

PART I

## CHAPTER I

### EXISTING INFORMATION ON DIAMOND

#### 1.1 Introduction

Since growth and dissolution of crystals take place through the surface of crystal faces, the crystal surfaces are the places where all phenomena concerning crystal growth and dissolution are most vividly reflected. From the study of the structure of crystal faces, therefore one may be able to predict the mechanism, process or history of crystal growth and dissolution. It is also possible to study the behaviour of internal imperfections or disorders of crystals such as dislocations, stacking faults etc., since their existence affects greatly the surface patterns formed by growth or dissolution. Surface structures of crystal faces also exhibit the differences in growth conditions, as well as the history that the crystals have experienced after their formation.

In recent years, the optical and interferometric techniques developed by Tolansky have been extensively in use for the topographical studies of the natural surfaces of crystals. By using these sensitive techniques, one can make a thorough survey of every minor detail of crystal surfaces and hence predict the mechanism of growth or dissolution even on an atomic scale.

Further information concerning the conditions

of growth mechanism of crystals can also be gained from the etch marks produced on the natural surfaces by some suitable solvents under proper conditions.

The topographical studies of natural surfaces and their etch patterns provide information with regard to the last stage of the history of growth of the crystal. The history of crystal during the growth can probably be obtained from the study of its cleavage surfaces. It can be considered that more information in this connection can be gained from the optical and interferometric study of the matched cleavage faces of crystals and their etch patterns.

In this laboratory, systematic microtopographical studies on various natural and synthetic crystal surfaces are being undertaken in detail and the present work on diamond takes its place in this series. The present chapter deals with the introduction on the existing information on diamond.

## 1.2 Historical review

Diamond has long been prized as a precious stone on account of its beauty, rarity and pre-eminence. It is distinguished from all other gem stones, by its remarkable properties of extreme hardness, high refraction, large

dispersion and brilliant lustre.

Mineralogically, diamond is composed entirely of the element carbon crystallised in the isometric system. Originally the words adams<sup>a</sup>, adamant and diamant were given to the very hard, colourless, transparent minerals now known as diamond, corundum, spinel, topaz and quartz.

A beautiful account of the history of diamond right from the biblical times has been recently given by Tolansky (1962) in his book 'The History and use of diamond'.

Diamonds are sold by carat. One carat corresponds with 0.200 gm.

### 1.3. Occurrence

Diamond occurs in nature in very limited localities and ranges in character from pure transparent single crystals to large conglomerate masses which are quite opaque. It is found in two distinct types of location, viz., the deep pipes from which it is mined as virgin material, or in water washed alluvial gravels which presumably came originally from a source similar to the deep mined diamonds. It may be supposed that the deep mined diamonds retain on their surfaces a

record of their history of formation at the close of their growth while those found in alluvial gravels may have suffered abrasion and even possible etching on their natural surfaces.

The authentic history of diamond mining begins with Jean Tavernier's visit to Goleonda, India (1663-68). During the years 1721 - 1820, Brazil was the chief source of world's diamond supply. Dodecahedral crystals are characteristics of the diamonds from Brazil and the name Brazilian diamonds, now used describes the shape and not the geographical origin of the diamonds. In the year 1866, the first South African diamond was identified. The finding of a fifty carat diamond in an intermittent stream led to the discovery of the first kimberlite pipe. Now 95 % of the world's output of diamonds comes from South Africa.

Crystals of diamond in their natural forms are also found near Panna in central India. A good description of the diamond deposits of Panna is given by Grantham (1964). Diamonds from Panna are distinctive for the high degree of curvature of the faces as shown in figure 1.

#### 1.4 Form and shape

Natural diamonds are found in a wide variety of forms and of these, two types dominate - the octahedron, often with fairly flat sides ( figure 2(a) ) and the twelve sided dodecahedron ( figure 2(b) ), frequently with rounded faces, meeting in very sharp, curved edges. The octahedron can be considered roughly as two square based pyramids with square bases joined and with opposing apexes. Well developed transparent octahedra are usually small and are only infrequently found. Dodecahedra are very variable in shape and many of the faces show fine striated line markings. Cubes (figure 2(c) ) do turn up at times but their surfaces are very rough.

