larger in size than those nucleated at a later stage of dissolution. Patel and Patel (1973) again etched \{111\} faces of different crystals by different etchants and different methods. Then they studied the etch patterns produced, and showed that all the microstructures had the same morphology as those observed on natural \{111\} faces. From their observations they concluded
that the trigons and the associated microstructures on natural \{111\} faces are all the result of dissolution and not of growth.

In addition to trigons on the octahedral faces, some other features are also observed, such as crystallographic slip. The slip shows up as a straight line running across the crystal face in the \langle110\rangle directions. Such slip lines pass exactly through the centres of trigons. Tolansky and Omar (1953) were the first to report crystallographic slip on the surface of a twinned diamond. They studied it interferometrically and they suggested that the slip plane made an angle of 70°5' with the surface. Tolansky, Halperin and Emara (1958) also observed linear discontinuities strictly in the \{111\} plane and suggested that they originate in slip which could have occurred while the diamond was still growing and presumably hot. The lines of slip were oriented strictly parallel to octahedral planes and some of the lines were traced continuously from one face to the neighbouring faces.

Varma (1970) has produced evidence to show that these linear discontinuities are the result of plastic deformation producing twinning. It was suggested that the twinning could occur even as the diamond is growing in nature. Patel and Agarwal (1967) confirmed the existence of crystallographic slip in diamond and reported that the slip line may terminate in the middle of a face and thus give rise to screw dislocations, which is in agreement with the spirals observed on natural \{111\} faces by Patel and Ramachandran (1967) on the octahedral faces.
3.3 **Characteristic features on natural dodecahedral faces:**

The dodecahedral form of diamond is often very rounded. It is believed that the curvature of diamond face could arise through one or more of several mechanisms:

a - A surface could become convex through successive layers diminishing slightly in extension, layer on layer becoming smaller.

b - A crystal originally *polyhedral* in growth shape, would tend to convexity if it is subjected to a solution process, since solution attacks edges and corners in preference to the face centres.

c - A diamond under high temperature and pressure conditions might well be plastic enough to suffer plastic deformation through alteration of ambient conditions after a given period of regular growth.

d - Raman and Ramaseshan (1946) conjectured a possibility that diamond might crystallize from the melt from a globule of melted carbon and as a consequence such diamonds will have a markedly rounded outline.

Fersmann and Goldschmidt (1911) attributed the curvature to partial dissolution. They conceived diamond to be immersed in a mother liquor allowing free movement of crystallization and solution currents to obtain a delicate balance between growth and solution, so that a current meeting the crystal may deposit diamond at one point as well as remove material elsewhere on leaving. These ideas have been further developed by Shafranov-sky (1940-1941).

Sutton (1928) explained the formation of the dodecahedral form by imagining preferential growth to occur at the edges and corners of the octahedron, resulting in a progressive diminution of the octahedron face, until the latter disappears completely.

Williams (1932) suggested that a dodecahedron would be formed if growth
on all the eight faces of octahedron occurred as a number of super-imposed triangular plates of diminishing size. Friedel (1924) explained the curvature as the result of a stage of plasticity through which diamond may pass during crystallization. Raman and Ramaseshan (1946) explained the curvature as a direct consequence of solidification from a drop of liquid carbon. This hypothesis was supported again by Ramaseshan (1946) who attempted to show that the curvature of the faces would correspond to the curvature of the liquid drop of carbon.

Frank and Puttick (1958) supported Fersmann and Goldschmidt's explanation of the formation of the dodecahedral form by dissolution of the octahedral form. Tolansky (1959) agreed with the view of Fersmann and Goldschmidt that the dodecahedral form has suffered marked solution. He tried to confirm that octahedra and dodecahedra are two independent forms caused by different conditions of pressure temperature and concentration.

Varma (1967b) studied the natural diamonds of dodecahedron form. He has shown that diamond grows by the deposition of layers in the (111) plane. Layers pile up one over the other, each successive layer getting progressively smaller in extent till a point summit could be reached and finally form a dodecahedron.

Moore and Lang (1974) studied also the morphology of natural rounded rhombic dodecahedral diamond by X-ray topography. They attributed this rounded habit to the dissolution of a sharp edged octahedral growth form. As a consequence of these conflicting theories, intensive studies were carried out to examine the surface microstructure of dodecahedral diamonds. Sutton (1928), Williams (1932), Tolansky (1955 and 1959), Tolansky and Emara (1956), Tolansky and Pandeya (1958), Varma (1967b) and Moore and
Lang (1974) have studied dodecahedral faces of diamond. They found that the dodecahedral faces show striations and some oriented network patterns.

Emara and Tolansky (1957) studied these striations by using multiple beam interferometry. They observed parallel lines or striations which are very shallow ruts, whose depths are varied between $50\,\text{A}^\circ$ up to $2000\,\text{A}^\circ$ and their width is about $\frac{1}{500}$ mm.

Varma (1967b) suggested that these striations or ruts on dodecahedral faces are the spaces between successive layers in the (111) plane. This was confirmed by the discovery of trigons in the narrow spacing between them. Secondly the appearance of geometrical network patterns which consist of a cross network of very shallow ruts, either curved or straight, enclosing small regions which are curved.

Thirdly, the dodecahedron face is characterized by boat shaped features. Sutton (1928), Williams (1932), Pandya and Tolansky (1954) observed boat shaped patterns on the dodecahedral faces and have interpreted them as etch pits.

Pandya and Tolansky (1954) observed that the boat shaped pattern has a keel, which was a so-called basal extension of a trigon. Varma (1967b) has also explained the boat shaped features to be small strips of layers containing trigons.

Microdisk patterns were also described by Sutton (1928). Further detail of such features was given by Pandeya (1959). In (1961) Pandeya and Tolansky showed that these disks are slightly elevated. They considered the crystals showing such of these disks to have been subjected to a solution or etch mechanism in the final stage of the crystal formation. They suggested that some microbubbles adhering to the surface would
locally prevent dissolution, leaving slightly raised disks on the surfaces.

3.4 **Characteristic features on natural cubic faces:**

The cubic diamond is very rare in nature compared with the octahedral and dodecahedral forms. The surface of the cubic form is very rough and pitted. It was reported by many workers who studied the microstructure of the cubic faces that the surface of these faces are full of square shaped cavities called tetragons (Sutton, 1928), having their sides in the \( <110> \) directions and their corners pointed to the edges of the cubic face, i.e. these cavities have so-called negative orientation with respect to the crystal face. Tolansky and Sunagawa (1960) suggested the name quadrons to match with the name trigons on the octahedral face. Such features are now normally referred to as tetragons.

Similarly to the case of trigons on octahedral faces, Fersmann and Goldschmidt (1911), Patel and Agarwal (1967) have attributed these cavities to natural dissolution, while Williams (1932), Tolansky and Sunagawa (1960), Harrison (1964) and Varma (1967c) have attributed these tetragons to growth. During the present work of this thesis, the cubic crystal of natural diamonds are studied in more detail to provide more information on the microstructure of such surfaces.
CHAPTER IV

EXPERIMENTAL METHODS FOR EXAMINING

THE SURFACE TOPOGRAPHY OF NATURAL

CUBIC DIAMOND
4.1 Introduction:

For the present study of the surface microtopography of cubic diamond, sixty crystals have been examined. All the crystals came from the Congo. They have different sizes, the length of their edges ranging from 1.2mm for the smallest crystal up to 3mm for the largest one, and weighing about 0.07 up to 0.12 carat. Their colours vary from white or colourless, to yellow, brown, grey and dark grey. The microstructure of the surfaces of these sixty stones were examined by optical, electron and scanning microscopy.

4.2 Vickers Projection microscope:

Figure (4.1) shows a Vickers optical microscope. The specimen is placed above the objective lens. The main collimating system of the microscope is carried on a movable arm to facilitate the change over from reflection to transmission. The collimating system of the microscope consists of a powerful mercury lamp, a condenser and an aperture controlled by an iris diaphragm, and some filters. An image of the source can be formed on the field iris. Translation movement of the lamp permits centering on the diaphragm. For visual observation, an eye piece with a reflector is pushed into the tube below the objective as shown in the figure. This completes the normal microscope system. Very slight refocusing is necessary when the visual system is changed over to the projection system.
Figure (4.1) The Vickers Optical Microscope
4.3 Method of Examination using Vickers optical microscope:

It has long been known that the cubic faces of natural diamonds are profusely covered with nearly square shaped depressions called "tetragons". Because of the faceted nature of the surface, light incident on the surface is specularly reflected from the facetted rendering observation by direct reflection microscopy generally very difficult. Many of the features do not show up at all, so it is often more satisfactory to study such a surface by means of a replica viewed in transmission. The first replication was done by Mohl (1940), who used collodion to reproduce the surface structure of a crystal. Faust (1949) was able to reproduce the surface micro-structure of a crystal with very high accuracy by using perspex. Harrison (1964) replicated the surfaces of natural cubic diamond by using the same substance "perspex" acrylin sheet of thickness $\frac{3}{16}$ inch, but with a modified technique. The replication was done by applying heat and pressure at the same time. The replicas so obtained were studied by ordinary light microscopy. The replicas used in the present work were also made from perspex, heated to $140^\circ C$-$160^\circ C$ when sufficient pressure was applied to reduce the thickness of the softened perspex. To get minimum residual strain, the replicas were returned again to the oven for about 15 minutes after the pressure had been applied. Then the replicas were allowed to cool to the room temperature very slowly over a period of several hours. A jig shown in figure (4.2) was used for applying the pressure to the perspex. Replicas of two opposite faces of a cubic diamond can be made in such a jig at the same time. The diamond crystal is held by four quadrants which are clamped between two annuli as shown in figure (4.3).
Figure 4.2: Jig for making replicas.

Figure 4.3: Specimen holder.
Two rounded pieces of perspex are put under and above the two opposite faces of the cubic crystal under investigation. Figures (4.4) and (4.5) are photographs of replicas for two opposite surfaces of a cubic crystal, which are seen to exhibit several tetragons, when they are examined under the Vickers projection microscopy in transmission.

4.4 **Topographical studies of surfaces by using the scanning electron microscope:**

The main advantage of using the scanning electron microscope (S.E.M.) is the speed and ease of obtaining information on the surface topography of the crystals. In the scanning microscope, there is no general illumination as the optical microscope. The interaction of the high voltage scanning primary electron beam with the specimen gives rise to secondary electrons, which may be collected and the information displayed on a cathode ray tube, where an image is formed as a result of any response of the specimen stimulated by the electron beam. The main advantages of the scanning microscope are:

a. A great depth of focus in comparison with an ordinary optical microscope, at relatively low magnifications.

b. The possibility of direct observation of the external form of real object, such as rough surfaces of diamond avoids the necessity to make the thin replicas which are necessary for use in direct transmission electron microscopy.

c. A wide range of magnification which is continuously variable.

d. The specimen is easily tilted or rotated.

The main disadvantages of the scanning electron microscope are:

a. Lack of highest resolution.
Figure (4.4)  (100) face
optical micrograph x 60

Figure (4.5)  (100) face
optical micrograph x 60
b. The vacuum environment of the specimen.

c. The inability to show up the internal detail.

As far as topographical detail is concerned, the images are closely similar to those formed by reflected light optical microscope, but with much greater depth of focus and at a considerably increased resolution.

To study the topography of the surface of any crystal by the scanning electron microscope, it is necessary to coat the crystal with a layer of suitable conducting material before examination. Silver is the easiest material coating for diamond. The usual apparatus for evaporating metal is an Edward 12EA coating unit, which consists of a glass bell-jar, connected to a vacuum system capable of bringing the pressure in the bell-jar to about $10^{-5}$ torr. Inside the bell-jar, there are several electric terminals, and a suitable position to mount the sample. The sample is rotated about two axes to get uniform deposition of the metallic coating on all the surfaces of the specimen. The tungsten or molybdenum filament is heated electrically, so that the coating material, i.e. silver, is vaporized. The current should be increased gradually until the filament starts to warm up, and then increased so that the silver vaporizes slowly. The sample should be far enough from the filament so that it is not affected by radiant heat.

After the specimen is coated with a suitable layer of silver, about 800Å, it is ready to be examined under the scanning electron microscope. Figure (4.6) is a photograph of the scanning electron microscope used. Figure (4.7) is an electron micrograph of cubic diamond at magnification of X50.
Figure (4.6) The scanning electron microscope

Figure (4.7) The surface of a cubic crystal

scanning electron micrograph x 50
4.5 Examination of the surface topography of the crystal by transmission electron microscopy:

The limited depth of focus of the optical microscope reduces its effectiveness in detailed studies of very rough surfaces. The lack of high resolution in the scanning electron microscope limited its use in the study of the finer details of the crystal surfaces. The transmission electron microscope, with its greater magnification and depth of focus was therefore used to complement the studies of rough surfaces of natural cubic diamonds. Sixty cubic crystals were studied. The six cube faces of each one were examined first by optical microscopy and then by electron microscopy. It is often more satisfactory to study the surface of any crystal by means of replication, especially if the electron microscope is to be used. The replica is a thin film of electron transparent material, corresponding exactly to the topography of the surface, which is opaque to electrons. Many techniques have been developed which enable almost all forms of specimens to be examined.

The first replication was done by Mohl (1940), who used collodion to reproduce the surface structure of a crystal. The next important step was made by Heidenreich and Perk (1943), who prepared the first replica by using vacuum evaporated material. They used silica which formed a very strong thin film capable of giving a very high resolution. A year later Keller and Geisler (1944) prepared thin electron transparent films of aluminium oxide. The technique of replication was described by Comer and Tuley (1955), who used it to study the relatively rough surface of a crystal. Replica techniques have been further developed by Bradley (1954) and (1959). Patel and Patel (1967a) also prepared carbon replicas for diamond surfaces, by evaporating NaCl as an intermediate layer. Miller
and Punglia (1970) developed a single stage replica technique for micro-diamond surfaces of size below 100 microns. It was recognised that, in order to get the best replication of the topography of the surface under examination, the replica should have the following characteristics:

1 - It should reproduce the surface structure faithfully to a high degree of accuracy.
2 - It should retain the details of the surface when stripped.
3 - It should itself contain no structure down to the resolution limit of the microscope.
4 - It should give adequate contrast for the various surface details.
5 - It should be very thin, \( \sim 200\,\text{Å} \), in order to transmit the electrons.
6 - It should be resistant to decomposition by electron bombardment.

A number of different materials are used in the manufacture of such replicas, but each one requires its own particular preparation technique. The choice of the material to be used, depends on whether a preliminary impression of the specimen surface is to be made, from which a final replica is to be obtained, or whether the material itself is to form this final replica. Also the choice of the material depends upon the type of the specimen, i.e. the size of the crystal, its shape, the solubility of the specimen, the surface structure and finally on the resolution desired. Platinum-carbon replicas produced by the two stage techniques were used in the present work to study the surface structure of natural diamond for cubic form of size 1-3mm on edge. The carbon-platinum replica films are usually about 200 to 500Å thick, evaporated under high vacuum (10^{-5} torr) so as to conform strictly to the surface structure. Carbon-platinum
is evaporated by passing an alternating current of 60 amperes at approximately 30 volts, through the contacting points of two electrodes, one carbon and the other carbon-platinum. The contrast produced by many replicas and other types of specimens in the electron microscope is often very low and it may be necessary to increase it by means of shadow casting. This consists of evaporating a thin film of electron-dense material such as carbon-platinum in our case, at a certain angle on the specimen or on the replica surfaces.

4.6 The shadow casting technique:

The technique of shadow casting, described by William and Wyckoff (1946), consists of depositing, by vacuum evaporation, a layer of electron-dense material on the specimen at a certain angle. It can be seen from the diagram that the areas shielded from the impinging beams of atoms by surface irregularities are not coated. So these areas are more electron transparent than the coated areas and resemble shadows in appearance. When examined in the electron microscope, they will appear lighter than the surrounding areas.

For shadow casting, it is desirable to have the specimen at a reasonable distance from the source to prevent any damage by heat radiation and to produce sharp shadows. The angle of shadowing is varied according to the type of structure under examination.

In our present work, the angle of shadowing was fixed at 25°, to get sharp shadow for our rough surface of the cubic diamonds. In order to avoid geometric distortion of the specimen topography by the application of an excessively thick layer of shadowing material, it is necessary that this material should be of high electron scattering power, and hence in
general, of high atomic number. The choice is thus limited to metals such as gold, platinum, palladium alloy and uranium.

The shadowing layer must have the least possible self-structure, and the best materials from this point of view are platinum and platinum-carbon deposits, (Bradly, 1959), since they are non-crystalline and have the advantage that the final replica can be made from the shadowing material. The carbon-platinum replicas suffer from lack of contrast, so in order to overcome this, the carbon-platinum film can be evaporated at an angle ("shadow casting"). Platinum-carbon shadow casting using composite platinum-carbon electrodes is capable of producing resolution of the order of 10Å. The platinum-carbon rods used in this work were supplied by Polaron Instrument Company.

By using the method of shadowing casting, with platinum-carbon electrodes, not only is the contrast enhanced, but step heights of the order of 50Å are satisfactorily measured. As shown in figure (4.8), if S is the width of the shadow, M is the magnification of the specimen, then the step height H is given by

\[ H = \frac{S}{M} \tan \alpha \]

where \( \alpha \) is the angle of the shadowing.

Recently many techniques have been developed for the replication of various type of specimen, depending on the extent, shape and the nature of the surface, Desmond (1965).

Because of the insolubility of diamond surfaces, and its chemical inertness under ordinary conditions, it requires special techniques. Various techniques can be applied depending further on the size and shape of the crystallites.

Since diamond is insoluble under normal conditions, the two stage process

* see the end of this chapter.*
Figure 4.8: Diagrammatic representation of a shadowed crystal.
replication has to be used to study the surface topography of cubic
diamond under the electron microscope. The crystals were in any
case too large to apply the single stage technique used for micro
crystals.

4.7 The technique of the two stage replica:

The technique is used for crystals of size more than about
100 microns, i.e. large crystals. In order to study the surface topo­
graphy of such crystals optically and electron optically, it is
necessary to mount the crystal in a suitable medium. This should be
softened when heated so that the crystal can be mounted with its face
perfectly flat for interferometric studies. Gelva is a suitable
material for mounting the crystal, and the following procedure was then
used:

1 - The plastic film of acetyl cellulose 0.034mm thick is cut into
pieces slightly larger than the specimen surface of the crystal
which is to be studied.

2 - A small amount of methylacetate is put in a small dish to be
used as a solvent for the plastic film.

3 - After mounting the crystal, it should be first cleaned with
dilute nitric acid, then with water and finally by preliminary
replication.

