The growth of diamond in the laboratory has made possible investigations of the crystal habit, color and surface structure as related to variations in the growth process. Many of the variations found in natural diamond have been reproduced. The preferred growing faces are the octahedral planes, with the exception of the low temperature cube forms, which grow on the cube face.

**INTRODUCTION**

The morphology of diamond has been of great interest from the time man first determined its composition and crystal habit. The early gem cutters were undoubtedly aware of the curious surface markings visible on many stones with the unaided eye. They also soon realized the directional properties of hardness and cleavage as related to the crystal orientation. Early observations on the occurrence of diamond were recorded by Fersmann and Goldschmidt (1911), Williams (1932), and others along with detailed speculation concerning the genesis and growth mechanism as related to the crystal variations observed. Later more detailed studies of diamond surfaces have been undertaken by Tolansky (1955) and others. There is great interest in diamond crystal growth and its relation to surface features since a diamond crystal represents a relatively simple atomic structure.

Now that diamond can be grown under controlled conditions, we have the opportunity to study the many variations in diamond crystals and can attempt to relate them to variations in the growth process. Many of the growth variations observed in natural diamond have been reproduced in the laboratory and the modifications of the process sufficient to yield these variations have been determined.

The high pressure, high temperature apparatus used for studying diamond growth characteristics was the taper piston device designed by Hall (1960). The diamond growth systems used have been described previously by Bovenkerk, *et al.* (1959).

One of the most interesting features of diamond growth is the apparent sharp boundary condition between growth and dissolution at the high temperatures at which the process takes place. Growth can be stopped at will by changing the pressure or temperature or both and the diamond crystal can easily be converted to graphite if the pressure is not main-
tained at these high temperatures. This may mean that the diamonds found in nature have been subjected to solution following growth in many cases. Therefore, the appearance of a natural or synthetic diamond surface is not necessarily representative of the surface as it was when the growth process was completed.

**Crystallography**

Diamond always crystallizes in the cubic system. The crystal forms commonly observed in nature are the octahedron, cube and rhombic dodecahedron.

In the growth of diamond in the laboratory compared to what is found in nature, there are many similarities and some apparent differences. A striking example of an apparent difference is the regularity of the crystal forms of diamond produced in the laboratory. If conditions are such that inter-growth, aggregation or gross dissolution are not present, the synthetic diamond has a regular, easily recognized crystal form. In natural diamond, perfectly straight-edged regular crystals are rare; more commonly, rounded crystals or irregular pieces having no easily recognized faces are found. This may be interpreted as meaning that in nature diamond grows in restricted or confined environments where the crystal more or less conforms in contour to the surrounding rock masses. A restriction in carbon reaching the growing faces uniformly may also account for this. The rounded crystal form could be produced by abrasion or dissolution after the diamond is formed. The growth of diamond in the laboratory supports the latter theory. In our synthesis of diamond where the crystallization occurs through a relatively thin film of metal catalyst with adequate graphite present, uniform deposition over the entire crystal face can easily take place. This metal film need never exceed a couple of hundred microns in thickness.

As in nature, we have found that diamond tends to the octahedron as the most common crystal form. However, under certain conditions only the cube and rhombic dodecahedra will result. The factors that influence the crystal habit have been examined and are discussed in the third portion of this paper.

**Crystal Surfaces**

A study of the surface topography of diamond shows a variety of surface markings. In the growth of diamond in the laboratory, an attempt was made to correlate these surface markings with the variables of the growth process. In doing so, it was anticipated that some information might be uncovered that would be helpful in elucidating the detailed growth mechanism.
Our experiments indicate that diamond prefers to grow by the piling up of sheets of material parallel to the (111) face. The cleavage and "grain" of diamond is parallel to these faces. Steps indicating the edges of sheets and the so-called "growth trigons," formed by intersection of these edges, can be found on laboratory made diamond. Fig. 1 shows synthetic diamond with these surface markings, which are identical in all characteristics to natural diamond. Note the large step parallel to the crystal edge composed of several growth layers. This step probably was caused by a deficiency of catalyst over the lower portion of the crystal face. There may be a wide range of trigon sizes. The trigon corners point toward the edges of the octahedral faces. The shallow depression represented by a trigon usually represents a difference in surface elevation of several hundred angstrom units. However, since trigons may exist too shallow to be resolved, the growth layers may be much thinner. Laboratory evidence indicates that these surface markings are found when the diamond was actually growing at the time it was removed from the selected conditions of temperature and pressure. The new growth appears to be added in plane waves advancing toward the octahedral edges, when trigons are observed.