Octahedra frequently occur in flat forms, of which there are two different kinds both of which are often well suited for interferometry. The first kind is called the portrait stone and it occurs as a flat effectively plane parallel thin plate of hexagonal outline. This is formed due to overdevelopment of two opposite octahedron faces, and the edges of the hexagon are the remaining octahedron faces. The other flat type is the triangular plate twin form called a 'macle', which appears as a thick triangular plate with a twinning plane parallel to the plane of the triangular faces, which are

octahedron faces.

Some diamonds are found in dark grey and even in black colour. They exhibit a more or less imperfect crystalline structure, and are known as black diamonds, bort or boart or carbonado. Boart is an imperfectly crystallised, translucent, dark coloured diamond and is therefore useless as a gem stone. Carbonado is the Brazilian term for a still less perfectly crystallised black diamond. Boart and carbonado are usually regarded as forms intermediate between diamond and graphite.

#### 1.5 Crystal structure and symmetry properties

All crystal shapes of diamond belong to the isometric or cubic system, but for the last many years there has been much controversy among crystallographers as to which class it should be assigned to. Since a few crystals of tetrahedral form are found it leads to the view that the symmetry is tetrahedral as in class 31. With this view of the symmetry of the crystals, the octahedral crystals can be regarded as two interpenetrating tetrahedra twinned about a cubic face and this interpretation is supported by the grooves often present along octahedral edges. The opposing view is that diamond belongs to class 32 with full octahedral symmetry and this is supported by the absence of



piezo-electric and pyro-electric effects. The tetrahedra are explained as being distorted octahedra with the suppression of alternate faces.

Hauy after very careful study came to the conclusion that the symmetry of the diamond is tetrahedral and his view was supported by many others including Mohr, Haidinger, Miller and Rose. Fersmann and Goldschmidt (1911) pleaded for the hemihedral structure of diamond. Vander Veen (1911) vigorously opposed the theories advanced by Fersmann and Goldschmidt and proposed a holohedral symmetry.

The results of the X-ray analysis of the crystal structure of diamond by Bragg and Bragg (1913) favoured the holohedral symmetry. According to them, the structure can be regarded as two interpenetrating face centred cubic lattices. The arrangement of the carbon atoms on the two interpenetrating f.c.c. lattices is shown in figure 3. All A atoms represent one face centred cubic lattice. The second face centred cubic lattice is displaced with respect to the first along a cube diagonal (Trigonal axis) by one fourth of its length. Four atoms of this lattice are represented by B, in the figure. It can easily be seen from the figure that every B atom of one lattice is surrounded

by four A atoms of the other lattice and vice versa. If these atoms are joined by heavy lines as shown in the figure, it can be shown that every carbon atom is linked tetrahedrally to four of its neighbours. The number of atoms per unit cell is eight. From X-ray measurements it is found that the edge length of the cell is  $3.567 \text{ \AA}$  and C-C bond length  $1.544 \text{ \AA}$ . While this fundamental Bragg structure has never been in doubt there has been considerable uncertainty over the texture or degree of perfection of the structure in actual diamonds. The planes shown passing through A A A are the (111) planes. The linking of carbon atoms in the lattice with the (111) planes horizontal is shown in the figure. When diamond is cleaved along the (111) planes, the vertical bonds shown in figure 4 are broken. The distance between two consecutive (111) planes is not constant.

Raman (1944, 1945) pointed out that by virtue of the special positions which they occupied in the crystal lattice, the carbon atoms in diamond might have tetrahedral configuration of electron orbital moments and spins. A tetrahedral axis has both direction and sense and the carbon atoms in the two Bravais lattices may therefore be oriented in space and with respect to each other in four different ways as shown in

figure 5, each of which corresponds to a possible structure of diamond. The cases I and II represent octahedral symmetry while cases III and IV represent tetrahedral symmetry. However the C-C bond length for Oh I and Oh II will be slightly different and these forms will form a lamellar structure with strains introduced. Lonsdale (1945) held that X-ray results were incompatible with this theory. In the first place (222) reflection should be absent in the mixture, but is observed for some type I stones, and further the predicted difference in interatomic distance between Oh I and Oh II is not found in the X-ray studies of type II stone.

#### 1.6 Cleavage

Dana and Ford (1948) define cleavage as the tendency for the crystals to break in certain definite directions, yielding more or less smooth surfaces.