4 - The small cut pieces of acetyl cellulose are moistened with
methyl acetate, then placed on the surface of the crystal and
lightly pressed. The single stage and the two stage replica techniques
are diagrammatically seen in figure (4.9).

5 - After the plastic film has dried (the solvent volatilizes in
S. Single Stage

T. Two Stage

Figure (4.9)
a few minutes), the replica is stripped carefully by picking it up with tweezers.

6 - In order to get the surface of the crystal very clean from any foreign materials, preliminary replicas are made, three or four times, at the beginning and then they are thrown away.

7 - As many as ten to twelve clean replicas are taken at a time, to ensure that true representation of the sample is obtained.

8 - All these replicas are pressed between two clean glass slides which are fastened lightly together by spring clips.

9 - The replica is then kept for about 30 minutes in an oven at 80°C, in order that the curling of replica films can be eliminated.

10 - The upper slide is then removed and the second one, with the reproduced surface upward, is subjected to platinum-carbon evaporation in vacuum.

11 - A clean glass slide is dipped in melted paraffin wax (melting point 65°C), then the replicas with the evaporated film are transferred on the wax film on the glass slide, as shown in the figure, with the evaporated platinum-carbon film side touching the melted paraffin.

12 - The slide is then placed in methyl acetate in a small container and left at room temperature to dissolve the acetyl-cellulose film, then the slide is transferred again to another dish of methyl-acetate where the temperature of the solvent is gradually raised to 60°C. The paraffin wax of the protecting film begins to dissolve and the evaporated replica films strip off the glass plate and float in the solvent.
13 - After repeating washing of the replica films in fresh methyl acetate, three times at least, they are washed again with acetone then transferred to a small dish filled with distilled water, where the replicas float on the surface of the water and are stretched flat by the surface tension of the water.

14 - The replica films are then picked out of the water and placed on the specimen grids to be examined under the electron microscope.

4.8 Classification of the types of diamonds by using Hilger spectrograph:

Diamonds have been classified as type I and type II according to their absorption in the infra red, visible and ultra violet regions. Type II diamonds transmit well in the ultra violet down to the absorption edge at 2200Å, but type I show absorption starting at 3300Å and increasing fairly rapidly at shorter wave lengths. The difference in the absorption spectra indicates that type II diamonds are more nearly perfect crystal than type I diamonds, i.e. type II diamonds are relatively free from some kind of defect or impurity which produces additional absorption in type I diamond. The existence of this absorption in type I diamond indicates the presence of some impurity or crystal defect which lowers the symmetry of the electronic structure.

Tolansky, Rawle-Cope (1969) identified nearly 6000 micro diamonds as type I or type II by observing their transparency with respect to the strong Hg line 2536Å obtained by filtering the light from a suitable Hg lamp with an aperture placed in a quartz spectrograph image plane.

In the present work, the sixty cubic diamond crystals have been examined
in a simple way by using a Hilger spectrograph to classify the diamond into type I or II according to their absorption to the ultra violet spectra. The experiment was carried out by placing the crystal against the slit of the constant deviation quartz spectrograph. The crystal was illuminated by the light from an intense quartz mercury source. The spectrum of each stone was photographed on a photographic plate.

From the spectrum recorded by each stone, it was found that the absorption started beyond 3000Å for all the 60 crystals. This revealed that the 60 crystals are all type I.

This method results in an underestimate of the depth of features such as terraced depressions with internal slopes at angles less than the shadowing angle. Figures quoted for depth in such cases are minimum values only and are estimated to $\pm 10\%$. 
CHAPTER V

EXPERIMENTAL WORK ON SURFACE

TOPOGRAPHY OF NATURAL CUBIC DIAMONDS
5.1 Introduction:

Although the cubic form of diamond is commonly produced synthetically, it is relatively rare in nature, small quantities being found in Congo and Tanganyika. As a consequence, relatively few studies have been conducted on the structure of this crystal form, moreover, the surface studies are not easy because their surfaces are very rough and pitted with many square shaped cavities which are called "tetragons", and sometimes called quadrons (Tolansky, Sunagawa 1960a). A detailed description of the surface topography of such faces is given in this chapter. The microstructures of the surfaces of sixty cubic diamonds were examined by optical microscopy, electron microscopy and by scanning electron microscopy. It was observed that the microstructures of the faces were similar for most of the crystals, with only a few exceptions.

5.2 Previous work on cubic diamond:

Fersmann and Goldschmidt (1911) were the earliest to report observations on cubic faces of diamond. Sutton (1928) also briefly described some cubic crystals. He reported that they deviated more from the true crystal form than other forms, and that the cubic faces depart from planarity, their edges being mostly rounded off to form faces which are dodecahedral. He pointed out that the rectangular depressions present in profusion on the faces are usually in negative orientation with respect to the crystal face i.e. their sides are at 45° to the cube edges. These observations have been generally confirmed by Williams (1932), Tolansky and Sunagawa (1959, 1960a), Tolansky and Harrison (1964), Varma (1967c), Patel, Patel and Agarwal (1967), Punglia (1972) and Moore (1972).
It was also reported by Evans and Sauter (1961), Patel and Ramanathan (1962), Harrison (1964) and Patel and Patel (1967) that etching of the cubic faces of natural diamonds produced pits in either positive or negative orientation, depending upon the etchant and temperature used. As with trigons on the octahedral faces, there is controversy regarding the origin of tetragons observed on cubic faces of natural diamond. Fersmann and Goldschmidt (1911), Patel, Patel and Agarwal (1967), and Patel and Patel (1975) have attributed these cavities to dissolution in nature, while Williams (1932), Tolansky and Sunagawa (1960a), Harrison (1964), Varma (1967a) and Punglia (1972) have attributed these tetragons to the mechanism of growth of the crystal. Tolansky and Sunagawa (1960a,b) conjectured that cubes grow by a plane sheet mechanism as revealed by layers and terracing. Just as the trigons on the \{111\} faces, so with the tetragons, the incompletion of growth layers leaves terraced pits, because of the sheet character of growth. They suggested the name "quadrons" to match with the name "trigons". They also established a number of distinctive differences between natural and synthetic diamonds of cubic form. They concluded that the differences between the natural and synthetic materials are due either to inclusions of metallic carbide in the synthetic crystal, or to different growth mechanisms for the two kinds of crystals. Seal (1962) and (1965) discussed the structure in relation to the kind of crystal growth which could have caused them and he observed that layer growth parallel to (111) plane was common. Varma (1967a) suggested that the cube is formed by a layer growth mechanism on \{111\} planes.

Patel, Patel and Agarwal (1967) studied the structures of the square shaped pits on the cubic faces of natural diamond, using an electron
microscope. They explained their observations by assuming that the square shaped depressions were formed by dissolution at the sites of dislocation, which were part of dislocation networks inside the body of the crystal. Patel and Patel (1968a) concluded that the point bottomed and flat bottomed square shaped pits on {100} faces of natural cubes are etch pits produced by natural etching of dislocations. Moore and Lang (1972) studied the internal structure of cubic natural diamonds by means of X-ray topography. They found that some crystals showed fibrous patterns. The fibres are seen to radiate from the central regions in the <111> directions towards the corners. Patel and Patel (1975) studied again dislocations on natural cubic diamond and observed rows of pits running approximately in <100> directions. They conjectured that such rows of pits are caused by the etching of dislocations along grain boundaries. They also conjectured that, since etching of crystal surfaces usually produces rows of etch pits along the grain boundaries, the rows of pits on {100} faces have also been formed by etching on such grain boundaries. They also observed rows of normal square shaped pits as well as rectangular spiral depressions. They suggested that the dislocations in the boundaries are a mixture of both edge and screw dislocations.

In order to decide the origin of the tetragon, i.e. whether they are formed by a growth mechanism or whether they are formed by etching in nature, it is desirable to study such faces in more detail and to give a full description of their microtopography.
5.3 **Optical studies on the structure of cubic faces:**

The surface structures were investigated directly by means of a Vickers projection microscope. The electron microscope, with its greater magnification and depth of focus, was used to complement the optical studies of the rough surfaces of the crystals. The scanning electron microscope was also a helpful tool for studying the surface as a whole at higher magnification without the need to replicate it. Figure (5.1) shows the structure of one face of natural cubic diamond, in which the square shaped depressions are clearly seen. Figure (5.2) is a further photograph taken by the scanning electron microscope and also shows the whole surface of another crystal face.

From the photographs we observe that the most obvious features of the surface are the rectangular depressions "tetragons" and that they vary in number from few to many hundreds on some faces. Figure (5.1) shows also some areas of flat facets which Harrison (1964) called cubic-like facets. The cubic facets usually occur between two or more tetragons or between the extensions of their tails as indicated in the photograph by the areas A, B and C. Some of them are markedly curved and the radius of curvature is very small, being less than 1mm (Harrison 1964). These two types of feature make up the entire surface of the cubic crystal.
Figure (5.1)  The (100) face showing tetragons and cubic facets. 
Optical micrograph X 80

Figure (5.2)  The (100) face of diamond  
S.E.M. X 100
5.4 Electron optical studies on natural cubic diamond:

This section describes studies of the fine detail of the surface of natural cubic diamond, using the high magnification obtainable by the electron microscope. This work is an extension to that of Patel, Patel and Agarwal (1967), who used electron microscopic techniques to study the \{100\} surfaces of natural diamonds. From their results, they attributed the existence of tetragons on cubic faces to natural etching. Punglia (1972) also used electron microscopic techniques during her studies on cubic diamond crystals and other forms. She concluded that the cubic crystals grow by layer deposition.

In order to obtain more information about the nature and possible origins of these natural tetragons, we have examined the surfaces on the six sides of each crystal of the sixty diamonds by means of the electron microscope. We only describe in detail the observations made on some of them, since the general features are common to most crystals. It should be pointed out that, of all the faces of cubic crystals which have been examined, only a few of them showed unusual features, and these will be discussed later in Chapter VI. It is well known that tetragons are found on the cube surfaces of natural diamond and also they can be produced by etching the cubic faces. The natural tetragons are not all alike, but they show many variations both in shapes and dimensions and possess some similar characteristics which can be summarized as follows from figures (5.3) and (5.4) for two different crystal faces we observe:

1 - The surfaces of cubic crystal consist of many rectangular pits having different sizes, which are all crystallographically oriented with their edges at $45^\circ$ to the edges of the cubic face.

2 - The tetragons are distributed irregularly on the crystal faces.
Figure (5.3)  (100) face of crystal No.(30)
Tetragrons of various size and shape  E.M. X 4000

Figure (5.4)  (100) face of crystal No.(32)  E.M. X 4000
3 - The neighbouring tetragons do not overlap with each other, but at the most they touch each other just like trigons on \([111]\) faces.

4 - Some tetragons are not perfectly square shaped as is shown in figure (5.5). The angles between the sides are not 90°, as are most of tetragons present on cubic faces. In this electron micrograph the sides of tetragons make angles 118°, 62° respectively.

5 - The shape of the small tetragons is similar to the shape of the larger ones when confined to the same area on the surface, figure (5.5).

6 - Some tetragons have rather complex features, where many small tetragons occur within the larger one. A good example of this phenomenon is shown in figure (5.6).

7 - Some tetragons have one side extended in the \(\langle 110\rangle\) direction, similar to the basal extensions observed in trigons on octahedral faces. Figure (5.7) shows some of these basal extensions or "tails" associated with some tetragons.

8 - The bottoms of almost all tetragons end in points i.e. the four sides of the tetragon are extended inwards to meet in a point. They are called point bottomed tetragons. Figure (5.8) reveals a selected region on a natural cubic face in which a number of point bottomed tetragons are seen. The photograph shows also the basal extensions associated with tetragons and shows also that the tetragons are elongated rather than squared.

9 - The pointed bases of some tetragons are not centered, but they are shifted towards one side as shown in figure (5.9).

10 - Some tetragons are terraced, as shown in figure (5.10), while some are not.
Figure (5.5) (001) face of crystal No.(2)

The tetragons are not square E.M. X 4000

Figure (5.6) (010) face of crystal (39)

Complex tetragons E.M. X 2500
Figure (5.7) The face (100) of crystal No. (3) showing the tails or basal extension E.M. X 4000

Figure (5.8) The face (010) of crystal No. (41) showing the basal extensions and point bottomed tetragons E.M. X 2500
11 - The terraced tetragon has a symmetrical structure with its base in the centre of the terracing as shown in figure (5.10), while the non-terraced ones usually have an asymmetrical structure, and their bases displaced to one side as shown in figure (5.9).

12 - Attention may also be drawn to the fact that although the outer boundaries of some tetragons are not perfectly square, their inner terraces make a perfect square. Figure (5.10) is again a good example of this type.

13 - The number of tetragons per unit area is not uniform on the same face. This is shown in figure (5.11).

14 - The cubic surface is composed of tetragons and cubic facets. Figure (5.12) shows some facets which are nearly flat and are of cubic or near to cubic orientation. They are enclosed between two tetragons or between two basal extensions of two tetragons (marked X in figure (5.12)). Sometimes the cubic facets are slightly curved and show bands as shown in figure (5.10) and are indicated by the areas A and B. Such observations show that the tetragons are not all alike and they show many variations both in their shape and size. Figure (5.13) shows four tetragons, having the same shape, but with considerable variations both in depth and size. Some of them have basal extensions in one direction, enclosed in between the cubic like facets. The big tetragon is terraced. It is noted also that the four tetragons are not perfectly square i.e. that the angles enclosed are approximately 70° and 110° respectively. Their depths range from 125Å for the smallest one to 375Å for the largest.

Another striking example of the variety in shapes of tetragons is shown in figure (5.14). Three tetragons are seen, which are also different
Figure (5.9)  The face (00\(\overline{1}\)) of crystal No.(35) showing that the centres are shifted towards one side of the tetragons  
E.M. X 2500

Figure (5.10)  The (010) face of crystal No.(38) showing the terraced type of tetragons  
E.M. X 3500
Figure (5.11)  The face (100) of crystal No. (32) shows the variation in distribution of tetragons  E.M. X 4000

Figure (5.12)  A cubic face of crystal No. (12) showing the cubic facets between tetragons  E.M. X 3000
Figure (5.13)  The face (100) of crystal No.(1)  E.M. X 4000

Figure (5.14)  The face (100) of crystal No.(3) showing the types of tetragons  E.M. X 3000
in size, depth and type. The biggest one is terraced with a flat base, square in shape and $\sim 750\text{Å}$ in depth. The second tetragon is also perfectly square with a flat base, and it is shallow, being approximately $120\text{Å}$ deep. The third is also a flat bottomed tetragon which is rectangular in shape with steep sides and overall depth approximately $110\text{Å}$. Figure (5.15) shows another type of tetragon with point bottomed base. Some tetragons are grouped on the base of a big tetragon, while some others are distributed on the surface. There is also an area which is smooth with no tetragons. Figure (5.16) shows another small area, several microns across, on the surface of natural cubic diamond, which contains many tetragons of different size, most of which are point bottomed. In contrast, figure (5.17) is nearly equal in area to the previous photograph, but the whole area contains two tetragons, both of which are terraced and have point bottomed bases. Their depths are $720$ and $340\text{Å}$, the larger being the deeper. These previous photographs reveal that the tetragons on (100) faces of natural diamond are not all alike, although they possess some similar characteristics, such as the basal extensions and the absence of overlap, but they show many variations in their shape and size. Figure (5.18) shows another good example of the variation in size, depth and type of tetragons. For example, near the bottom of the photograph on the left side, there is a terraced tetragon with flat base, on which there are two other small tetragons, one flat and the other point bottomed with steep sides. Similarly, there is another big tetragon at the top with steep sides and flat base which has also two point bottomed small tetragons on its flat base. There is another small flat bottomed tetragon on the right of the photograph. The rest of the tetragons are
Figure (5.15)  The (100) face of crystal No. (23)  E.M. X 4000

Figure (5.16)  The (100) face of crystal No. (32)  E.M. X 4000
Figure (5.17)  The (010) face of crystal No.(8)  E.M. X 3500

Figure (5.18)  The (00\bar{1}) face of crystal No.(9)  E.M. X 4000
all point bottomed and they have different sizes and depths.

It is quite clear from the previous photographs that most tetragons in a particular limited area on a cubic face have nearly the same shape, as in figures (5.5), (5.8) and (5.13), but also there is a considerable variation in their sizes and types. Therefore, since it is very important to specify not only the face but the type of the crystal, it is necessary to determine whether it is type I or II (Halperin 1954). The sixty cubic crystals were examined for transparency to the ultra violet region, and all of them were completely absorbent below 3000Å, which means that all of them are type I diamond.

Also from our discussions on the previous photographs, we can classify tetragons into two distinctly different types with respect to their bases.

1. Flat bottomed tetragons
   - terraced sided flat bottomed
   - steep sided flat bottomed

2. Point bottomed tetragons
   - terraced sided point bottomed
   - steep sided point bottomed

Figures (5.19), (5.20) are further examples, differentiating the two types of the point and flat bottomed tetragons. The point bottomed tetragon in figure (5.19) is a steep sided one and about 100Å deep, whereas the smaller one is very shallow and flat bottomed of approximately 20Å deep and the large one is a terraced tetragon of about 65Å of step height and ended inwards with a flat base. Figure (5.20) shows also the types of tetragons, the flat based ones and the point bottomed with terraced sides, noting that the flat bottomed tetragons are of different shapes, i.e. terraced and steep sided flat tetragon.
Figure (5.19) The (010) face of crystal No. (8) showing the types of tetragons E.M. X 4000

Figure (5.20) The (100) face of crystal No. (2) showing the types of tetragons E.M. X 4000
5.5 Classification of tetragons according to their bases:

Two types of tetragons are found on natural surfaces of cubic diamond. This leads us to study them in detail, to investigate their origin whether they are all due to growth mechanism or to dissolution in nature. Actually not much work has been performed on such classification of the tetragons: only Patel, Patel and Agarwal (1967) reported the point bottomed, flat bottomed and terraced tetragon, whereas much work has been done on the classification of trigons.

Before proceeding to a classification of tetragons on the basis of the present observations, a discussion will be given of the way in which trigons have been classified. Halperin (1954) characterized trigons which are found on natural \{111\} faces of diamond, that they are mostly shallow with their bottoms flat, especially on nearly perfect crystals, but on imperfect crystal faces they are, however, much deeper and their sides are extended down and inwards to meet in a point: these are called the point bottomed trigons. Wilks (1961) observed that the majority of trigons on \{111\} faces of natural diamond are low angle pyramids and another variety has steep sides with a flat base. She found that all of these low angle trigons are simply pyramids; some are truncated with flat bases and some have slightly concave sides. She determined the inclination of the sides of the steep trigon and showed that the sides of the trigon were inclined to the octahedron surface at an angle of $70^\circ_2$, which are the sides of the octahedron planes. She concluded that the low angled pyramids may have formed due to etching of dislocation lines. She could not decide the origin of the steep sided flat trigons.