These trigons or surface steps are not always found on synthetic diamond after its formation. When conditions are such that the growth is followed by holding the diamond at a temperature above the growth
temperature and a little outside the diamond stable region, etch pits are found on the (111) face (Fig. 2). The sides of the triangular pits are parallel to the octahedron edge. Etch pits have also been produced by slowly dissolving the surface of natural and synthetic diamond in fused potassium nitrate at 500 to 600° C. These etch pits probably mark imperfections of the atomic arrangement in the crystal lattice. The marking of imperfections or dislocations by etching is an established art in studying crystals in other materials. The etch pits are rather uniform in size as shown and the depth and diameter depends on the degree of etch. Fully developed pits have about an eight to one width to depth ratio.

![Etch pits on octahedral face as removed from high pressure cell. 300X.](image)

It is considered that these etch pits are produced by a dissolution process. If at constant pressure the temperature is increased after the diamonds are formed until conditions exist where diamond is no longer stable the diamond is converted to graphite. This process has been demonstrated many times in diamond synthesis studies. If the increase in temperature is only enough to cause slight instability, dissolution is slow and etch pits are produced. Greatly increased temperatures under these conditions produce a more catastrophic attack of the diamond. Very rough surfaces may be produced on diamond in this manner. It has been observed that cube faces appear to etch more rapidly than the octahedral faces under these conditions.

Synthetic diamond may be etched at one atmosphere in the same manner as natural diamond. The octahedral and cube faces lightly
etched at 600° C. in fused potassium nitrate are shown in Fig. 3 and 4. Fersmann and Goldschmidt probably were the first to study etch pits and propose the dissolution process.

Still another surface characteristic is found on the faces of cube diamond grown under conditions of minimum temperature and pressure for each catalyst. Under these conditions diamond appears to grow by the addition of layers to the cube face only. A cross section of the diamond clearly shows the layered structure. The stepped surfaces on these faces resulting from the edges of the layers is shown in Fig. 5. The use of the
interference microscope shows the step height to average about 300 Å with the center of the face higher than the edges giving a slope of about 1 to 300. In contrast, natural cube faces always have a rough pitted surface, the surfaces of which are (111) planes. The layered structure on the cube face is apparently a double growth spiral on a dislocation. One can follow the edges to form closed loops. Although single growth spirals have been observed, the double growth spiral is much more common.

The diamond which grows almost exclusively on the cube face is almost always black, possibly due to graphite between the layers. X-ray analysis of these crystals shows a distorted crystal structure due to the
inclusion of much foreign material. This results in a weak structure easily cleaved and crushed. This form of diamond has not been observed in nature.

Another type of surface marking is commonly found on synthetic diamond. This surface detail resembles a network of veins or streams (Fig. 6). In many cases, the detail looks more like dendrites. This pattern can be found on both octahedral faces and the cube faces (Fig. 7) of the diamond. This surface condition is considered to be a reflection (or) imprint of the dendritic structure of the metal catalyst. If the catalyst film is stripped off the crystal face after the diamond is removed from the growing media, and the metal film examined metallographically, the same dendritic structure is seen in the catalyst film. During the last stages of the growth of the diamond with this surface pattern, the catalyst is in a semi-solid state with dendrites freezing in the metal and being mirrored on the diamond surface. Carbon may still be migrating in the unfrozen portion of the catalyst building up or dissolving the diamond surface. The last stages of growth then occurred at a temperature near the carbon-metal eutectic. Trigons are found only when higher temperatures occur relative to the carbon-metal eutectic.

If diamonds, such as shown in Fig. 7, are etched in potassium nitrate at 550 to 600° C., the dendritic pattern slowly disappears and the veined structure of Fig. 6 remains. Further etching brings out etch pits, triangular on the octahedral and rectangular on the cube faces.