That diamond could be cleaved along (111) planes had been known to Indian lapidaries, who developed the art of cleaving, for a long time. The process of cleaving has been described by Boot (1604) and Wollaston (1816). Even at present, the same method, which consists of rubbing a kerf in the stone with a diamond chip and giving a sharp blow to one end of a metal blade whose other end is inserted in the kerf,

is used in industry. Figure 6 represents an octahedron prepared for cleaving by rubbing some kerfs. The kerfs can be distinctly seen in the figure. A schematic diagram of an octahedron with the (111) cleavage plane shaded is shown in figure 7. The figure also shows the cleaved out portion separated from the octahedron.

Although in diamond (111) cleavage is by far the easiest to achieve and is therefore the most commonly observed, other cleavages are also reported. Sutton (1928) remarks that (110) cleavage and also conchoidal fractures have been observed. Williams (1932) has stated that he did not see any cleavage parallel to either (110) or (100) planes. Ramachandran (1946) found (211) cleavage. Ramaseshan (1946) in a study of 15 crystal fragments observed (111), (211), (110), (322), (331), (221) and (332) faces. The (111) face was most common while the (221) and (110) were not uncommon.

Why the (111) plane in diamond should be the plane of easy cleavage was first explained by Ewald (1914) and again by Kraus and Sawson (1939) and Ramaseshan (loc. cit). Recently, Brunton (1962) has expressed the view that the octahedral planes turn out to be the cleavage planes not because they have the lowest

cleavage energy but because they are also the growth planes and as such occasionally contain layers of faulted growth lacking the cohesion of the perfect structure.

Pandya (1954) from his observations that occasionally some cleavage lines terminate along a line, oriented crystallographically, has suggested that there is evidence of dislocations. Following Gilman (1955) and Hirsch (1956), Wilks (1958) considered that the cleavage lines in the case of diamond were in fact associated with the presence of twist boundaries of screw dislocations.

#### 1.7 Classification of diamonds

Diamonds have been classified as type I and Type II in relation to their absorption in the infrared, visible and ultraviolet regions (Robertson, Fox and Martin (1934) ; Sutherland, Blackwell and Simeral (1954); and Clark, Ditchburn and Dyer (1956) ). Type II diamonds transmit well in the ultraviolet down to the absorption edge at  $2200 \text{ \AA}$  but type I diamonds show absorption starting at  $3300 \text{ \AA}$  and increasing fairly rapidly at shorter wave lengths. This difference forms the basis of a convenient method of discriminating the two types.

Most diamonds are extremely good 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 conductors. He proposed the classification of the non-conducting type II diamonds as type II a and the semi conducting diamonds as type II b , and this nomenclature has been generally accepted.

Halperin (1956) showed that the density of trigons is less on type II diamonds, suggesting a greater density of screw dislocations on the natural faces of the type I diamonds. Seal (1956) using a reflection electron microscope found a difference in the roughness of the cleavage surfaces of type I and type II diamonds. In type I local changes of the height of several microns were frequent while type II was much smoother. He found that certain type I diamonds showed a "mixed" behaviour since regions of type II cleavages were often found in this cleavage surface. Wilks (1958) concluded that the cleavage surface of a type II diamond exhibited a more regular pattern, whereas there were in general, more cleavage lines and also a great number of the so called river systems on type I diamonds.

According to Dyer et al (1965), four broad .

classes of diamond have been recognised. They are designated as Ia, Ib, IIa and IIb. The characteristic optical absorption features of these several types can largely be explained in terms of the presence or absence of nitrogen in different forms. Type Ia diamonds contain nitrogen platelets of about  $10^{15} / \text{cm}^3$ . Kaiser and Bond (1959) showed that type I diamonds can contain upto 0.23 % of nitrogen. Dyer et al (loc.cit.) showed that type Ib diamonds contain nitrogen but in smaller amounts than type Ia, and in dispersed form. Type II diamonds in general do not appear to contain nitrogen (Kaiser and Bond, loc. cit.)

## 1.8 Physical properties

### (a) General

Mellor (1946) has described the physical properties of diamond in detail. Recently Berman (1965) has given a detailed account of the various physical properties of diamond.

Gem diamonds have a density of  $3.53 \text{ gm. cm}^{-3}$  but the touch black coke-like aggregate may have a density as low as  $3.15 \text{ gm. cm}^{-3}$ . It is the hardest known substance. Boron nitride recently synthesized by General Electric Company and called Borazon is the next hardest material known. Silicon carbide, tungsten

carbide and aluminium oxide rank below Boron nitride in hardness in that order. Diamond occupies position ten on Moh's scale of hardness. Carborundum is nine on the same scale. But the difference in hardness between them is quite great, diamond being 85 times as hard as carborundum. Further diamond is a very strong material and therefore resists compression. It has the best compressibility property of any known material (Tolansky, 1962).