Varma (1967a) observed that every flat bottomed trigon he has examined
contained many small tiny pyramidal trigons within its base. He con­
jectured that all trigons originate by a growth mechanism. Wilks and
Wilks (1971) again have listed diamonds according to the intensity of
their birefringence patterns. They observed that the number of
pyramidal trigons on diamond is correlated to birefringence in diamond,
but there is no correlation between birefringence and flat bottomed
trigons. They argued that a flat bottomed trigon could only have been
formed by a growth process because the flat bottom of a trigon was at
exactly the same level as the surface, separated from the surface by an
elevated ridge, and that all the pyramidal trigons are due to etch.
This confirmed Tolansky and Wilcock's hypothesis (1947), when they
argued that a flat bottomed trigon could only have been formed by a
growth process, because they observed that the flat bottom of a trigon
was exactly at the same level as the surface of the diamond crystal.
By using X-ray topography and the phase contrast microscopy, Lang (1963)
studied the origin of trigons on natural octahedral faces. He observed
that the pyramidal trigons are always associated with dislocation
outcrops and that no dislocation outcrops at flat bottomed trigons.
Patel and Patel (1965) and (1968a) have reported their observations on
the origin of the small point bottomed and flat bottomed trigons which
are either isolated or appeared to be within a large flat bottomed trigon.
They explained that the trigons nucleated at the sites of the termination
of dislocation on these layers and that trigons nucleated earlier will be
larger in size compared to trigons nucleated at a later stage of
dissolution. They postulated that the trigons which are nucleated at dis­
location loops will become flat bottomed trigons.
Patel and Patel (1969) again found that during the process of etching
of diamond of the octahedral faces, pits of rectilinear sides and sharp corners similar to trigons on natural diamond are produced. These etch pits were of two types, a) point bottomed and b) flat bottomed. They suggested that the dislocations might be running small distances within the body of the crystal giving rise to the flat bottomed trigons. It was also observed by Halperin (1956) that on a certain part of a crystal face the deeper trigons are smaller in lateral dimensions than the shallower ones, and that the micro-structure of a rough face is more complicated.

It was found by Angus, Dyble (1975) that the point bottomed pits with shallow slopes are formed from small initiating defects, e.g. dislocation outcrops. Flat bottom pits with steep sided outer faces (70' 32') are formed by etching along shallow defects, e.g. ring cracks of inclusion. Also Patel (1961) etched diamond in KNO₃. He classified the etch pits produced into point bottomed, flat bottomed and terraced pits. He postulated that pits are initiated on linear defects in the body of the crystal. The pits so nucleated will be point bottomed in the initial stage. The pits will remain point bottomed by increasing etching till the point bottom of the pit reaches the end of the linear defect and then the pit will gradually convert into a flat bottomed type. If any new defect appears after on the flat bottom of the pits, a new pit will be nucleated at this place which explains the formation of pits within pits. He explained the phenomenon of the eccentricity of some point bottomed pits which do not coincide with the centre of the triangular boundary of the pit. The eccentricity of the point bottom increases with the time of etching. Even in the case of flat bottom, this was explained by postulating that the linear defects may not be perpendicular to the
cleavage face, but they may be inclined to it.

By the analogy with trigons on \{111\} faces and as a result of the above work, we may classify tetragons according to their shape and type into:

1. The flat based tetragons:

   Starting with the first type of classification of tetragons with flat bottoms, figures (5.21) and (5.22) are two examples of this type. They show several flat based tetragons with a considerable difference in both of their depths and sizes. Figure (5.21) shows that all the flat based tetragons are non-terraced with steep sides, whereas the tetragon in figure (5.22) is a terraced one. From these two photographs, we can classify also the tetragons with flat bases into two different side shapes as follows:

   a. Terraced or "step" sided flat bottomed tetragons:

   b. Steep sided "non-terraced" flat bottomed tetragons.

a. Terraced sided flat bottomed tetragons "step sided":

   Figure (5.23) is a good example of a flat bottomed tetragon with step sides "terraced". It is very obvious from this photograph that the descent of the sides to the bottom can take place in several abrupt steps. The tetragon is very deep, about 1000\(A^0\), with average step height 200\(A^0\), where the sides appear as regularly stepped. This type of tetragon is very infrequent on the surfaces of cubic diamonds.

b. The non-terraced flat based tetragons "steep sided":

   This type is more common than the previous one, because it was observed nearly on all the crystal surfaces which have been examined. Figure (5.24) is an example which reveals the flat based tetragons with non-terraced sides. The photograph shows a number of well shaped squared tetragons with three of them nearly the same size and depth which is
Figure (5.21) The (100) face of crystal No. (3) showing the non-terraced flat bottomed tetragons E.M. X 4000

Figure (5.22) (010) face of crystal No. (12) showing a terraced flat bottomed tetragon E.M. X 4000
Figure (5.23) (100) face of crystal No. (3) showing a very deep tetragon with flat bottomed and terraced sides.

Figure (5.24) (100) face of crystal No. (10). Some flat based tetragons with non-terraced sides.
about 50°, and they are very shallow with flat bases and rectilinear sides. Another small flat bottomed tetragon which also has steep sides with one side missing and of a considerable depth, about 100°, is seen in the photograph. The upper tetragon which is near the right corner is a steep sided tetragon with a "point bottom", i.e. different from the flat bottomed type, as will be discussed later. It should be noted that sometimes we observe a collection of small tetragons having different sizes and shapes, on the bottoms of flat based tetragons where they form complex features. Figures (5.25) and (5.26) show two examples of assemblies of small squared depressions on the bases of flat tetragons. The photograph of figure (5.25) reveals a shallow tetragon which is non-terraced, together with another two tetragons which are point bottomed and enclosed between two of their sides a flat area which is a cubic facet, such as we discussed earlier, all together on the flat base of a big tetragon, forming a complex one.

2. The point bottomed tetragons:

This type of tetragon is found in profusion on the surfaces of natural cubic diamonds. Figures (5.27) and (5.28) show some of these tetragons on a very small area of a few square microns on the surfaces of natural cube. The two micrographs represent two different crystal faces. It is noticed that the tetragons are different in size and depth, but they are nearly all of the same shape, with their sides meeting inwards in a point to form point bottomed tetragons. These are again classifiable into two groups, as follows:

c. Terraced point bottomed tetragons (step sided).

d. Non-terraced point bottomed tetragons (steep sided).
Figure (5.25)  The (100) face of crystal No.(1). Assemblies of pits on a flat based tetragon  E.M. X 4000

Figure (5.26)  The (100) face of crystal No.(32). Many small tetragons on a flat based one  E.M. X 4000
Figure (5.27) The (010) face of crystal No. (2)
Point bottomed tetragons

Figure (5.28) The (010) face of crystal No. (32). Another shape
of point bottomed tetragons
c. **Terraced point bottom tetragons "step-sided":**

Most of the terraced tetragons are large compared to the non-terraced ones. Figures (5.29) and (5.30) are two examples of this type. Figure (5.29) shows three tetragons which are all point bottomed with terraced sides. They are large, ranging in size from 400° up to 700°. They are also well formed and have rectilinear sides with sharp edged layers. On the same photograph there are three small tetragons which are non-terraced and have point bottoms. The photograph shows the big difference in size between the terraced and non-terraced tetragon, although all of them are of the same type. Figure (5.30) shows another two tetragons of nearly the same size and depth, which is about 500° and both are terraced. Their sides make an angle of about 35° with the cubic plane.

From these photographs and our studies on the point bottomed tetragons with terraced sides, we observe that the inner terracing of the tetragon is perfectly square, but that the outer boundaries deviate from the square shape. Furthermore, all the terraced tetragons have a symmetrical structure, especially the inner area with their sides meeting together in a point which lies very near to the centre, while the non-terraced tetragons usually have an asymmetric structure with their point bottoms deviating from the centre towards one side, as we will discuss later.

Also it is quite clear that almost all the terraced tetragons with point bottoms are large and very deep compared to the non-terraced ones. Their sides make an angle of 35° with the cubic plane.

d. **The steep sided point bottomed tetragons, i.e. non-terraced tetragons:**

This type of tetragon is found in profusion on all the faces of cubic diamonds. Figures (5.31) and (5.32) show assemblies of this type
Figure (5.29) The (010) face of crystal No. (38) showing point based tetragons with terraced sides

E.M. X 4000

Figure (5.30) The (0010) face of crystal No. (30) showing point bottomed tetragons with terraced sides

E.M. X 3500
Figure (5.31) The (100) face of crystal No.(3). Tetragons with point bases having steep sides  E.M. X 3500

Figure (5.32) The (100) face of crystal No.(18). Tetragons with point based and steep sides  E.M. X 3500
of tetragons on the faces of two different crystals. It is obvious that all the tetragons are non-terraced and are shallow of maximum depth 150A, compared to the terraced ones. Also the non-terraced tetragons have small dimensions. It is also observed that the sides of each tetragon meet in a point at the base and that the bases are not quite central, but deviate towards one side of the tetragon (figures (5.31), (5.32)). A further observation on some tetragons, especially the point bottomed ones with steep sides, is the extension associated at one side of the pit which looks like a tail (Figure 5.31).

As a result of the above classification, we concluded that:

i - The structure of tetragons may differ from one type of crystal to the other,

ii - The terraced sided tetragons have been formed by a different mechanism from those which have steep sides and will be discussed later,

iii - It was observed also that the terraced tetragons are very deep compared to the non-terraced,

iv - The terraced tetragons, either point bottomed or flat bottomed have big dimensions with a symmetrical structure, especially near to the central region of the tetragons.

v - The point bottomed tetragons have their sides inclined with 35° to the cubic plane which is the angle of the octahedral plane with the cubic face. This means that the sides of point bottomed tetragons are coincident with the octahedral plane

vi - It was observed that the tetragons are distributed at random on the surface with a variety of size and depth, and in general have rectilinear sides and sharp corners.
vi - the most common type on the surface are the non-terraced tetragons with point bottomed bases, whereas the flat bottomed tetragons are relatively few.

5.6 Some other features observed on the surfaces of cubic crystals:

Tetragons are distributed at random with a variety of size, depth and shape, with some tetragons found together on the base of a big one, whereas some of the smaller tetragons appear to be isolated as if they develop independently.

One of the most interesting observations made on the cubic faces of natural diamond is the arrangement of some tetragons in rows, either across the diagonal of a big tetragon, or parallel to the \( \langle 010 \rangle \) direction. Figures (5.33), (5.34) and (5.35) show the arrays of small tetragons across the diagonal of big ones on three different faces.

There is another type of array in which some tetragons arrange themselves on the side wall of a big tetragon parallel to the \( \langle 110 \rangle \) directions and figure (5.36) is a good example of this type.

It is also observed that there are some small tetragons which are found over a considerable area on the surface and are arrayed in a very long row which look like a step line on the surface of the crystal. This line lies parallel to the \( \langle 010 \rangle \) direction. They are of very small size. This type of arrangement is seen in figures (5.37) and (5.38), where the line of tetragons in the first photograph is a continuation of the line of tetragons in the second one. They are more or less of the same size.

Figures (5.39) and (5.40) are further examples of the array of the tetragons in a line, which is also a continuous one, found on another crystal face, i.e. the line of tetragons in figure (5.39) is a continuation to that one of figure (5.40).
Figure (5.33) The (100) face of crystal No. (32). A linear array of tetragons along the diagonal direction E.M. X 4000

Figure (5.34) showing an array of small tetragons across the diagonal of a big one E.M. X 4000
Figure (5.35)  The arrangement of tetragons on the diagonal of a big one E.M. X 4000

Figure (5.36)  The arrangement of tetragons on the side wall of a big one parallel to $\langle 110 \rangle$ direction E.M. X 4000
Figure (5.37) showing the arrangement of tetragons in a row

E.M. X 2500

Figure (5.38) shows the continuation of tetragons of the previous photograph

E.M. X 4000
Figure (5.39)  A long line of small tetragons

Figure (5.40)  A continuation line of tetragons of the above
photograph
Patel and Patel (1975) also observed rows of pits running parallel to the \(\langle 100 \rangle\) direction on the cubic faces of natural diamonds. They conjectured that such rows of pits are attributable to the etching of dislocations along grain boundaries, where it produced square pits as well as rectangular ones. This accords with our observations. Other interesting features observed on the faces of cubic crystals, are the block pattern shown in figures (5.41) and (5.42). The pattern appears as rectangular blocks piled up one over the other and they are all oriented in one direction.

Omar, Pandya and Tolansky (1954), Tolansky (1955), Berman (1965) and Punglia (1972) have observed such remarkable block features on quite a number of octahedral faces when they were etched in KNO\(_3\) at higher temperatures over 600\(^\circ\)C. They attributed such features to etching.

5.7 External structure and defects on cubic faces:

Sometimes the surfaces of some crystals are marred by cracks or furrows. Figure (5.43) is an optical micrograph of a perspex replica which shows the surface of crystal No. (45) which has a linear crack over the diagonal of the surface, with several tetragons on both sides of the crack. Figure (5.44) shows a similarly furrowed surface. Another crystal showed a very peculiar phenomenon. A small cubic crystal is attached to one side of a big cubic crystal No. (15) as seen in figure (5.45). By using higher magnification to examine the surface topography of the small crystal, it was found that it has the same surface structure on its face as the large one. Figure (5.46) shows the tetragons on the surface of the small crystal to have slightly different orientation of those on the surface of the big crystal.
Figure (5.41) The (010) face of crystal No. (41)
A block pattern feature  E.M. X 2500

Figure (5.42) The (010) face of crystal No. (41)
A block pattern feature  E.M. X 2500
Figure (5.43) The (100) face of crystal No. (45). Crack across the diagonal of a cubic crystal. Optical micrograph X 50

Figure (5.44) The (100) face of crystal No. (45). Defects on the surface. Optical micrograph X 50
Figure (5.45) Crystal No. (15) showing the attachment of a small cubic crystal to the big one S.E.M. X 50

Figure (5.46) showing the orientation of the pits on the surface of a small crystal S.E.M. X 100
CHAPTER VI
EXAMINATION OF OCTAHEDRAL AND
DODECAHEDRAL FACETS ON CUBIC DIAMONDS
6.1 Introduction:

It has long been known that octahedral faces of diamond crystals are characterized by a number of triangular depressions called "trigons". Almost all of these depressions are equilateral in shape with rectilinear sides and sharp corners. They are also crystallographically oriented in one direction on untwinned faces with their corners pointing to the edges of the octahedral face. The features seen on the cube faces are generally quadrilateral or rectangular depressions called "tetragons" as we have discussed in the last chapter.

The cubo octahedral form is also found in nature, the surface of such crystals are composed of cubic faces as well as octahedral faces. They are all small in size, of the order of a few microns (Punglia 1972). As we have discussed in the previous chapter, the general characteristics of the cubic faces are however very nearly the same, with a few exceptions. Figures (6.1) and (6.2) show two opposite faces (100) and (100) for one cubic crystal. They reveal the structure of the faces and the distribution of tetragons on them.

Of the sixty crystals we have examined, about eight crystals are peculiar and show trigon depressions in addition to tetragons on their faces. Also other facets such as dodecahedral facets have been observed and are characterized by striations.

Sutton (1928) reported the presence of dodecahedral facets at the edges of cubic crystals. In (1964) Harrison examined the edges of some cubic diamonds which looked rounded and striated; he called them dodecahedral faces. When he tilted the crystal so that it was oriented approximately in such a way that an octahedral plane of the crystal was perpendicular
Figure (6.1)  (100) face of crystal No. (45)
Optical micrograph X 60

Figure (6.2)  (100) face of crystal No. (45)
Optical micrograph X 60
to the optical axis of the microscope, he observed trigons. This occurred when the facet was exactly octahedral and was present only at the corners of the cubic crystals.

Varma (1967c) also studied natural diamond crystals of cubic form and observed trigons at different places at the corners. This was observed only by setting the cubic crystal such that the (100), (001) and (010) planes were equally inclined to the line of the viewing microscope. He concluded that the cubic layers were therefore formed by a layer growth mechanism and that the layers were in the \{111\} planes. Some cubic faces were also examined by Seal (1960). Their surfaces were so rough and pitted that the sides of the hills present on the face had octahedral orientation and the tops had cubic orientation. In this case trigons and the four sided pits "tetragons" appeared in close proximity. Patel, Patel and Agarwal (1967) studied the cubo-octahedral form. They observed some trigons on the \{111\} faces very close beside the tetragons on the cubic faces on the same crystal. Punglia (1972) has also studied the cubo-octahedral form of synthetic diamond and found that the cubic faces of these crystals are smooth and specular, unlike the faces of the natural cubes. Moreover, she has found that this type of crystal is of minute size i.e. of the order of $10^{-4}$ cm. She has observed that in addition to their smoothness some showed remarkable surface pittings, which are crystallographically oriented and are related to the symmetry of the face, with their sides parallel to \(<110>\) directions. These pits are not very deep and have flat bottomed bases. Their sizes are fairly similar. Most of them have sharp corners forming an angle of $90^\circ$ and their sides are usually rectilinear. Trigons have also been found on the octahedral facets and the tetragons on the cubic facets, and all are together on the cubo-octahedral crystal faces.
6.2 **Topographical studies of octahedral facets at the corners of cubes:**

Of the sixty cubic crystals which we have examined optically and electron optically, a few of them (4 crystals) show octahedral faces at their corners characterized by the presence of trigons. We have studied the topography at these corners by means of replica techniques (perspex replicas for use in the Vickers optical microscope, and two stage replicas for the electron microscope). Also the scanning electron microscope has been used to examine the corners directly after coating with a silver layer. The two photographs shown in figures (6.3) and (6.4) have been taken by the optical microscope and show two opposite corners of a *buncahed* cubic crystal. The photographs show an area of octahedral faces present at the crystal corners, which is characterized by depressions of several trigons having different sizes. Most of them are terraced with flat bottomed bases, and they are all crystallographically oriented in one direction with their corners directed towards the edges of the (111) plane. It is quite obvious that the octahedral faces seen in the two photographs are surrounded by three areas of dodecahedral faces which are also characterized by striations. The dodecahedral face is also present at the rounded edges of the cube. Figure (6.5) is a further photograph, taken by optical microscope for another crystal, which shows two corners of the crystal, having the octahedral faces with trigons on them. At the left and right sides of the photograph there are two areas of octahedral faces and in between there is a big area of (110) face with many striations. Figure (6.6) is a scanning electron micrograph, showing one corner of the whole crystal, which reveals the octahedral face with many trigons. The other faces are out of focus and even the trigons are also not very clear. By using a higher magnification, four times the
Figure (6.3) The corner of a cubic diamond with trigons on the (111) face

Figure (6.4) Another corner, which is an octahedral face with trigons

Optical micrograph X 100

Vickers microscope X 100
Figure (6.5) Two corners of \{111\} face at the left and right parts with trigons enclosed between is (110) face with striations. Vickers micrograph X 100

Figure (6.6) The whole crystal showing the octahedral face. S.E.M. X 50
magnification of figure (6.6) it is easy to recognise the octahedral faces at the corners of the crystals and their topography, as shown in figure (6.7). The trigons are all oriented in one direction, having their corners pointed to the edges of the octahedron. Most trigons appear to be equilateral and have a pyramidal shape. The majority have terraced sides. It is also noticed that most of the trigons are deep with point bottomed bases and few are flat bottomed and they look very shallow. Figure (6.8) shows another octahedral face found at the corner of another crystal. It is evident that the trigons in figure (6.8) are relatively small and not very deep. It is quite clear that each octahedral face at the corners of a cubic crystal is surrounded by three dodecahedral planes, which are present at the rounded edges of the cube. They are characterized by striations as will be discussed later.

The truncated corners of the cubic crystals have been examined in the magnification range 3 to 4K, by replicating them, and then examining the replicas in the electron microscope. Figures (6.9) and (6.10) are two good examples revealing the corners of two crystals and showing the octahedral faces with many trigons. Although the density of the trigons on the two specimens is different, they show some similarities. The obvious features of these micrographs are:

1 - The trigons found on the (111) faces at the corners of the cube have different sizes, as shown in figure (6.10).

2 - All the trigons are crystallographically oriented.

3 - The trigons are equilateral with rectilinear sides and sharp corners.

4 - Some trigons have terraced sides as in figure (6.9), while some are non-terraced as those in figure (6.10)
Figure (6.7)  The (111) face at one corner of a cubic crystal

S.E.M. X 200

Figure (6.8)  Trigons at the (111) plane on the corner of cubic crystal

S.E.M. X 200
Figure (6.9) A small area of octahedral face found at the corner of cubic diamond. It shows trigons of different sizes.

E.M. X 3000

Figure (6.10) The (111) face at the corner of cubic diamond. Trigons with flat and point bottomed bases.

E.M. X 4000
5. Some trigons are complicated, including on their surfaces smaller ones as in figure (6.10).

Figure (6.11) shows a complex trigon which is very big with a flat base, containing many small trigons, some of them are very tiny with point bottomed bases and two of them have flat bases. Figure (6.12) represents another small area at the corner of a cube which shows that the trigons are varied in depth.

It is observed that, in general, trigons with flat bases are very shallow compared to trigons having point bottomed bases. Figures (6.3) up to (6.12) provide confirmation that at the corners of some cubic crystals there exist some areas of octahedral faces with many trigons. These octahedral faces are parallel to the \{111\} plane of the bulk of the crystal.

6.3 **Topographical studies of dodecahedral faces at the edges of the cubes:**

Many studies have been done on dodecahedral diamond crystals and it is found that this form of crystal is often very rounded.

Emara and Tolansky (1957) have studied the surface topography of dodecahedral crystals of diamond and observed striations on their surfaces. These striations are found to run approximately parallel to the long diagonal of the rhomb which forms the dodecahedral face. Emara and Tolansky have studied these striations interferometrically and called them ruts or channels on the surface. They have observed that these ruts or striations are of the order of $\frac{1}{100}$ mm wide and from 100 to $200\,\AA$ deep.

Harrison (1964) has also studied the dodecahedral faces which are found at the intersection of every pair of cubic faces on some crystals. He has observed that these \{110\} faces, like the cubic faces, are characterized by a faceted structure.
Figure (6.11) A small area of (111) face at the corner of cubic crystal

E.M. X 3000

Figure (6.12) An area of (111) face at the corner of cubic crystal

E.M. X 4000
Varma (1967b) has studied the dodecahedral form by setting up the crystal so that the three faces, namely (110), (011) and (101), can be simultaneously seen. He has observed that the striations go around all the three faces which are in fact the spaces between successive layers and that the spacing between these layers look like ruts or channels. Varma has concluded that dodecahedron is an initial octahedron modified by growth occurring on all the octahedral faces in the form of parallel layers of progressively diminishing size, giving rise to a pyramidal hill at the pointed top.

In the present work, a different method is used to study the surface topography of dodecahedral faces present at the edges of cubic diamonds. We have replicated the edges between every pair of cubic faces of some crystals which have rounded edges, by mounting the crystal very carefully on a piece of flat glass with its cube edge horizontal, in order to reproduce the face (110). The dodecahedral replicas are then examined optically by using Vickers optical microscope.

Figure (6.13) shows the dodecahedral face at one edge of cubic diamond which is rounded. The photograph shows the feature of striations over the surface, between the edges of cubic faces. These striations run adjacent perpendicular to the cube faces. At the two sides of the photograph, left and right, there are two small areas of octahedral faces which are present at the corners of cubic crystals. Trigons are visible on these (111) faces.

Figure (6.14) is another interesting photograph showing the three faces (100), (110) and (111) simultaneously. At the top of the photograph there is an area of octahedron which is characterized by trigons. The (111) face is enclosed by two areas of dodecahedral faces which show many
Figure (6.13)  The rounded edge of cubic crystal which is characterized by striations  Optical micrograph X 100

Figure (6.14)  Simultaneous view of three faces (110), (111) and (100)  Optical micrograph X 100
striations. Also there is an area of cubic face with some tetragons. The tetragons are not clearly observed because the replica has been mainly done for the \{110\} faces.

The rounded edges of cubic diamond for four crystals have also been examined by the scanning electron microscope. The dodecahedral faces at the edges are examined directly on the crystal itself after it has been mounted on a flat piece of glass with the (110) face at the top. It was coated with silver under vacuum before examination. Figure (6.15) shows the striation features over the surface between two cubic faces. Figure (6.16) shows the three faces together i.e. the cubic face with some tetragons at the upper part of the photograph, there is a small area of smooth octahedron with few trigons at the lower part of the photograph, while in the middle is a striated dodecahedral face.

To study the dodecahedral surface in detail, the higher magnifications of the electron microscope and two stage replica techniques are used. Figure (6.17) is a good example which shows two faces together. The replica has been taken mainly for the edge between two cubic faces, together with a part of the cubic face itself. The lower part of the photograph reveals the cubic face with some tetragons which are mostly flat bottomed and are very shallow. The upper part of the photograph is a dodecahedral face characterized by striations which are also of different depth and width. Figure (6.18) is another interesting electron micrograph which was taken for another cubic crystal. It shows similar features of the two facets together. At the left of the photograph there is a part of the striated dodecahedral face, while the rest shows an alternation of striated dodecahedral facets and cubic facets with some tetragons. The two facets are alternated in different parts on the surface of the cubic crystal No. (31). This crystal No. (31) is peculiar
Figure (6.15) Striations at the rounded edges of cubic crystals

S.E.M. X 200

Figure (6.16) Three faces, the (111) plane with trigons, the (110) with striations and the cubic face with tetragons

S.E.M. X 100
Figure (6.17) The dodecahedral face which is striated and the cubic face with tetragons E.M. X 4000

Figure (6.18) Alternating dodecahedral faces with striations and the cubic faces with tetragons E.M. X 4000
because it shows many facets on its surfaces such as (111), (110) and cubic faces and other uncommon features as will be discussed later. Figure (6.19), another cubic crystal with rounded edges, shows that the striation features resemble layers which are all crystallographically oriented. They have different widths and their depths range from 50\(\text{Å}\) to 350\(\text{Å}\). At the lower part of the photograph there is a small triangular pit on one of these striations. This confirms Varma's hypothesis (1967b) that dodecahedron is formed by a piling up of layers in the (111) planes, on which trigons could be seen at the spaces in between the different layers. Also in the middle of the photograph there is a striation having a quadrilateral pit which is also crystallographically oriented with its corners directed towards the edges of the cube. Figure (6.20) is another photograph which represents a small area of dodecahedral face at one edge of a cubic crystal and is also striated. The striations are different in their appearance to those which we have seen before, being broader and more rounded at their end and extended inward to a point. From these observations we conclude that some cubic crystals with rounded edges show dodecahedral facets at their edge with striations, which are different in the thickness of the layers comprising them.
Figure (6.19) Striated dodecahedral face with a triangular pit and a quadrilateral pit  E.M. X 4000

Figure (6.20) A dodecahedral face with striations  E.M. X 4000
6.4 The topography of the octahedral facets on cubic crystal:

Of the numerous crystals which have been examined, only about \(\frac{1}{8}\) of the total show trigons on their surface in addition to tetragons. These octahedral faces with trigons are different from those found at the corners. Such triangular depressions have been studied in more detail by the electron microscope at a higher magnification range between 2.5k up to 4k. Most of our observations are original and reported for the first time.

Crystal No. (11) is a rather unusual crystal. It is grey in colour, is about 1.2mm on edge and its weight is about 0.06 carat. Nearly all its six faces show a number of octahedral facets which overlap with the cubic faces. Figures (6.21) and (6.22) reveal two different areas of a few microns in diameter on one face of the crystal No. (11). The two photographs show similar features i.e. octahedral facets which are characterized by the trigons juxtaposed to the cubic faces with some tetragons. The octahedral and cubic facets are observed many times in different parts on the crystal surfaces, next to each other and sometimes overlapped together. Figure (6.23) shows another part of a cubic surface which composes of an octahedral facet with trigons juxtapose to tetragons. From these observations we conclude that some cubic diamonds are multifacets. The predominant facets are the cubic ones with tetragons and the cubic-like facets which are sometimes slightly curved. The octahedral facets also occur in many cases as we have seen in the previous photographs. Few cases of dodecahedral facets have also been observed overlapping with the cubic faces. Figure (6.24) shows the overlapping of the three facets together on a very small area i.e. the cubic facets with few squared tetragons; the dodecahedral facet which is striated and
Figure (6.21) The face (010) of crystal No. (11) showing two adjacent facets: (111) and (100) E.M. X 4000

Figure (6.22) The (010) face of crystal No. (11) showing the two adjacent facets E.M. X 4000
Figure (6.23)
The face (010) of crystal No.(11) showing the adjacent facets
E.M. X 3000

Figure (6.24)
The facet (100) of crystal No.(31) showing the three facets, each facet has its own character
E.M. X 4000

Figure (6.25)
One face of crystal No.(13) showing very small areas of (111) facets on the cubic surface
S.E.M. X 1000
the octahedral facet with trigons. Each of these facets is crystallographically oriented and has its own character.

Seal (1960) has examined some cubic surfaces which are rough and pitted. He has attributed the appearance of the adjacent trigons and four sided pits to the presence of hills which have sides of octahedral orientation and a cubic top.

Our observations are different, a good example of this being shown in figure (6.25) for one face of crystal No. (13) where there are some small areas of octahedral facets exist on the cubic face.

From these previous photographs, it is clearly seen that these triangular pits possess all the characteristics of trigons such as:

1 - The triangular depressions have rectilinear sides and sharp corners.
2 - The triangular depressions are crystallographically oriented.
3 - They have different sizes and shapes e.g. the trigon in figure (6.21) is a point bottomed one, whereas the trigons in figures (6.22), (6.23) are flat bottomed.
4 - Their depth is also varied approximately from a very shallow one 50Å° to 400Å° for the point bottomed trigons.
5 - Some trigons have terraced sides.

This means that the triangular pits which are observed on these (111) facets possess all the characteristics of trigons on the natural octahedral diamonds.

Also the tetragons on the cubic facets vary in their shapes, sizes and depths. They also possess the same characteristics as the tetragons found on cubic crystals and discussed before in chapter V. Therefore the octahedral facets on (100) surfaces do not look like a side of a hill, but they are actually small areas of octahedral facets which exist on the cubic surface.
Many examples of this phenomenon are observed on different crystals. Crystal No. (31) is another unusual crystal which has multi-facets intersecting together. This crystal is yellowish in colour and has side lengths about 2.7mm with rounded edges which show the dodecahedral faces characterized by striations. By examining its faces under Vickers optical microscope, its structural detail could not be easily detected because of the relatively low magnification compared to that attainable with the electron microscope. The two electron micrographs in figures (6.26) and (6.27) reveal a very small area of a few square microns which show the fine structures of the face (100). It is quite clear that the surface is composed of two different types of crystallographic facets, which are overlapped together in many areas over the crystal surface. Figure (6.26) for example, reveals three areas of octahedral facets, two of them have a big trigon with a point bottomed base. The trigons have the same direction i.e. they have the same crystallographic plane. They border on a very small area of cubic facet which has some tetragons. These tetragons have the same orientation as the rest of the others which are found at different places on the surface. Another small octahedral facet is also visible at the bottom of the photograph with many small point bottomed trigons which are in turn crystallographically oriented and have the same orientation as the big ones. Figure (6.27) further reveals the intermixing of the two types of facets where there are two areas of octahedral facets bordering on a very small area of cubic facet containing parts of tetragons.

From the two latter photographs it is quite clear that the tetragon depressions are not deep, between 50 - 100A° and have almost flat bases.
Figure (6.26) The face (100) of crystal No. (31) showing the interfaces of the two types of facets together
E.M. X 4000

Figure (6.27) Another area on the same surface (100) of crystal No. (31). The two facets (111) and (100) interface together
E.M. X 4000
They are fairly similar in size, with sharp corners of nearly 90° and with rectilinear sides, whereas the trigons are different in their size, depth and shape. Some are terraced with point bottomed bases as are the two big ones in figure (6.26), whereas the other trigons are different in their sizes, but almost all are point bottomed with steep sides and are different in depths.

Figures (6.28) and (6.29) show two different faces of the crystal No. (31). They reveal the different shapes of trigons on the octahedral facets which are adjacent to the cubic facets. The tetragons in figure (6.29) are not squared in shape, like those in the three previous photographs, but their angles are 60° and 120° respectively. They are more or less of the same size with flat bases. Their depths are ranging from 50A° up to 200A°.

Crystal No. (30) is another special crystal which shows also some uncommon features on its faces. It shows a big tetragon with two small triangular pits at its lower side as seen in figure (6.30). At the middle of the photograph, there are a number of elongated tetragons which are arranged in a long row. This row is interrupted by an octahedral facet with a small trigon, which is point bottomed.

Many electron micrographs have been taken to show that the surface topography of some cubic crystals sometimes have uncommon features, such as these which are composed of two different facets or more, very near to each other. These facets display tetragons on the cubic facets and trigons on the octahedral facets and the striated dodecahedral facets respectively.

The occurrence of trigons at different positions on the surfaces of cubic diamonds, indicates that these crystals are composed mainly of layers
Figure (6.28) Adjacent facets (111) and (100) on the surface (100) of crystal No. (31)  
E.M. X 4000

Figure (6.29) Adjacent facets over a very small area of the surface (001) of crystal No. (31)  
E.M. X 4000
Figure (6.30)  The (010) face of crystal No. (30) showing a (111) facet with cubic face  E.M. X 4000

Figure (6.31)  The (111) face with layer growth  E.M. X 4000
which are deposited on the \{111\} planes. Figure (6.31) reveals a very small area of the octahedral facet existing on a cubic face of crystal No. (31). It shows many terraced trigons and most of them are point bottomed with truncated corners, especially at the outer boundaries, which supports the layer growth hypothesis of Tolansky and Wilcock (1946, 1947) and other workers. Van der Veen (1913) was the first to suppose that trigons have been formed by three growth sheets approaching from three sides. He has imagined that the advanced sheets halt at their ends to leave a triangular pit. Tolansky and Wilcock (1947) have suggested the possibility that the advancing growth layers in the form of plane waves inclined at 60° to each other, are stopped due to some disturbance to form the trigon. Tolansky (1960, 1962, 1965) has argued that the trigons are formed, filled and formed again, but we have not observed a trigon which is partly filled. Varma (1967a) has given the evidence that diamond grows by the deposition of layers parallel to the \{111\} planes. He has pointed out that these layers pile up one over another, each succeeding layer is getting progressively smaller in extent and that the trigons affect growth in a definite way. Figures (6.32) and (6.33) are two further electron micrographs taken for the crystal surfaces No. (31), showing the growth layers which are deposited parallel to the \{111\} planes. These growth sheets are inclined to each other at 60°. If there exists any defect in the body of the crystal, a very tiny trigon may start to appear at the site of the defect, so that when the new growth sheets parallel the \{111\} planes proceeding from the three sides of the small trigon, they are arrested at 60° to
Figure (6.32)  Growth layers in the (111) plane  E.M. X 4000

Figure (6.33)  The intersection of layers on the (111) plane  E.M. X 4000
form the terraced sides of the trigons. This could be observed in the two previous photographs, where the trigons are all terraced and have very rectilinear sides with sharp corners. The trigons are all crystallographically oriented and have different sizes. The truncated corners of some trigons indicate that the rate of the advancing growth sheets in one direction is faster than the others.

6.5 **Trigons on the side wall of tetragons:**

One of the most unusual features is to find a triangular depression on the side wall of a tetragon as shown in the electron micrograph of figures (6.34) and (6.35) which have been taken for two different faces (010) and (001) of crystal No. (13). Figure (6.34) shows a triangular pit with flat bottom on the side of a flat based tetragon which has terraced sides, whereas figure (6.35) shows a small triangular pit on one side of a flat bottomed tetragon whose sides are steep.

Seal (1960) has first reported a case of a trigon occurring on the side wall of a tetragon on a cubic face. Harrison (1964) has examined about fifty cubic diamonds by optical methods, but he has failed to find such a feature on the surface of any crystal he had examined. Patel, Patel and Agarwal (1967) have found by chance a triangular depression on one side of a tetragon. They have described it as an etch pit on the (111) plane which is the side of the tetragon. In the present work we have observed such uncommon features many times on the side walls of several tetragons repeated on the faces of twelve crystals out of the sixty. Figures (6.36) and (6.37) have been taken for two different crystals and they reveal more clearly the triangular pits on the side walls of the
Figure (6.34)  The (100) face of crystal No. (13). A triangular pit on the side wall of a tetragon  E.M. X 4000

Figure (6.35)  (00\bar{1}) face of crystal No. (13). A trigon on the side wall of another tetragon  E.M. X 4000
Figure (6.36)  Crystal No. (38), face (001). A trigon on the side wall of a tetragon  E.M. X 4000

Figure (6.37)  Crystal No. (30), face (001), showing the same feature  E.M. X 4000
flat based tetragons.