All diamonds are non-conductors of electricity but all are excellent heat conductors, superior even to iron and steel. Some diamonds conduct electricity when they are subjected to radioactive emanations. It has been found that the current conducted is proportional to the intensity of radiation. Proportional counters used for measuring radioactivity are based on this principle. It has been found that when diamonds are irradiated with electrons or neutrons they develop a number of interesting properties. The most striking change is one of colour. During neutron irradiation they first become pale green, then dark green and finally, after a large enough dose, black. Similar changes occur after irradiation with 1 MeV electrons. In addition to these colour changes the diamond also becomes paramagnetic. The strength of the magnetic moment is roughly proportional to the dose of

irradiation. Both the colour and the magnetism are removed or greatly reduced by annealing e.g. by keeping the diamonds for 10 minutes at  $1000^{\circ}$  C.

It was first thought by Friedman (1948) and Hofstadter (1948), that the only diamonds which are used as counters are type II and this was explained on the basis of Raman theory, as showing that high trap densities exist in the mosaic type I, while conduction is possible along the lamellae in type II. Ess and Rossel (1951) concluded that, to explain the counting characteristics of diamonds two types of imperfections were necessary (1) impurity centres (2) imperfections like lattice dislocations.

Although the curvature of diamond is very common, very few precise measurements have been made for its determination. Ramaseshan (1944) from the measurements made on some diamonds from Sir C. V. Raman's collection, came to the conclusion that the curvatures are highly variable, both in an individual diamond and also between different specimens.

Vander Veen (1911) explained the curvature to arise as a result of the growth of the crystals by layer deposition. But according to Fersmann and Goldschmidt (1911), the curvature and the grooves found on the edges

of some octahedra have been explained by assuming solution currents to exist in the mother liquor. Friedel (1924) attributed the external forms of diamond due to the forces acting on it in the plastic state. This view was later on confirmed by Sutton (1928). Kucharenko (1946) considered the curvature to be due to minute crystal facets whose inclinations with one another are very small and therefore taken as a whole to give the effect of continuous roundness.

Raman and Ramaseshan (1946) from their experiments, came to the conclusion that the diamond was formed from the solidification of carbon which had assumed the liquid form under conditions of high temperatures and pressures. They explained that the thermal agitation of atoms in the liquid state prevented a perfect ordering of the valence bonds within the liquid. Hence molten carbon would assume a rounded shape.

(b) Optical and other special properties

Diamond has a high refractive index (2.417 at  $5890 \text{ \AA}$ ) and a high dispersion. When it is free from strain it is isotropic, being a cubic crystal, but many natural diamonds show strain bands when examined between a polariser and an analyser. It has been stated that sometimes part of this strain may be annealed by heating

in vacuum to 1600° C. but more commonly the strain can not be annealed unless the diamond is heated very strongly. This must be carried out under pressure to prevent graphitization. Strain does not greatly affect the properties of diamond as a gem though it may make the shaping more difficult or hazardous. The 'fire' of a gem stone depends first on its high refractive index, which implies a low angle of total reflection, and secondly on its high dispersion.

Luminescence which is exhibited by nearly all diamonds has been explained by Raman as being due to the interpenetrative or lamellar twinning of different possible crystal structures in diamond. He has shown the relation between the quality of luminescence and the interpretation of different structures. The spectroscopic and the X-ray studies confirm that luminescence is essentially physical in origin and not due to the foreign atoms present as impurities.

Sunandabai (1944) has shown a striking relation between ultraviolet absorption spectra and character of fluorescence. Extensive scientific research has recently been done in connection with these phosphorescing and fluorescing properties of diamond, especially in relation to structure and to impurities.

The birefringence in diamond was first observed by Brewster in (1815) and later by Friedel (1924),(1932); from examinations of many diamonds of diverse origin. They found that a feeble birefringence was shown by all diamonds irrespective of source. Recently Tolansky (1966) has criticised Friedel's theory and has proposed an alternative explanation of the fact that almost all diamonds (natural and synthetic) appear to be birefringent. Seal (1966) has reported studies on the inclusions, birefringence and structure in natural diamonds. Very recently Lang (1967) has shown that by optical and X-ray techniques many different causes of strain birefringence in diamond can be distinguished. According to him, the perfect diamond, free from strain, is an elusive ideal.