From the four previous photographs we noticed that all the triangular pits are crystallographically oriented with their sides in the \(\langle 110 \rangle\) directions. They have nearly rectilinear edges and sharp corners, so they possess all the general characteristics of the trigons observed on the natural octahedral faces of diamond. The microstructures of these trigons are not clearly seen because there is a difference in the angle of shadowing between the cubic face in general and the octahedral facets on which the trigons are present. In several cases, there are flat based trigons present on the side walls of flat based tetragons as we have observed in the four previous photographs, although some of them do not show clearly that they have flat bases. Figures (6.38) and (6.39) are further examples which confirm our observation that the triangular pit is of the same type as the tetragon on which it is present, i.e. if the tetragon is a flat based one, so the trigon existing on its wall is also flat bottomed. The photograph of figure (6.38) shows that the tetragon has steep sides ending with a flat base and the trigon present on its wall has steep sides and is also flat bottomed. The other photograph of figure (6.39) confirms this observation i.e. the steep sided tetragon with a flat bottomed base has on its sides two adjacent trigons which are also flat bottomed with steep sides. The two trigons possess some similarity in that they have rectilinear sides with sharp corners, but they do not look equilateral because of the difference in the angle of shadowing on the two sides. This feature is repeated on the side wall of another two tetragons as shown in figure (6.40) which shows a steep sided tetragon with a small flat bottom. On one of its side walls there is a trigon which is also
Figure (6.38) Crystal No. (13) showing a steep sided flat trigon on the side wall of a steep sided tetragon  E.M. X 4000

Figure (6.39) Crystal No. (30) showing two flat bottomed trigons on two sides of a tetragon  E.M. X 4000
Figure (6.40) Crystal No. (23). A steep tetragon with a flat bottom on which there is a trigon with small flat area
E.M. X 4000

Figure (6.41) Crystal No. (30). A point bottomed tetragon with a point bottomed trigon on one of its sides
E.M. X 4000
steep sided and has a flat based bottom. At the top of the photograph there is another tetragon whose bottom is not clear, but on two of its sides there are two flat bottomed trigons.

In many cases, pyramidal trigons are also observed on the sides of some tetragons which have also point bottomed bases. Figures (6.41) and (6.42) show this type of pyramidal trigon on the side walls of a point bottomed tetragon which differs from those in the previous photographs from figures (6.35 - 6.40).

In general, it appears that tetragons which have flat bottom bases, also have flat bottomed trigons on their side walls. Tetragons which are point bottomed have also point bottomed trigons. In other words, the trigons, which exist on the side wall of tetragons, follow the shape of the tetragons themselves.

Figure (6.43) is a striking case which has been observed on the face of crystal No. (12) showing a flat bottomed tetragon with steep sides. On one of its sides, there is a trigon which is well defined having a complicated surface structure. This trigon has rectilinear edges with sharp corners and is crystallographically oriented. On its bottom there is another small triangular pit which has a different orientation to the big trigon. This might be explained as an etch pit, produced at a later stage of growth. Such a feature has not been seen before on any surface of all the other crystals which we have examined.

We concluded that this phenomenon of a triangular pit on the side wall of some tetragons is most probably produced by the dissolution process in nature. The triangular depression exists on the side wall of a tetragon and follows the type of the tetragon itself.
Figure (6.42) Crystal No. (37). A point bottomed trigon on the side wall of a tetragon E.M. X 2500

Figure (6.43) Crystal No. (12), with a trigon pit E.M. X 4000
6.6 **Trigons of opposite orientation:**

It is very interesting to find approximately parallelogram shaped figures instead of trigons as is shown in figure (6.44). It is confirmed that these are depressions which indicate that they are apparently formed by pairs of trigons, oriented opposite to each other on a certain boundary. The photograph shows two of such features, one in the middle and the other at the bottom of the photograph near the left side. The two trigons of each pair are not exactly the same although they roughly form the shape of parallelograms.

Patel (1964) has described some pairs of trigons observed on the two sides of a twin boundary on the octahedral face of a twinned crystal of diamond. The two pairs of trigons form either parallelogram or hexagonal shapes. It is clear that they are formed by pairs of trigons oriented opposite to each other on the two sides of a twin boundary running across its diagonal. These trigon pairs are touching each other along this boundary. He has etched the crystal in KNO$_3$ at 550°C and has observed that the twin boundary is preferentially attacked during etching and the etch pits produced having opposite orientation which reveals that this region of the crystal is twinned. He has noticed that the etch pits produced in a particular region are oppositely oriented to the natural trigons and the original trigons have been truncated due to etching. He has conjectured that these trigon pairs might have been found due to etching of dislocations on the twin boundary.

Bermann (1965) has found on a small region of a fine untouched octahedron face that there are a few triangular shapes of both orientation, i.e. trigons opposite to each other. He has firstly attributed them to local twinning and, then, he has suggested that one set might be due to growth
Figure (6.44)  Crystal No. (45)  Parallelogram shape composed of two opposite oriented trigons  E.M. X 2500

Figure (6.45)  Crystal No. (45)  Two trigons having opposite orientation  E.M. X 2500
and the other to natural etching.

Varma (1972) has obtained evidence for deformation twinning in diamond and that diamonds in nature are likely to be subjected to severe shear stresses at their origin and these stresses might have plastically deformed the crystal, producing twinning.

From our studies on the morphology of cubic diamond, we have observed such features of trigons opposite each other. Figure (6.45) is another example on another area of the same crystal surface. At the top of the photograph, there is a trigon pair. The lower trigon has the same orientation as the other trigons present in the photograph and it is opposite in direction to the one above. The two trigons have nearly the same size but they are different in shape. The upper trigon has a flat base, while the lower trigon is a complex one and composed of two small trigons, one with a flat base and another smaller one which is faint but appears to be pointed. Another pair of trigons is shown in figure (6.46) which reveals that the two trigons opposite to each other, are not symmetrical, and have different dimensions and depths. The two trigons are shifted such that they do not form a parallelogram shape as we have seen before in figure (6.44). Figure (6.47) shows another pair of opposite trigons which are also shifted from each other along the edge separating them. The photograph shows that the occurrence of trigons in opposite directions does not necessarily mean that the two crystal regions are twinned, but that there are two opposite octahedral facets. Each facet is characterized by the presence of one trigon or more which are crystallographically oriented. In figure (6.47) the lower facet has two trigons which are not equilateral. This is most probably due to the difference in the angle of shadowing or the angle of observation of
Figure (6.46) Crystal No. (45) trigons opposite to each other
E.M. X 2500

Figure (6.47) Crystal No. (3) trigons of opposite direction
E.M. X 4000
the replica itself. The trigons on each facet are crystallographically oriented. They are flat bottomed and of considerable depth, about 100 Å. Figure (6.48) further confirms our observation of the presence of multiple octahedral facets which have different orientation on the surface of some cubic crystals. The photograph shows at least four octahedral facets which are opposite to each other. The photograph shows also trigons of opposite orientation. Another cubic surface of crystal No. (45) also shows many trigons opposite to each other with a curious distribution as shown in figure (6.49). It shows that the left part of the photograph consists of several octahedral facets which are opposite to each other alternately. The right part of the photograph shows a cubic facet with a number of tetragons having different sizes. From these photographs, we conclude that some cubic crystals show many octahedral facets which are overlapped with cubic facets, over the crystal surface. The occurrence of trigons in different places on the body of the crystal and which are sometimes opposite to each other, means that the octahedral facets in these regions may closely alternate, having opposite orientation. Also the occurrence of octahedral facets in many regions on the cubic crystal, confirms that the cubic crystal is formed by layers in the (111) planes in addition to cubic planes.
Figure (6.48) Crystal No. (33) Layers of (111) of opposite orientation

Figure (6.49) Crystal No. (45) Many trigons having opposite directions
CHAPTER VII

ETCHING OF DIAMONDS
7.1 Introduction:

When a crystal is attacked by a suitable solvent, the dissolution takes place in a manner which is related to the molecular structure of the crystal, forming cavities which are known as etch pits. The shape of these etch pits, which relate to the internal structure and the symmetry of the crystal face is, no doubt, determined by the nature of the solvent. In other words the regular geometry and the external shape of a crystal reflect the arrangement in which the units of construction are built up during the process of growth. When a crystal is attacked by an etchant, etch patterns related to the internal molecular structure are thus produced.

Daniel (1816) first tried to correlate the nature of the etch figures with the molecular structure of solids. Then Honess (1927) defined etch pits as cavities produced by the action of some natural or artificial solvents upon the faces of crystal. The shape and distribution of these cavities have been attributed to the solvent and to the molecular configuration of the face upon which they occur. These cavities of different shapes and different orientations are produced on different crystallographic planes which are susceptible to different solvents under certain temperatures. It has long been known that etching of a surface takes place preferentially along scratches, edges and the sites of dislocations.

Gilman, Johnston and Sears (1958) studied the dislocations and etch pits produced in lithium fluoride. They observed that the shape of etch cavities depended mainly upon the nature of dislocation and on the exact composition of the etchant.

Goldschmidt (1904) explained the formation of both etch pits and etch
hillocks as resulting from etching produced by the movement developed in the solvent. The chemical action between the corrosive etchant and the substance upon which it was acting gave rise to currents, some of which were directed towards and some away from the surface. The interference of ascending currents with descending currents tended to form eddies, which was a starting point for the formation of a pit. The tendency of any solvent to produce a regular and hemispherical hole was offset by the force of crystallization which constantly endeavoured to keep the corroded surfaces bounded by crystal planes. The result was the occurrence of etch pits. Goldschmidt, however, added further suggestions:

1 - The etch pits are located at the places where the defect points exist.

2 - Etching takes place along fine scratches, cracks and edges.

3 - Small particles of dust on the surface provide the corrosive etchant with the point of attack.

4 - Bunching of etch pits are produced on the strained parts of the crystal.

5 - The sites of impurities are preferentially attacked by etching.

The explanation for the origin of etch pits and their development are given on the basis of dislocations. That is, an etch pit can be formed when a dislocation meets a crystallographic surface. The studies by X-ray diffraction on the crystal structure, indicate that nearly $10^6$ dislocation lines thread through a square centimeter of the surface. However, the studies of crystal growth indicate a value of about $10^4$ to $10^6$ of dislocations per cm$^2$. This order of magnitude agrees very well with the density of etch pits observed by Dekayser (1955) and Tolansky.
and Omar (1954). Tolansky and Omar (1954) have etched diamond in KNO₃ and reported that the number of etch pits per square cm is of the order 10⁶ on octahedral faces.

7.2 Etching diamond crystals:

Etching is the most convenient method for revealing dislocation points in crystals, because etch pits are nucleated at the sites of defects on the surface. The existence of several types of etch pits confirms that etching is sensitive to more than one type of dislocation. However, when different crystallographic planes are susceptible to different solvents, the etch pits produced have different shapes as well as different crystallographic orientations. Etching study is, therefore, a powerful method for determining the orientation of the surface of a crystal.

The most important feature of natural figures found on diamond surfaces is that they are oriented in different ways from the etch patterns produced in the laboratory. For example, trigons, which have been observed on natural octahedral faces, are oppositely oriented to those produced by etching in the laboratory. This observation has led quite a number of workers to conclude that the naturally occurring trigons together with other features appearing on the crystal faces are features of growth. So much work has been done to find out the relationship between natural features of growth and those produced by etching.

Early experiments on the etching of diamonds were carried out by Luzi (1892) when he heated diamonds at a high temperature of 1770°C in blue ground. Another series of experiments on etching diamonds was continued by Fersmann and Goldschmidt (1911). They explained the presence of
natural trigons on octahedral faces of natural diamond on the basis of an etch mechanism. They etched with potassium nitrate and soda fluxes at 900°C, thus producing triangular and rounded etch figures on the faces. Sutton (1928) etched octahedral faces of diamonds with KNO₃ at 900°C and roughly obtained rounded and equilateral triangular etch pits, but when he heated the dodecahedral faces of natural diamonds, he observed boat shaped features. Again he continued his experiment by etching some polished faces of natural cubic diamonds and obtained concentric squares oriented in conformity to the cubic faces. Williams (1932) carried out his experiment on etching and studied the etch phenomenon in more detail. He used fused potassium nitrate at 900°C to etch diamonds. Nevertheless, he observed cavities which were both flat bottomed trigons and pyramidal ones. On prolonging the etching, the trigons overlapped. Moreover, he noted that by etching the crystal more, no rounding off of the corners or edges occurred. Wilcock (1951) realized that etching used in the previous studies on diamonds was too heavy, so he started to use mild etching, by heating the diamond crystals at lower temperatures starting from 200°C to 600°C, in fused potassium nitrate. More precise work was done by Omar, Pandya and Tolansky (1954) when they etched diamonds in fused KNO₃ starting from quite a low temperature. They observed that etching started to affect the octahedral faces at 525°C along existing rings, cracks, micro-ring cracks and scratches if they existed on the surfaces. Moreover Omar et al. noted that at a low temperature well shaped etch pits started to appear over most of the octahedral faces. For example, etching for one hour at 550°C produced small triangular shaped etch pits. They also reported that etching inside the natural trigons was notably less severe than elsewhere
on the surface. They considered this phenomenon as an evidence that trigons are growth features. However, they found out that etching above 575°C caused the etch pits to increase in size, so that ultimately they devoured neighbouring ones and consequently decreased in number. They also reported that most of these etch pits had flat bottomed bases with rounded corners. A third stage of etching was observed in which the flat bottomed pits changed into pyramidal ones, and finally gave rise to remarkable block patterns.

Further studies on etching of diamonds were carried out by Pandya and Tolansky (1954). They examined the etch features produced on polished cubic and dodecahedral planes obtained of octahedral crystal. The dodecahedral faces showed boat shaped features on their surfaces, whereas on cubic faces, squared etch pits were produced, oriented such that their sides were parallel to the \( \langle 110 \rangle \) directions. When they etched a polished dodecahedral section of an octahedron at 550°C, micro etch pits were obtained. The density of these pits varied over the surface. In addition to the pits on dodecahedral faces, they discovered a crystallographically oriented rectilinear pattern which had hexagonal shapes and whose sides were approximately parallel to the edges of the section. This rectilinear pattern was also observed on cubic faces. Pandya and Tolansky also studied the effect of etching on a polished cubic section of an octahedral crystal at 550°C. They observed both squared etch pits and a striking rectangular pattern. Moreover, etch pits within a group were marked to be of a uniform size. Further etching at 700°C gave a heavier pattern revealing lamination within the crystals. Emara and Tolansky (1957) studied again the effect of etching on natural dodecahedral faces. They observed that etching preferentially took place along the
solution channels presented on natural faces. This led them to conclude that these channels were most probably due to etching and they gave evidence that the original outlines on the surface were less resistant to etching than the rest of the surface and that etching was presumably taking place along dislocation networks. However, they related the boat shaped depressions to the more vigorous etching and concluded that the natural etching would be very gentle compared with etching in laboratory. According to Tolansky and Patel (1957) the shape of etch pits on diamond surfaces was determined by the rate of etching. They found out that etching with potassium nitrate at 475°C for a long time, i.e. more than 24 hours, produced etch pits with rectilinear sides, whereas etching at 525°C for a short time of about three hours only, was faster and heavier and produced pits with round corners then changing to hexagonal shapes. It was, however, concluded that the etch pits could be arbitrarily made either rectilinear or curvilinear in outline depending on the rate of etching. Patel and Tolansky (1957) again studied the etch pits produced by etching of cleavage octahedral faces. They observed that the etch pits produced were classified in three different ways:

a) random small pits; b) striking linear arrangement and c) individual isolated pits, usually larger in size than the others. The isolated pits were divided in turn into two distinctive types, i.e. flat bottomed and pyramidal trigons. Moreover, the etch patterns on pairs of matching cleaved surfaces were almost identical especially the isolated pits. This led them to conclude that when the cleavage cut passed through regions of imperfection, then each imperfect point became a nucleus for an etch pit. The etch pits thus produced on both sides matched. Moreover
by etching cleaved blocks, a striking stratigraphy was revealed, showing that the individual stratigraphical sheets go right through the whole crystal. They concluded that the different degree of etching which occurred on different layers was due to different conditions of growth such as pressure, temperature, concentration, impurities, etc.

Omar and Kenawi (1957) studied the effect of etching diamonds of octahedral form, by etching them on hot molybdenum filaments at $1000^\circ C$ in a vacuum chamber which contained a very small amount of oxygen. After some hours, rectilinear etch pits were formed. The pits were oppositely oriented to the growth trigons, but they possessed all the similarity of natural features with rectilinear sides and sharp corners. Some of these pits had terraced sides.

Further experiments on gas etching of diamonds were carried out by Frank and Puttick (1958). They used various agents such as chlorine and wet hydrogen at $800^\circ C$. They tried to produce etch pits of negative orientations as natural trigons, but they did not succeed. They tried again by heating another crystal in fused kimberlite at a higher temperature of $1450^\circ C$ and thus produced sharp edged triangular etch pits with negative orientation similar to natural ones.

Evans and Sauter (1961) proceeded with their experiment on gas etching on natural octahedral and dodecahedral diamonds and also on polished cubic faces. They etched diamonds in air at low pressure and high temperatures ranging between $800^\circ C$ and $1400^\circ C$. They observed a change in etch pits orientations. As the temperature of etching continuously increased, the etch pits on cubic and dodecahedral faces started to change their orientations at about $1400^\circ C$. Whereas on the octahedral faces the change occurred at $1000^\circ C$, having pits with negative orientations which were
similar to the natural trigons in that respect. To find out which gas was responsible to form etch pits of similar orientation as natural ones, they subjected octahedral faces to various mixtures of gases. They found that oxygen and water vapour are the main responsible factors in producing the well shaped etch pits with negative orientations. They also observed that by using carbon dioxide at 900°C the diamond crystal was heavily attacked. Patel (1961) etched natural and cleaved diamonds of octahedral form by using fused KNO₃ at about 525°C and for a limited period. He examined the etch pits produced and classified them into three different groups; a) flat bottomed trigons; b) terraced trigons and c) point bottomed trigons. He assumed that the formation of the point bottomed pits originated usually at linear dislocations which were not completely etched away, but in the case of flat bottomed trigons, the dislocations were completely etched away by further etching. He gave an explanation that when a new defect appeared on the surface of a flat based pit a new etch pit nucleated at the site of this defect and thus accounted for the formation of a pit within a pit. He interpreted further the eccentricity of the point bottomed pits as due to linear defects in the crystal which might not be at right angles with the cleavage faces but inclined to them. Further explanations of linear and point defects on crystal surfaces were described again by Patel (1962). He observed that the etch pits produced at point defects were always equilateral triangular shapes, whereas etch pits of different shapes were developed at the sites of other types of defects, such as linear defects. He found that etching of cleavage faces in their early stages of etching revealed the etch patterns. These patterns were developed by further etching into pits of triangular and trapezium shapes.
depending on the type of defects either of point defects or linear defects respectively. He observed that the linear defects were of different sizes, but all of them were crystallographically oriented.

Patel and Ramanathan (1962) also examined etch pits produced on natural and polished faces of octahedral diamonds. They etched the crystal in strong oxidizing agents such as potassium chlorate and sodium perchlorate at various temperatures. Etch pits of both negative and positive orientations were produced. They observed that when etching the octahedral faces with NaClO₄, etch pits of positive orientation were formed at 500°C, then changed to negative pits at 600°C and again to positive at 960°C. However, when they etched polished cubic faces of diamonds by KClO₄ at 600°C for 4½ hours, squared etch pits having their sides parallel to the cube edges, were formed. By etching another polished cube face, with the same etchant at a higher temperature of 840°C for only one hour, they obtained squared etch pits with sides inclined at 45° to the cube edges.

Finally, they concluded that KClO₄ was a strong agent and that the energy of oxygen atoms which were obtained by heating such etchant might exceed the value obtained from KNO₃, although the temperature was the same.

Evans and Phaal (1962a) continued their experiments on etching different faces of diamonds at temperatures between 650°C and 1350°C. Their experiment was carried out by passing a stream of purified oxygen over the faces to be etched, at the required temperature and under the pressure range of 5 x 10⁻² to 0.5 torr. They observed that the rate of etching was linear dependent on the oxygen pressure. At 650°C the octahedral and dodecahedral faces showed surface blackening which was attributed to carbon depositions, but at the same range of pressure on cubic faces, the surface blackening started to appear at 850°C. When they increased
the pressure to atmospheric, the blackening of the surfaces started to appear at higher temperatures of about $700^\circ$C in the case of (110) and (111) faces. They found that cubic faces were etched at the lowest temperature below $1000^\circ$C, above which the reaction rate was the same for all faces.

Patel and Agarwal (1966) have done further studies on the rate of etching on different faces of natural diamonds. They reported that the rate of etching varied on different faces of diamonds, etched in KNO$_3$. They observed that the rate of etching was faster on the octahedral faces, while it was slowest on the dodecahedral faces and moderate on the cubic faces. This meant that the cubic faces had the rate of etching intermediate between the other two principle faces, i.e. (111) and (110).

Again about a hundred octahedral faces of diamonds had been examined by Patel and Ramachandran (1967). They observed the normal triangular depressions on all faces, in addition to a hexagonal spiral depression which was present on only one face of the octahedron crystals. They concluded that the spiral depression might have been formed by a dissolution process and therefore they attributed the formation of trigons to the same process, since the spiral and the trigons were found on the same face side by side. Again Patel and Bahl (1965) conjectured that all the octahedral faces of natural diamonds which showed trigons on their faces might have been subjected to dissolution in nature and not to a growth mechanism. Varma (1967d) also studied the etch pits and trigons on (111) faces of natural diamonds. He observed that the trigons were related to the features surrounding them. He reported that the dimensions of etch pits changed with continuous etching, whereas the trigons present on natural octahedral faces could not change their dimensions with further
etching. Therefore, he concluded that trigons differed from etch pits in this vital respect and that trigons on natural diamond were not etch pits produced by natural dissolution, although their appearance was similar in shape or even in their orientation. Patel and Patel (1968) carried out their experiment on etching diamonds with NaNO₂ solution. Etching was performed on octahedral faces having flat and point bottomed trigons. They observed that the bottoms of the point based trigons were preferentially attacked than the flat bottomed ones and changed by further etching into flat bottoms. This evidence led them to conclude that the point bottomed trigons were originally nucleated at the sites of dislocations. They also reported that no change by etching was observed in the case of flat bottomed trigons.

Patel, Patel and Agarwal (1967) also studied the effect of etching on natural cubic diamond faces by heating the crystal in a carbon arc with a drop of solution of sodium nitrate in water at the required temperature. They then studied the etch pattern produced and concluded that tetragons were etch pits produced by etching dislocation points on the natural cubic faces. They reported that the point bottomed tetragons were developed at the dislocation points and that the dislocations giving rise to them had not been completely etched away, but part of them still remained in the body of the crystal terminating in the point bottom of the tetragon. They also assumed that the flat bottomed tetragons located at the dislocation points were completely etched away before the process of natural etching was stopped. By etch experiment, they observed that the point bottomed tetragons remained either point bottomed or turned to flat bottomed by further etching, depending upon whether the dislocations producing them were still present or had been etched away. By increasing
the time of etching, all the tetragons changed to flat bottomed. They also observed, during etching, that etching proceeded in two distinct directions: a) parallel to the surface; b) in the direction of dislocations. They conjectured that when the dissolution along the surface was faster than that along the dislocation, the tetragons reduced in size by successive etching.

Patel and Patel (1969) further tried a number of etching experiments by changing the etchant as well as the method of etching until they succeeded in producing etch features exactly similar to the trigons on natural octahedral faces. Most of them had flat bottoms. They finally concluded that the trigons on (111) faces might have been produced by etching in nature. Again Patel and Patel (1973) studied the triangular etch pits produced by etching the (111) faces of diamonds in NaNO₂. They observed trigons with salients in the [112] direction without neighbouring trigons. Also some triangular etch pits, surrounded by three oppositely oriented triangular hillocks, were formed. They reported that these triangular etch pits produced by etching had similar characteristics to the natural trigons and some of them were associated with wings and had a fish shaped structure. These features were described by Bedarida and Komatsu (1966) when they studied the octahedral faces of natural diamonds. Therefore, Patel and Patel concluded that the trigons and the associated microstructures found on natural octahedral faces were formed as a result of dissolution and not of growth. Grigor'ev (1974) etched cleavage faces of octahedral natural diamonds. He used melt NiS as an etchant and the experiment was performed at 700°C. He obtained areas of positive and negative etch pits. He observed that etching was more expedient on the areas with negative orientation. Increasing etching did not lead to the
overlapping of trigons, but further etching resulted in a decrease in the number of old trigons and causing no change in their shape. However, he confirmed the possibility of the formation of trigons on octahedral faces with negative orientation by dissolution under natural conditions. Tolansky, Miller and Punglia (1972) also studied the effect of etching and the change in orientation of the etch pits produced on cubic faces of diamonds. They observed that some of the square pits changed their orientation at 600°C having their sides along $\langle 100 \rangle$ instead of $\langle 110 \rangle$ direction. They interpreted the phenomenon of reorientation as being inhibited by agitation of the crystal during etching. They observed that only the deeper and larger pits underwent such reorientation. They also reported that no change in the orientation of pits on the octahedral faces occurred by heating the crystal up to 800°C.

Angus and Dyble (1975) studied again the slope of the sides of etch pits. They observed that the etch pit slopes were functions of the sizes of the initiating defects. They showed that the point bottomed pits with shallow slopes less than 2° were formed from small initiating defects, i.e. dislocation outcrops, and that the flat bottomed pits with steep sides 70° 32' were formed by etching the large shallow defects such as ring cracks of inclusions. Finally they concluded from their results that natural trigons were formed by an etching mechanism.

Evans and Rainey (1975) heated type I and type II diamonds to higher temperatures ranging from 2000 to 2300 °C under pressure. They observed that type I diamonds changed from colourless to yellow after being heated for one minute at 2250°C. They assumed that the yellowing was due to the scattering of light in cubic planes. Whereas type IIa diamonds did not turn yellow as a result of the above treatment.
Mendelssohn et al. (1976) believed that etching experiments on diamond in various laboratories produced etch pits with orientations depending mainly upon the temperature. They carried out their experiments of etching diamond in carbon dioxide at a temperature in the region of 900°C. At such a temperature they produced a number of features bearing a striking resemblance to those found not only on, but also inside the natural diamonds.

7.3 Experimental work on etching:

It is long known that etching effects on diamonds are produced by strong oxidation under high temperature. In the laboratory experiments it is very convenient to produce etching on diamond by heating the crystal in a hot flux of potassium nitrate between the temperatures 400°C and 620°C or by hot flames rich in oxygen.

Etching experiment has been done on various crystallographic faces of diamond in stages by successively heating the crystals in hot potassium nitrate for a limited time at different temperatures. It was observed that the etch pits initially produced were very small and then became bigger by increasing the time of etching until they ultimately coalesced. The natural faces of cubic diamonds are extremely rough and pitted and therefore they are unsuitable for precision etch studies. For this reason much more extensive studies have been done on studying the surface topographic and etch phenomenon of the octahedral faces.

However Seal (1962) and (1965), Harrison (1964), Patel, Patel and Agarwal (1967) and Punglia (1972) have studied the effects of etching on polished and natural cubic faces of diamonds.

In the present work more attention has been paid to the cubic crystals
of natural diamond, on which etching was carried out in order to study the stratigraphical patterns produced by etching and to examine the shape of etch pits and whether they are similar to those tetragons which are observed on natural faces or are different.

After studying the surface topography of cubic crystals, optically and electron optically, etching experiments have been performed by heating the crystal in a nickel crucible containing about 10 grams of potassium nitrate in an electric oven, thermostatically controlled to \( \pm 10^\circ C \) between room temperature and \( 600^\circ C \). The diamond crystal is removed from the etchant soon after etching time has been completed. It is then transferred to a small tube containing nitric acid which removes the solidified melt from the surfaces, leaving the diamond clean. It is then washed again several times with distilled water. It is further cleaned in the usual way for replica microscopic examination. For every etching experiment, a fresh quantity of \( \text{KNO}_3 \) is used. The temperature in our experiment was started from \( 400^\circ C \) for a short interval of one hour in each stage of etching so as to study the effect of light etching on the surfaces of the crystal. It has been established already that, if the rate of etching is slow on the one hand, the etch pits become strictly rectilinear in outline. Whereas if, on the other hand, it is fast, the corners of the pits are rounded off (Patel and Tolansky, 1957).

We, therefore, started our experiment on three cubic crystals which had few natural tetragons on their faces; by contrast the result of the cubic crystals mostly had very rough surfaces. The three crystals which have been etched, have the usual point bottomed tetragons as well as flat bottomed ones on their faces. They are colourless and of relatively small size, with edge length range between 1.8 and 2.2mm,
weighing approximately 12 to 25 mg. before etching.

Crystal No. (8) is the smallest one and has truncated corners. Its six faces are relatively smooth and contain tetragons as is shown in figures (7.1), (7.2), (7.3) and (7.6). It is worthy to note the characteristics of tetragons on these faces, which are as follows:

1 - The natural tetragons are not very deep and most of them are point bottomed.
2 - Their sizes are fairly similar with few exceptions.
3 - They have rectilinear sides and a few of them are terraced.
4 - The tetragons do not overlap each other, but just touch, like the natural trigons on \{111\} faces.
5 - The crystal surfaces are relatively smooth, where there are large areas without tetragons.
6 - The bottoms of most point bottomed tetragons are not quite central.

We start etching the crystal by applying the previous method in fused potassium nitrate at a temperature of 400°C for one hour. It is observed that up to 540°C no etch pits are produced. Etching at 550°C starts to form little apparent effect as shown in figure (7.4). In this photograph the natural pits and those produced by etching are clearly distinguished. They have the following characteristics:

1 - The etch pits produced at 550°C are squared and have a small size.
2 - Some of the etch pits are incomplete, being at different stages of formation with two or three sides only.
3 - Most of the etch pits at the temperature 550°C have the same orientation as the natural tetragons.
4 - Some etch pits are still too small to be distinguished clearly.

By etching the same crystal again at a higher temperature 580°C, a striking change can be seen in figure (7.5) for the same face, where the
Figure (7.1)  The surface (100) of crystal No. (8) with a few number of tetragons  

Optical M. X 60

Figure (7.2)  It shows the face (010) of crystal No. (8)  

Optical micrograph X 60
Figure (7.3) surface (001) for crystal No. (8) before etching

Figure (7.4) The same surface (001) after it has been etched in KNO₃ for one hour at 550°C. The etch pits start to appear

Figure (7.5) The same surface (001) of crystal No. (8) after it has been etched in KNO₃ at 580°C for one hour
Figure (7.6) Surface (\{100\}) of crystal No. (8) before etching

Optical micrograph X 60

Figure (7.7) The above surface (\{100\}) of crystal No. (8) after it has been etched in \(\text{KNO}_3\) at 580°C

Optical micrograph X 60
etch pits have become clearer and bigger.

Figures (7.6) and (7.7) show another face of the same crystal No. (8) after etching at the temperatures 550°C and 580°C respectively, comparison of the two photographs shows that more etch pits have been produced at this temperature 580°C, and most of these pits have different orientations from the natural ones, although a few of them have the same orientation as tetragons. Moreover, we observe that the distribution of the pits is not uniform over the surface. It may also be seen from figures (7.5) and (7.7) that:

1 - Some of the etch pits have their sides parallel to the edge of the cube itself.

2 - The etch pits are squared in outline and some of them are round off at the corners and this is quite contrary to the natural ones.

3 - Some of the etch pits are overlapped.

4 - The natural tetragons with point bottomed bases have been etched further and change to flat bottomed bases with rounded corners.

5 - The etch pits attack the edges and cracks presented on the surface more than the smoothed area. As seen in figure (7.7), the etch pits attack the corners more than the middle of the face.

6 - The pit density is not uniform, some areas are more resistant to etching.

7 - The etch pits are small generally compared to the natural ones.

8 - There are no etch pits inside the natural tetragons.

Figures (7.8) and (7.9) are further examples which illustrate the (100) face of another crystal No. (47) when it has been etched at 600°C in fused KNO₃. The time of etching is only ½ an hour in every stage. At 600°C the etch pits are of reasonable size to reveal their shape.
Figure (7.8)  Face (100) of crystal No. (47) The surface before etching

Optical micrograph X 60

Figure (7.9)  The same face (100) of crystal No. (47) after it has been etched in KNO$_3$ at 600$^\circ$C
Figure (7.10) The face (100) of crystal No. (3) before etching
Optical Micrograph X 60

Figure (7.11) The same face (100) of crystal No. (3) after it has been etched in KNO₃ at 570°C
Figures (7.10) and (7.11) are two further examples which show another surface of crystal No. (3) before and after etching. The etch features observed have the same characteristics as those seen before on the other surfaces.

From these results obtained on etching the natural cubic faces of diamonds in KNO₃, it is observed that hollow squared etch pits are produced at low temperatures, starting from 540°C. Some of them are oriented in the same direction as the natural tetragons, with their sides at 45° to the edges of the cubic face and some others have their sides parallel to the cube edges. It has also been observed that at low temperature the etch pits produced have rectilinear sides and by increasing the temperature and the time of etching, the etch pits start to round off and overlap. The results also show that the etch pits produced in the laboratory are different in their shape and size from the natural tetragons as we have discussed before. Also it is remarkable that the pit density is very low or negligible within growth tetragons. However, there is a random distribution of the small etch pits over the surface. Moreover, it is observed that the point bottomed tetragons are more attacked and by successive etching are changed to flat bottomed tetragons with rounded corners, whereas the flat bottomed tetragons remain the same by etching and have concaved bottoms. By increasing the rate of etching the natural tetragons do not overlap as do the artificial etch pits. These results confirm Patel and Patel's hypothesis (1968) that the point bottomed tetragons have been developed at the sites of dislocation. By etching the crystal, the dislocations at the bottom of tetragons are either etched away, leaving flat bottomed tetragons, or some portions of them still exist in the crystal, where
point bottomed tetragons remain as we have seen.

7.4 Etching on polished cubic faces:

Our experiment is carried out on the polished cubic faces of natural cubic diamond. A colourless cubic crystal about 1.8 mm edge and weighing 0.07 carat is sawn into two equal halves parallel to the cubic plane (100). This operation is performed by Dr. M. Seal (D. Drukker and ZN. NV. Amsterdam).

One piece of the cut crystal is polished on the sawn face and also on the natural cubic face, in order to remove most of the natural features from the surface. At one corner, there is still an area about $\frac{1}{3}$ of the face area which shows tetragons, as shown in figure (7.12). The face is then cleaned and coated with 700 Å silver layer for the examination by multiple beam Fizeau fringes to study the smoothness of the polished face. This shows that the surface is not quite flat but has a very slight curvature. The same half is also examined by polarized light as shown in figure (7.13). After examining the smoothness and the strain on the cut crystal, it is etched in potassium nitrate for half an hour in every stage, starting from 500°C up to 590°C in intervals of 10°C. Figure (7.14) shows the surface after it has been etched at 500°C, where the rate of etching is still very slow and does not produce any etch pits.

By increasing the rate of etching, it has been established that even at 540°C, etching on the polished face is still too mild to produce etch pits. At 560°C, the surface is lightly etched and shows very tiny etch pits. Figure (7.15) reveals the same region of the polished face after further exposure to etchant for $\frac{1}{2}$ an hour at 570°C. At this temperature
Figure (7.12) The polished face of crystal No. (3) with its $\frac{1}{3}$ area still unpolished, showing tetragons

Optical micrograph X 60

Figure (7.13) The same slice of the cut crystal examined in transmission between a polarizer and analyzer

Optical micrograph X 60

Figure (7.14) The same face of the cut crystal after it has been etched in KNO$_3$ for $\frac{1}{2}$ an hour at 500°C

Optical micrograph X 60
the small etch pits start to appear clearly and variations in the pit density are evident on the surface. By increasing the temperature to 580°C for a further half an hour, the etch pits become larger and clear as shown in figure (7.16). The final shape of etch pits become more clear and pronounced after the temperature is increased 10°C further at 590°C. Figure (7.17) shows the pattern of etch pits produced at this temperature. Examination of the figures reveals that no new etch pits are produced. The pit density is not uniform, being much higher in some areas than others, i.e. some regions on the surface are more resistant to etching than others. A higher magnification of etch pattern shows that:

1 - The etch pits produced are square shaped and actually seem to have their sides either parallel to the cube edges or inclined at 45° to them.

2 - Etching at 590°C has not produced any new etch pit.

3 - There is no significant variation in the size of etch pits formed, i.e. they have more or less the same size, which is very small compared to the natural tetragons.

4 - Most of the etch pits are rounded off at their corners.

5 - Some of the etch pits are gathered together as groups where the density is high, while some others are seen to be isolated.

6 - There are some areas without any pits, which are resistant to etching.

7 - There are no traces of any basal extension associated with any etch pits as is the case with natural tetragons.

8 - There are no pits within pits to form a complex feature as observed in natural tetragons.
Figure (7.15)  The same face of the cut slice after it has been etched at $570^\circ C$ X 80

Figure (7.16)  The same face of the cut crystal after it has been etched at $580^\circ C$
Figure (7.17)  The same face of the cut crystal after it has been etched in \( \text{KNO}_3 \) at 590°C

Figure (7.18)  The other slice of the cut crystal No. (3) before etching  
S.E.M. X 100
Most of the etch pits are flat bottomed and all their sides are non-terraced.