Most diamonds, apart from those specifically selected as gem stones, contain some impurities, usually in the form of a mineral inclusion. When a diamond containing a mineral inclusion is examined by transmitted polarised light it is usual to observe strain birefringence within the diamond. The strain is always the greatest in the region immediately adjacent to the inclusion. The inclusion is thus being held under pressure by the diamond at room temperature. Henriques (1965) has made a study of the thermal expansion of the

inclusions in diamond.

(c) Thermal properties

Diamond has a much higher thermal conductivity at room temperature than other hard materials and this plays an important part in the industrial use of the stone. Diamonds of gem quality have thermal conductivities at room temperature greater than any other substance. A type II specimen conducts heat five times better than copper, and this difference is accentuated at lower temperature, the ratio being twenty-five at liquid air temperature.

Measurements of specific heat and thermal expansion were used with existing data to predict conditions under which it might be possible to synthesize diamond. Wright (1965) extended the measurement of the thermal expansion coefficient of diamond from  $900^{\circ}\text{C}$ . to  $1700^{\circ}\text{C}$ . His results on two type II specimens gave values of about  $4.7 \times 10^{-6} /^{\circ}\text{K}$  at  $800^{\circ}\text{C}$ . to about  $5.5 \times 10^{-6} /^{\circ}\text{K}$  at  $1700^{\circ}\text{C}$ .

1.9 Chemical properties

The diamond is highly resistant chemically. It consists of carbon, but usually a small percentage of impurity is included in it. The opaque or dull

59564

stones usually contain more impurity. Its great resistance to chemical attack helps it to be cleaned by standard reagents without producing any damage. In fact diamonds are most likely to suffer damage by chipping than by any other means.

Although chemically resistant, diamond is easily oxidised to carbon dioxide at high temperatures without producing any ash. It converts to graphite when heated in absence of oxygen. It can also be attacked by hot oxidising agents. In fact etching of diamond can be carried out by using a proper oxidising agent at the required temperature for a specific time. A great deal of structural information can be obtained by controlled etching.

#### 1.10 Uses

It is principally as a gem stone that the diamond, has for centuries been prized. It is distinguished from all other gem stones by its remarkable properties of extreme hardness, high refraction, large dispersion and brilliant lustre.

In the past when the art of cleaving and polishing was not known, the octahedron diamonds often found early in India, were used, uncut and without

further treatment, as gems.

Large transparent plates of diamond of reasonable thickness have been prized in the past and were specifically called "portrait stones" because they were used as "windows" to cover miniature portraits painted on ivory to be worn on the bosom. Such a miniature portrait covered with a diamond window, was considered a particularly decorative ornament for wear.

#### In industry

In the period just before and during the last war diamond emerged as an important industrial material. Diamond is a technological hard material of the greatest importance. It can now be regarded technically as a fundamental strategic raw material. Of the annual world out put of mined diamonds, which is some 5 tons, only 1 ton is used for gem stones, the remaining 4 tons being consumed in Industry as a hard abrasive or a cutting material.

The uses of diamond in Industry are growing rapidly in two broad categories :

- (1) Single individual diamonds
- (2) Crushed grit

The range of uses is enormous, it varies

from lathe cutting tools to gramophone needles, from the truing and shaping of precision grinding wheels to the cutting and drilling of glass. Then again diamond rock-saws, diamond rock drills, diamond wire-drawing dies, even indeed diamond micro-tome cutting knives, all these are but a few of the multifarious industrial uses of singly mounted diamonds.

Many basic components of mass-produced engines and automobiles etc. are rapidly shaped by accurately made silicon carbide grinders of precise form and dimension. These grinders wear with use and they must be continuously reshaped and trued and it is done with diamond, the only material hard enough to retrue the carbide grinders. Further the diamond grit bonded wheels have a fierce cutting and abrasive action and are extensively used for polishing, grinding, cutting and shaping; for gear wheel teeth, manufacture of hard tools sawing of rocks etc. These are but a few of the extensive uses of the newer bonded wheels.

#### Miscellaneous

There are many specialised scientific uses of diamond such as, for the cutting of fine line gratings, for hardness indenting test tools, for the fine stylus used in some instruments and it can even be used as a

detector for atomic radiations.

The semi conductive diamonds can easily replace germanium and silicon, bearing in mind their semiconductive properties. The diamond, will withstand much higher temperatures than germanium or silicon.