From these results, it is quite clear that the etch pits on a polished cubic face are significantly different in their appearance and in their characteristics compared to the natural tetragons on cubic faces. These results also show that most probably these etch pits are initially developed at the weakness points on the surface such as dislocations or impurity centres. Moreover, no new etch pits have been formed on further etching because all the dislocation points have been etched away giving rise to the etch pits formed at the beginning of etch process.

7.5 Etch patterns on cut sections of cubic crystals:

A considerable number of etching experiments have been reported on the natural and cleavage \{111\} faces of diamond, but not much work has been done on etching sections of cut diamond, especially the cubic form. The present work adds some information about etching sections of cubic diamonds. Three crystals have been sawn, each into two approximately equal parts by a cut parallel to one of the cubic axes. The three cubes which have been used to study the etch pattern produced on their surfaces, have been previously examined by X-ray topography by Moore and Lang (1972). The three cubes are nearly of the same size, i.e. the side length is approximately 2\text{mm} and the weight about 0.08 to 0.1 carat. They are of different colours, one is colourless, one is yellow and the third is brown. Etching is performed slowly on the two halves of each cube together to get the same time of etching at the same temperature and under the exact conditions. Temperatures from 500\text{oC} up to 600\text{oC} are used. Every stage of etching the temperature is increased by 20\text{oC} until 560\text{oC}, when the etch
pits start to appear, after which it is increased by 10°C in intervals. The time of etching is \( \frac{1}{2} \) an hour at each stage in order to produce light etching on the surfaces.

7.6 The etch patterns on the two cut halves of the colourless crystal:

Preliminary etching on the two halves of the colourless cut crystal has been performed in fused potassium nitrate starting at 500°C for \( \frac{1}{2} \) an hour. The etchant is put in a nickel crucible and heated in a muffle furnace at temperatures maintainable to within \( \pm 10°C \). The two pieces are cleaned, then replicated as usual by perspex to be examined under Vickers optical microscope. Also carbon and platinum replicas are used for examination at higher magnification under the electron microscope. Figure (7.18) reveals one half of the cut crystal before etching when it is examined by the scanning electron microscope.

At 500°C no etch pits are formed. The experiment is carried out by increasing the temperature to 520°C, then to 540°C, respectively. In each time and after etching, the two halves are taken away from the fused KNO\(_3\) and thoroughly cleaned in concentrated nitric acid, then washed with distilled water several times before they are examined under the optical microscope. Up to 560°C no etch pits could be observed clearly, just very tiny pits are observed. Further etching for \( \frac{1}{2} \) an hour more at 570°C leads to the features shown in figures (7.19) and (7.20). The photographs reveal that the etch pits which start to appear are very small. They are concentrated at the centres and near the edges of the cube. Figures (7.21) and (7.22) show the shape of these etch pits produced at 570°C, evident under the electron microscope. The photographs show that the pits have rounded corners and some of them have six sides. They overlap together.
Figure (7.19)  The cut polished face after it has been etched at 570°C for 1/2 an hour. Optical micrograph X 60

Figure (7.20)  The corresponding face to the above polished face after it has been etched in KNO₃ at 570°C for 1/2 an hour.
Figure (7.21) Some etch pits produced on the polished face at 570°C E.M. X 1500

Figure (7.22) Some etch pits produced at 570°C on the polished face of the colourless crystal E.M. X 1500
over some areas. Prolonged etching is required, so the two halves of the cut crystal are heated again for half an hour at 580°C. Their surfaces are cleaned then the replicas examined under the optical and electron microscopes. By careful study of figure (7.23) taken by the optical microscope after etching at 580°C, it may be seen that no new etch pits are produced, but the size of the etch pits increases to become more pronounced. By using double the magnification as in figure (7.24) it reveals the etch pits more clearly at the central region of the cube. Most of the etch pits are approximately squared and have their sides either parallel to or inclined at 45° to the cube edges. Some of the pits are rounded off at the corners. Figures (7.25) and (7.26) are further photographs representing the two polished faces of the cut crystal No. (3) after etching in KNO₃ at 590°C. They show the whole area of the two matching faces with the final distribution of etch pits on their faces which form such patterns of heavy and light areas of etch pits. At the temperature 590°C the etch pits overlap together in many areas. Figures (7.27) and (7.28) show the central regions of the two faces taken with higher magnification. The two photographs show that the etch patterns on the two corresponding polished faces are not identical. Although they have the similarity that the etch pits are first concentrated around the central regions, after which there is a region almost free from any etch pit, followed by a narrow etched region and followed again by a free region with very few etch pits. The outer region like a pathway is heavily etched and finally, near to the edges, a lightly etched region exists. Such combinations of areas, each with its own degree of reaction to etching are quite noticable, whereas some other areas are resistant to etching.
Figure (7.23) The etch pattern produced on the cut polished face after etching at 580°C for $\frac{1}{2}$ an hour

O.M. X 60

Figure (7.24) The etch pattern at 580°C. The central area of the above photograph

O.M. X 120
Figure (7.25) The final etch pattern produced by etching at 590°C on one face of the cut crystal
Optical micrograph X 50

Figure (7.26) The etch pattern on the other face of the cut crystal at 590°C
Optical micrograph X 50
Figure (7.27)  The central area of fig (7.25) Optical micrograph X 150

Figure (7.28)  The central area of figure (7.26) Optical micrograph X 150
These results support Tolansky and Rawle-Cope's hypothesis (1969) that diamond is formed by layers of type I and type II alternating with each other and that etching preferentially attacks type I because it is far from perfection.

In general, the etch pits are square shaped and appear to have similar sizes and shapes. By using higher magnification, it is evident that the etch pits are more clear under the electron microscope and, as shown in figures (7.29) and (7.30) reveal different shapes of etch pits on the cut faces of crystal No. (3) after they have been etched at 590°C. It is quite obvious from figure (7.29) that most of the etch pits are point bottomed. Some of them show complex features and have small etch pits on their bottoms. Moreover, the pits overlap together in many areas over the surface. Also large square shaped depressions are produced, which have flat bases and concave sides. A good example is shown in figure (7.30) which reveals etch pits with flat bottomed bases having concaved sides. A part of a triangular shaped pit is observed on the side wall of a squared etch pit. The triangular pit does not look as well formed as a trigon although it is crystallographically oriented. Therefore, it may be a part of a triangular etch pit formed on the side wall of a squared etch depression such as the several cases we have observed before on natural tetragons, or most probably it is a tear in the replica itself and gives the shape of a triangular depression. Also it is observed that the sides of most etch pits on the polished faces are slightly curved and all without exception are non-terraced. Another type of etch pit is shown in figure (7.31) which reveals an isolated etch pit with steep sides, being slightly bent and meeting inwards to form a flat bottomed pit. A further electron micrograph of figure (7.32) is a good example which shows
Figure (7.29) The point bottomed etch pits E.M. X 1500

Figure (7.30) Flat bottomed etch pits with a triangular shape on the side wall E.M. X 1500
Figure (7.31)  A flat bottomed etch pit with a steep curved side

E.M. X 1500

Figure (7.32)  The shape of etch pits with small etch pits developed on the base of a big one

E.M. X 1500
a complex etch feature with two small pits on its bottom. The small pits have different orientations and are also different in their shape, one of them has a flat bottom, while the second is a point bottom with steep sides and is oriented with 45° to the others. By specular examination of figures (7.25) and (7.26) it shows that there is a striking shape which looks like a chain of screw driver shapes radiating from the centre of the crystal and directed along the diagonals. Such structure is observed here for the first time and is present only on the colourless crystal No. (3). The shape of such a feature becomes more pronounced in figure (7.27) in which the central area of figure (7.25) is enlarged three times. The structural detail of these features has been examined at a higher magnification, using the phase contrast microscope together with the electron microscope. The electron microscope reveals that the screw driver shape is in fact composed of rows of etch pits which are square or elongated, touching each other and having different widths to form the shape of the screw driver. Good examples of such shapes are shown in figures (7.33) and (7.34). They reveal the various shapes of the pits, some of which are elongated having different widths as shown in figure (7.34), while other pits are approximately squared with smooth bottoms as in figure (7.33). They touch each other from one side to form the shape of a chain. They are more or less of the same depth which is about 30 to 50Å. There is a continuation of such shapes but it is difficult to get them on the same micrograph because of the high magnification used, although these two photographs are taken by the lowest magnification of the electron microscope. Figure (7.35) illustrates two parts of two shaped screw drivers lying beside each other. Each is composed of many
Figure (7.33)  A part of the screw driver shape which consists of small etch pits with four sides

Figure (7.34)  Another part of the screw driver shape which contains many etch pits of different sizes
small etch pits touching each other to form the shape along the \langle 110 \rangle directions. The pits are very shallow, only a few angstroms deep, and all have the same orientation as the natural tetragons. Figure (7.36) is a further photograph showing the end part of one of the screw driver shapes, having a complex feature on its base. There are some rounded pits with six sides and on the base of which a square flat bottomed pit of positive orientation is found, having its sides parallel to the cube edges. It is quite clear that the screw driver shapes end near the corners of the cube, where there exists parallel etched octahedral facets as shown in figure (7.25) and as described by Suzuki and Lang (1976). They have reported the occurrence of \{111\} faceted growth set within larger regions of crystal where the non-faceted mode of growth is dominant. Lang (1974a and b) has examined the internal structure of well shaped cubic crystals by X-ray section topography. He has observed column axes in \langle 111 \rangle directions which are repeated near the corners, so as to fill each cube growth sector.

Cathodoluminescence produced from cut and polished surfaces of natural and synthetic diamonds has been used recently by many workers to reveal the dislocations on surfaces. The intensity of C.L. is strongly affected by the presence of impurity on the surface and accounted for the number of dislocation points on the surfaces.

Cathodoluminescence photographs are, therefore, taken for the two cut pieces of crystal No. (3) with different filters. The filters are blue, green and yellow. The luminescence images show nearly the same patterns for the two polished faces and which are similar to the etch patterns obtained by the optical microscope. Figures (7.37) and (7.38) show the cathodo-luminescence images for the two cut faces taken with the green
Figure (7.35) A four sided etch pit overlaps with two parallel screw driver shaped features  
E.M. X 1500

Figure (7.36) Small etch pits with four sides on the base of eight sided pit with other pits of different shapes and sizes on the bottom of the end of a screw driver shaped feature  
E.M. X 1500
Figure (7.37) Cathodo-luminescence pattern of the cut crystal No. (3)
S.M. X 50

Figure (7.38) Cathodo-luminescence pattern on the other slice of the cut crystal No. (3).
S.M. X 50
filter. We observe dark areas at the centre regions of the C.L. images, which reveal the presence of impurities and dislocation points in those areas and show that the central areas are of type I diamond. The brightest areas surrounding the central regions have relatively low defect concentrations which means that they are type II. Alternative layers of type I and type II diamonds are then formed as shown in the two photographs.

Collins (1970) has studied defects in diamonds using an electron beam to stimulate luminescence in diamond. Kiflawi and Lang (1974) have studied the mixed growth habit of mainly (111) and (100) forms in combination in diamond. They have studied the luminescence effect produced from cut and polished surfaces of natural and synthetic diamond, stimulated by electron bombardment. Woods and Lang (1975) have also used the cathodo-luminescence, optical absorption and X-ray topography to study polished sections of synthetic diamonds. They have reported that the cube growth sector display a bright yellowish green cathodo-luminescence with particularly marked growth banding parallel to traces of the cube growth surfaces. Again Kiflawi and Lang (1975) have tried to correlate X-ray topographic and cathodo-luminescence topographic studies to examine defects in diamond.

Sobolev, Yu Dubov (1975) have studied the intensity and colour of the luminescence emitted by natural diamonds. Vishevsky (1975) has also examined the internal structure of synthetic diamond by using cathodo-luminescence. He has shown that in the growth process, impurities and inclusions are differently adsorbed by cubic and octahedral faces. He has observed that the (111) faces adsorb impurities more intensively than (100) faces. He has also reported that the internal structure of
natural diamond is more homogenous than that of synthetic diamonds. Finally he has concluded that natural diamond crystal grows under more stable conditions than synthetic diamonds. This shows that luminescence emission depends mainly upon the concentration of impurities and the number of dislocations in the crystal. Therefore the luminescence patterns are representative of the impurity distribution in the crystal, which reveal in turn the internal structure of the crystal.

7.7 The etch patterns on cut sections of two other cubic crystals:

Two other crystals of cubic diamond, loaned by Dr. Moore, have also been sawn in half and the cut faces on the two halves are then polished. The etch experiment is then carried out on the polished faces by successive stages, starting from 500°C up to 610°C following the same procedures as described earlier. The two sections of each crystal were mounted after every stage of etching so that the etched faces could be replicated. The replica obtained was examined by Vickers projection microscope, the scanning electron microscope and by transmission electron microscope.

The optical photograph of figures (7.39) and (7.40) reveal the etch patterns produced at 590°C on the two sections of crystal No. (2) which is yellow in colour. The two photographs look nearly similar where some of the etch pits form rows in the $<110>$ directions along the diagonals of the cubes and in between there are other types of rows formed by etch pits which are either parallel to $<100>$ or to $<111>$ directions. The rows parallel to the $<100>$ directions form a square shape around the middle of the crystal. Moreover, the two photographs illustrate that there is no
Figure (7.39) The etch pattern produced on the surface (100) of the cut crystal No. (2) O.M. X 60

Figure (7.40) The etch pattern on the other polished face of the cut crystal No. (2) O.M. X 60
area free from etch pits on the surface and which is resistant to etching. However, it is observed that the density of etch pits over the surfaces is not uniform, although the size and shape of the pits look similar even by using a higher magnification.

The third crystal No. (1) which is also cut into two equal sections by a cut parallel to the cubic axes, has a brown colour, and its edge length is 1.8 mm. Figures (7.41) and (7.42) reveal the etch patterns produced on the polished faces of the two cut sections after having been etched at 610°C with fused KNO₃ for ½ an hour. At this temperature an enormous number of small etch pits are developed. Around the central area, as in figure (7.41) there is a 'flower shape' which is free from etch pits but it shows inside some parallel facets of etched octahedral facets which are also seen in figure (7.42). Moreover, the two etch patterns show rays of etch pits along the diagonals of the cubes. In between there are several rows of etch pits parallel to the \langle 111 \rangle and \langle 100 \rangle directions which are similar to the etch patterns of crystal No. (2). By using the scanning electron microscope, the etch pattern of one of the cut sections is revealed again in figure (7.43). It is obvious from this photograph that there are some etch pits which appear to have a relatively large dimension. By using a higher magnification, ten times that of figure (7.43), it is possible to observe such etch pits in figure (7.44) which are large. Most of them have different orientations with their sides parallel to the cube edges, whereas the majority of the small pits have their sides oriented with 45° to the cube. Actually the pits of larger dimensions have started to appear at 570°C on the two polished surfaces of the crystal and initially they are developed before the smaller pits. They appear as rod shaped features on the surface of
Figure (7.41) The etch pattern produced at 610°C on the polished face of cut crystal No. (1) O.M. X 80

Figure (7.42) The other polished face of the cut crystal No. (1) after it has been etched at 610°C O.M. X 80
Figure (7.43) The etch pattern of figure (7.41) S.E.M. X 50

Figure (7.44) The etch pattern of the same face at higher magnification S.E.M. X 500
the two sections. By increasing the temperature and time of etching the rod shapes are developed into etch pits having big dimensions and all are point bottomed. Patel (1962) has observed such pits in the early stage of etching which consist, as he described, of small linear rods which are crystallographically oriented in the $<110>$ directions, being of different lengths. He has interpreted them as caused by etching of linear defects in the surface.

It is observed also that all the etch pits on the polished surfaces of the two pieces are point bottomed. Examination of such pits at a higher magnification, using the electron microscope, shows that the polished faces are covered with numerous etch pits. Figures (7.45) and (7.46) show some of the pits which are point bottomed and most of them have non rectilinear edges as in figure (7.46). Whereas figure (7.45) shows well shaped etch pits of nearly rectilinear sides, the distribution of etch pits on the surface is not uniform. Some areas show heavily etched pits as in figure (7.46).

The variations in the distribution of pits produced by etching as observed in the etch patterns of figures (7.25), (7.26), (7.39), (7.40), (7.41) and (7.42) could be attributed to the variation of dislocations on the surface and the presence of regions heavily etched are due to high dislocation density on the surface. The defects are either linear defects or local precipitation of imperfections which are developed to etch pits by etching the crystal.

The stratigraphical etch pattern on natural polished cubic faces which reveals the growth history of natural diamonds has been studied by Seal (1962) and (1965), Tolansky and Harrison (1964), Frank (1967), Wilks (1969) and Lang (1974a and b).
Figure (7.45) The etch pits produced at 610°C on the polished face of crystal No. (1) E.M. X 1500

Figure (7.46) Another area of etch pits produced at 610°C on the same face E.M. X 1500
Seal (1962) believed that during the growth of diamond, there is a series of fluctuations in the external conditions which give rise to a series of layers of more or less perfect material. This is in turn represented as a series of light and heavy areas of etch pits. Our results as shown in figure (7.25) and (7.26) support his assumption. The photographs show heavy areas of etch pits at the central regions which means that they are of low perfection in their structure and this is attributed to the presence of impurities or defects during crystallization. The central part, which is heavily etched, is followed by a region of perfect structure, then a narrow area which is imperfect and so on.

Wilks (1969) has done some studies on polished cubic faces and found good agreement with the patterns described by Seal (1962, 1965). She has reported that the etch patterns produced as a result of etching reveal the growth history of diamond, which has taken place in the form of layers parallel to the octahedral plane in type I crystals. Kinks in straight patterns have also been interpreted as a local interruption in layer growth (Seal, 1965).

Tolansky and Rawle-Cope (1969) have conjectured that the original diamond is a mixture of type I and type II. Tolansky and Harrison (1964) have reported that by etching a section of octahedral crystal parallel to a cubic plane in KNO₃ at 650°C, etch patterns are produced. They have added that most diamonds show a type II core, then an alternation of type I and type II layers. Moreover, they have shown that etching preferentially attacks type I diamonds (dislocated layers) before type II. The dark parts of etch pattern are actually masses of small etch pits which are type I, whereas the bright part is free from etch pits and is type II diamond.
Shah and Lang (1963) have studied also the unusual distribution of precipitation in diamond by X-ray topography and have shown that the central region of type I stone is densely populated with small inclusions. X-ray studies indicate that these are precipitated after the growth of the stone. These inclusions correspond to some impurities incorporated during growth.

Seal (1965) has studied again the growth history of diamond as revealed by etching cross sections of diamond of octahedral and cubic forms. He has interpreted the rectilinear structure of etch patterns he obtained as parallel plane sheets which are in turn parallel to the $\{111\}$ planes. He has added that this kind of growth on the $\{111\}$ planes is common but it is not the only kind of growth prevalent. Moreover he has observed that there is no correlation between the internal structure of natural diamonds and geographical origin.

Frank (1967) has pointed out that certain types of natural diamonds have been bounded during their early stage of growth by a combination of different forms. This means that, beside the normal flat octahedral facets, there has also been non faceted hummocky surfaces whose mean orientation is roughly $\{100\}$.

Moore and Lang (1972) have used X-ray topography to study the internal structures of the three cubes which have been cut and etched by KNO$_3$ in this work. From their results two quite different modes of crystallization of diamonds are described. They have reported that in the colourless crystal a mixed habit of growth is observed. This means that normal faceted $\{111\}$ growth combines with rounded surfaces of the mean $\{100\}$ orientation. They have attributed the dark central areas in the photographs to correspond to growth on cuboid surfaces, whereas the $\{111\}$
growth sectors are light. Moreover, they have observed that the \{100\} surfaces are dominated in the outer parts of the crystal. They have again described the structure found in the other two crystals (yellow and brown ones) as fibrous or columnar structures. They have reported that the fibres seem to emanate from the central regions in the \langle111\rangle directions and are directed towards the four corners. They have added that in the region between the corners there appears to be mixtures of fibres in the two directions, i.e. the \langle111\rangle and \langle100\rangle directions.

Lang (1974c) has again classified diamonds according to their growth history into normal or abnormal. The normal growth is recorded by concentric and complete octahedral growth layers and show only the octahedral habit. He has shown that most of the dislocations originated at the crystal's centre of growth and are radiated out to the crystal face, while the abnormal mode of growth comprises a combination of forms which are the normal faceted \{111\} form together with the non faceted hummocky surfaces having mean orientation \{100\}, i.e. the cuboid growth sectors.

Suzuki and Lang (1976) have studied the growth of diamond of mixed habit in which crystallization has proceeded simultaneously on both the normal \{111\} facets and the non crystallographic surfaces of mean orientation \{100\}.

From these previous researches and with the analogy of our results, it is clear that natural diamonds grow in nature in different ways. Some diamonds have a rather complicated growth history and are grown by a combination of facets crystallized in the normal \{111\} planes beside the cuboid form which has mean orientation in the \{100\} planes. Whereas many diamonds grow normally by crystallization in layers parallel to the \{111\} planes, sometimes growth may occur on planes other than \{111\} planes.
GENERAL DISCUSSION ON THE RESULTS
The mechanism of growth of diamond is not yet fully understood, in spite of the fact that much work has been done to obtain information about the growth mechanism by studying the internal and external features. It is not always clear whether these features are due to growth or to dissolution in nature. This work provides new information about the cubic diamond, both in its normal state and after being etched, by examining microscopically details of a large number of these cubic crystals. Electron microscopy has been used to fully resolve the microstructures of the surfaces. It is observed that the cubic faces have numerous square shaped depressions (tetragons) which are crystallographically oriented. All tetragons have rectilinear sides and sharp corners pointed towards the edges of the cube. Figure 8.1 shows a selected area of a natural cubic face with a number of tetragons which have been classified according to their bases as point bottomed and flat bottomed tetragons (Chapter V). Each type is sub-divided again according to its sloping sides, which can be terraced and non-terraced. It is observed that the terraced tetragon often has a symmetrical structure with its base lying at the centre of the point bottomed tetragon, whereas the non-terraced tetragons usually have asymmetrical structures with their bases displaced to one side. It is, however, noticed that the terraced tetragons of the two types, the flat bottomed and the point bottomed, have big dimensions and are very deep compared to the non-terraced ones.

By measuring the dimensions of the sides of some point bottomed tetragons which are relatively large, their sloped sides may be obtained by applying the following equation:
Figure (8.1)  Selection of tetragons  
E.M. X 4000
\[ \phi = \tan^{-1} \frac{d}{r} \]

Where \( \phi \) is the angle of the slope, \( d \) is the depth of the tetragon and \( r \) is the shortest distance from the side to the centre point of the tetragon. It is found that most of the sides of big tetragons which are point bottomed, make an angle of about \( 35^\circ \pm 2^\circ \) with the cubic face. This value of the angle is of the same magnitude as that of the octahedral plane with its neighbouring cubic face. This confirms that the sides of the point bottomed tetragons are in fact lying in and parallel to the \{111\} planes.

By studying the morphology of thousands of tetragons on several cubic faces together with those produced by etch experiments on natural and polished cubic faces, we can show some conclusions about the origin of tetragons together with the help of the previous work which has been done over several years on the morphology of diamonds. From these results, we observe that the tetragons provide evidence which indicates growth as the mechanism of origin.

a - Evidence for a growth mechanism:

1 - The tetragons on natural cubic faces show a big variation in their shape, size and depth, whereas the etch pits produced in the laboratory have more or less the same size and depth.

2 - Natural tetragons always have rectilinear sides and sharp corners, while etch pits generally have curved sides and rounded corners. Sometimes etch pits have rectilinear sides under special conditions of etching, such as light etching (Tolansky and Patel, 1957).

3 - Natural tetragons always have their sides inclined with an angle of \( 45^\circ \) to the cube edges, while etch pits have their sides either parallel to or inclined at \( 45^\circ \) to the cube edges as shown in figure (7.31).
Evans and Sauter (1961), Patel and Ramanathan (1962) and Tolansky, Miller and Punglia (1972) have reported that etching produces etch pits having their orientation like the tetragons on natural faces or rotated through 45° with respect to them, depending upon the etchant and the temperature used.

4 - The natural tetragons sometimes have basal extensions associated with their sides, whereas etch pits have not. Omar and Kenawi (1957) have etched octahedral diamond and produced etch pits which have basal extensions similar to the natural ones.

5 - Natural tetragons cannot alter their size by increasing the time of etching, while etch pits are enlarged with continued etching and ultimately overlap with each other as etching proceeds.

6 - Some of the natural tetragons have terraced sides, whereas etch pits do not show terraces. Patel, Patel and Agarwal (1967) have etched cubic faces of diamond and produced terraced square shaped pits but with rounded corners. Omar and Kenawi (1957) have reported the occurrence of step formation on the walls (terraces) of triangular etch pits on octahedral faces.

b - Evidence for a dissolution mechanism of tetragon formation:

1 - Laboratory etching sometimes produces etch pits having rectilinear sides and sharp corners and have the same orientation as natural tetragons, only when the rate of etching is slow and under certain conditions, such as temperature and etchant.

2 - The etch pits produced by etching polished cubic faces are of two types as are the natural ones. The flat bottomed and point bottomed etch pits are of relatively different sizes but not with so large a difference as the natural ones. (Figure (8.2) is an example which shows
Figure (8.2) The types of etch pits. E.M. X 1500
etch pits of the two types.

3 - The development of small pits on the bottom of a big one is also produced by etching. A good example is shown in figure (7.32).

4 - Rows of natural tetragons, on the faces of cubic crystals, are observed to run parallel to \( (100) \) directions. These rows of tetragons have been attributed to etching of dislocations along grain boundaries on the surface. Logically, if these rows of natural tetragons are attributed to dissolution in nature and they have the general characteristics of the natural tetragons, the natural tetragons on the same surface can be attributed to the same mechanism.

From all the foregoing observations on the evidence of growth and dissolution, it may be concluded that the balance of probability is strongly in favour of the theory that natural tetragons on cubic faces arise at the sites of dislocations by dissolution in nature and before the growth of the crystal is completely stopped, where the diamond crystal is subjected to the exact required temperature and pressure.

This means that growth and dissolution on diamond crystals have occurred alternately. Initially, diamonds grow, partially dissolve, then grow again. It is suggested that if there is any dislocation existing on the surface of diamond after growth, then due to its environmental surroundings a very tiny pit starts to initiate at the site of this dislocation. The pit takes the same shape of the crystal face on which it is formed. When the growth of diamond starts again, the new growth sheets advance from the four sides, they stop around the small pit and touch each other at their ends with an angle of 90°, leaving a tetragon depression. The advancing layers on the \( \{111\} \) planes, one over the other, form the side walls of the tetragon and they finally give rise to
a terraced tetragon. This explanation for the formation of point bottomed tetragons with terraced sides agrees with Varma's hypothesis (1967a) that defects affect growth in a definite way. Figure (8.3) confirms our suggestion of the existence of a plane sheet mechanism, as revealed by a terraced tetragon. It shows how the advancing layers between the sides of two neighbouring tetragons proceed and become slightly curved, forming cubic like facets.

The variation in the depth of terraced tetragons can be explained by the same mechanism, that the tetragons initiating at the sites of defects in the early stage have large sizes and depths whereas small tetragons which are relatively shallow and small in size are formed at a later stage of growth.

The non-terraced tetragons with steep sides are also produced by the dissolution process in nature at the site of dislocation on the surface (Lang 1964) and these are most probably produced after the growth has been completely stopped, forming the point bottomed tetragons of steep sides.

The flat bottomed tetragon with non-terraced sides is also produced by the same mechanism as the point bottomed tetragon, but with the difference that the dislocation on the flat bottomed tetragon is completely etched away, leaving a flat bottomed tetragon.

The point bottomed tetragons (terraced and non-terraced) are known to be nucleated at the sites of dislocations (Lang 1964). They will remain point bottomed if the dislocations giving rise to them still exist (Patel and Patel, 1968).

Flat bottomed tetragons (either terraced or non-terraced) show that the dislocations causing them have been completely etched away before the
Figure (8.3) Terraced tetragon E.M. X 4000
process of natural etching is stopped.

In the laboratory, etching the natural tetragons causes the point bottomed tetragons either to remain point bottomed or change to flat bottomed, depending upon whether the dislocations causing them still remain in the body of the crystal or are etched away.

The eccentricity of the point bottomed tetragons may be explained by postulating that the dislocations giving rise to them are not perpendicular to the cubic face but may be inclined to it (Patel 1961) or most probably, the rates of the advancing layers coming from different sides being not equal.

The basal extension associated with one or more sides of some tetragons may also be attributed to the higher speed of the advancing layer from one side more than the others, leaving a basal shape which is different in its level from the surrounding areas with a step less than 100Å (Harrison 1964).

When an advancing layer is confined between two basal extensions of two neighbouring tetragons, the advancing layers are slightly curved and form the bands on the cubic like facets as shown in figure (8.4).

The explanation of the formation of the complex tetragons which sometimes appear on natural cubic faces may be due to the fact that the advancing growth layers proceed from the four directions and before being arrested by the presence of a tetragon, they include between their ends more than one tetragon. Also it has been suggested by Patel (1961) that when a new defect appears on the flat bottom of a large tetragon, a small tetragon is initiated at this defect, forming a complex feature.

The occurrence of tetragons of the same shape on a limited area on the surface as it has been shown in figures (5.5) and (5.8) suggests that the
Figure (8.4)  Cubic like facet  E.M. X 4000
type of defects causing these tetragons are all of the same type. Finally from these observations, we can conclude that diamond has grown, then partially dissolved and then regrown again. The growth of diamond occurs by crystallization in layers parallel to the \{111\} planes and sometimes parallel to other planes such as cubic planes. That is why cubic surfaces are found to be multifaceted. The predominant facets are the cube and the octahedral facets. Dodecahedral facets are also found on the cubic crystal but there is a difference in level between the cube faces and other facets.

The occurrence of trigons at different areas on the body of the cubic crystal and also on the side wall of some tetragons, as we have discussed earlier in chapter VI, confirms the fact that cubic crystals of natural diamond are mainly formed by layers in the octahedral planes beside the cube planes. Figure (8.4) shows that the advancing layers may pile up on the \{111\} planes to form tetragons.

Etching the natural and polished faces of cubic crystals is also performed. As is expected from the crystallography, the etch pits produced are square shaped with their sides either parallel to or incline at 45° to the cube edges. It is known that the orientation and shape of etch pits depend mainly on:

1 - The etchant used [Gilman and Johnston (1957) and Frank and Puttick (1958)].


By increasing the time of etching, the etch starts to overlap. The stratigraphical etch patterns on polished cubic faces of the cut crystals
Nos. (1), (2) and (3), reveal the structure of the crystals. The different degree of light and heavy areas as revealed by etching in figures (7.25) and (7.26) is attributed to different conditions of growth in the original crystal which in turn gives rise to the defects laid down during the crystallization of diamond. The density of the etch pits is proportional to the number of defects in the crystal, since etching starts more at the sites of lattice defects such as dislocations and impurities. As a result, it is clear that the defects may be impurities which cause the layer to grow in abnormal orientation (Frank 1943), thereby producing type I diamond. They may also be due to aggregation of vacancies which give rise to dislocations, i.e. to type I diamond as revealed by the heavy etching.

As a result, it is assumed that diamond is formed of layers of type I and type II material (Rowle-Cope and Tolansky 1969). Referring again to the etch patterns of figures (7.25) and (7.26), it may be seen that at the centre point of the crystal, there is a heavily etched area, which indicates that it is of type I diamond. The centre is surrounded by alternate layers of type I and type II material and as the crystal grows larger, type I diamond predominates especially near to the edges of the cube. That is why the sixty cubic crystals which have been examined are type I and show absorption in the ultra-violet region beyond the wavelength 3000Å°.

Cathodo luminescence photographs of the two cut pieces of crystal No. (3) are also functions of dislocations in the crystal material. The two images of figures (7.37) and (7.38) reveal the distribution of impurities and dislocation sites on the polished faces, which are accorded to the patterns obtained by X-ray topography (Moore, Lang 1972).
The striking depression features which have the shape of screw drivers and radiate from the centre of the crystal along the diagonal of the cube, are found to be composed of very shallow etch pits 100Å° with flat bottoms. These pits touch each other and form the chain shape, which ends near the corners of the cube. At their ends there exist faint etched octahedral facets like those described by Suzuki and Lang (1976) as {111} re-entrant faceted which are localized within the region of non-faceted growth, presented in diamond of mixed habit growth, during which crystallization proceeds simultaneously on normal {111} faces and non-crystallographic faces having mean orientation {100}. In this case growth can propagate on the pair of re-entrant facets forming a column of octahedral growth inserted within the surrounding matrix of non-faceted growth material.

Planes of the form {111}, in facets, combine to produce faceted re-entrants on the surface of growing crystals, where the non-faceted modes of growth are dominant.

The other type of etch pattern as has been described by Moore and Lang (1972) and by Lang (1974a, b), is shown in figures (7.39), (7.40), (7.41) and (7.42). The figures reveal the fibre patterns which radiate from the centre of the cube, towards the edges, and across the diagonals of the cubes. It is observed that the etch pits are arranged in rows along the diagonals of the cubes, starting near the centre and directed towards the corners of the cube. Small rows of etch pits are also present in the area between the diagonals; some of them are parallel to the cubic planes while others have the <110> directions. The rays of etch pits which are parallel to the <110> directions form a square shape around the middle area of the crystal as in figures (7.39) and (7.40).
Lang (1974b) has interpreted these fibres as representing growth in column with repeated branching in $\langle 111 \rangle$ directions, so as to fill the space between the axes defining the corners of each cube growth sector.
Angus, J. and Dyble, T. (1975) Surface Science 50, 157
Bravais, A. (1866) Etudes Cristallographiques (Paris)
Buckley, H.E. (1951) Crystal Growth (Wiley, New York)
Custers, J.F.H. (1952) Physica 18, 489
Daniel, F.J. (1816) Quarterly J.Sc. 1, 24
Evans, T. and Phaal, G. (1962a) Phil.Mag. 7, 843
Evans, T. and Sauter, D.H. (1961) Phil.Mag. 6, 429
Feust, R.C. (1949) Ph.D. Thesis Victoria University of Manchester
Fersmann, A. and Goldschmidt, V. (1911) Der Diamond (Heidelberg Winter)
Frank, F.C. and Puttick, K.E. (1958) Phil.Mag. 3, 1273
Frankel, J. (1945) J.Phys. USSR 2, No. 2, 391
Frankel, J. (1946) Kinetic theory of liquid (J.Phys. USSR 2, 392)
Friedel, G. (1924) Bull.Soc.Fran.Min. 47, 60
Goldschmidt, V. (1904) Zeit Sch.fur Kryst. 38, 656
Lang, A.R. (1969) Crystal imperfection (Final report contract AF 61-449 Aerospace Research)
Mahl, M. (1940) Z.Techs.Phys. 21, 17
Orwan, E. (1934) Z. Physik 89, 634
Patel, A.R. (1964) Physica 30, 505
Patel, A.R., Goswami, K.N. and Desat, C.C. (1964) Phil. Mag. 10, 931
Polanyi, M. (1934) Z. Physik 89, 660
Raal, F.A. (1957) Amer. Min. 42, 354
Seager, A.F. (1953) Mineralogical Mag. 30, 1
Seal, M. (1960) Diamond 4, No. 4
Seal, M. (1962) First Internat. Conf. on diamond (Paris) 361
Seal, M. (1965) Amer. Min. 50, 105
Shafranovskii, I.I. (1941) Dokl. Akad. SSSR. 31, No. 8
Smekal, A. (1933) Physik Z. 31, 229
Sobolev, E.V. and Yu Dobov, I. (1975) Sov. Phy. Solid state (USA) 17, 726
Sutton, J.R. (1928) The Diamond (Murby, London)
Tammann, G. (1898) Z.Phys.Chem. 25, 441
Tolansky, S. (1959) Ind.Diam.Rev. 19, 6
Tolansky, S. (1968) The strategic Diamond (Oliver and Boyd Ltd.)
Van der Veen, A.L.W.E. (1913) Z.Kristallogr. 51, 545
Varma, G.K.R. (1967a) Phil.Mag. 16, 959
Varma, G.K.R. (1967b) Phil.Mag. 16, 621
Varma, G.K.R. (1967c) Phil.Mag. 16, 657
Varma, G.K.R. (1967d) Phil.Mag. 16, 611
Varma, G.K.R. (1972) Scripta Metall. 6, 383
   (John Wiley and Sons)
Volmer, M. (1922) Zeit Phys. 9, 193
Volmer, M. (1939) Kinetic der Phasenbildung Leipzig
Wilcock, W.L. (1951) Ph.D. Thesis Victoria University of Manchester
Wilks, E.M. (1961) Phil.Mag. 6, 1089
Williams, A.F. (1932) The Genesis of the diamond 2, 423
Wulff, G. (1901) Z. Krist. 34, 449