Another type of cube diamond can be grown that is different from the black cube described previously. The diamond may start as an octahedron and grows to a symmetrical cubo-octahedral shape and finally to
a cube with very small (111) faces at the corners. Cubes grown in this manner are not necessarily black in color nor do they incorporate as much impurity in the crystal. The (111) faces grow faster, leaving the cube faces predominating. Under marginal growth conditions, it appears that the growth may be almost completely stopped on the cube faces. Higher temperatures appear to favor growth on the octahedral faces exclusively and the cubo or cubo-octahedral habit of crystal is not produced. The cube and octahedral faces produced may be very flat or slightly concave. Again, this crystal form is not observed in natural diamond.

The fact that the two different growth habits are dependent on the temperature at which the growth occurs can be demonstrated readily by growing under both conditions consecutively. The temperature is first maintained so as to grow a cubo-octahedron and then lowered about 40° C. to the cube face growing condition. The finished diamond in section shows the center clear cubo-octahedron surrounded by the black opaque layered cube growth in the same orientation as the center crystal.

Rhombic dodecahedra are rarely found in laboratory grown diamonds. When they are found, however, the entire yield will consist of dodecahedra. Since they are so rare and since the conditions where they are grown are those where dissolution is suspected, the rhombic dodecahedron is not considered to be a true growth form in the case of synthetic diamond. All the dodecahedra examined show rough faces with deep striations as shown in Fig. 8. Frequently, octahedra are produced with dodecahedral faces starting to form. Again, this takes place where etching or dissolution of the crystal is occurring and etch pits are found.
on the octahedral faces. Evidently preferred dissolving on the 110 face must occur under certain conditions of physical and chemical environment. These conditions must be common in nature since the rhombic dodecahedron is often found in natural diamond or else the natural dodecahedron represents a type of growth we have not been able to reproduce.

If one looks at the crystal model of diamond and studies the octahedral, cube and dodecahedral surfaces, the surface roughness varies when observed on an atomic scale. This roughness is an indication of the relative ease with which atoms may be removed from the surface by a solution process. The octahedral face presents the smoothest surface and the cube and dodecahedral faces, the most open or roughest surfaces. Near conditions of diamond growth, the octahedral face is less likely to dissolve than the cube or dodecahedral faces. It appears that slightly different equilibrium conditions exist for the three different crystal faces and these differences in surface energy of the crystallographic planes partially account for the crystal forms of synthetic diamond described above. For example, a crystal can start as a cube or dodecahedron and grow with the crystal filling out to the octahedral form.

**Crystal Habit Variations with Growth Rate**

The growth rate of synthetic diamond is very high but has been varied over a range of nearly two orders of magnitude with at least one-third millimeter per minute as the maximum. The rate is influenced primarily by the pressure, temperature and temperature gradient so that the farther into the diamond stable region, as we have determined it, and the steeper the gradient, the higher the growth rate.

At high growth rates, it is difficult to prevent nucleation so that diamonds start growing simultaneously at many closely spaced intervals on the catalyst-graphite interface. This leads to intergrowth and clustering of the crystals. The crystals grow into each other at random angles and new crystals may nucleate and grow right on established growing faces at high growth rates. The edges of the octahedra may tend to grow faster with growth advancing toward the centers of the faces. This leads to a hoppered surface and a skeletal structure. That is, the growth is initiated at the edges of the faces and the initiation of growth layers is faster than the rate at which the growth proceeds across the crystal face. A typical intergrown diamond cluster showing hoppering and skeletal growth is shown in Fig. 9.

A mosaic of many small oriented crystallites of diamond can be grown. This structure may take many forms; an example of one form is shown in Fig. 10 which has been etched to bring out the oriented crystallites making up the large octahedral face. A structure, similar to natural carbo-
nado diamond, can be grown with the crystallites joined to form a dia-
mond to diamond bond by intergrowth. The structure may be porous
with foreign material filling the voids. The carbonado is a polycrystalline
diamond formed by small crystallites grown together. The carbonado is
grown at the lowest temperatures of formation with spontaneous nu-
cleation at closely spaced intervals giving a relatively small grain size.

The “ballas,” a rare form of natural diamond with radial symmetry
composed of apparently spherically grown layers, has not been synthe-
sized to our knowledge.

In general, as the growth rate is slowed down, the crystals become
better in quality. The crystals generally incorporate less impurity and
the skeletal or hoppered structure may not be formed. This is only a gen-
eral observation as the action of the catalysts vary; that is, some cata-

![Fig. 9. Hoppered and skeletal growth. 50X.](image)

![Fig. 10. Mosaic diamond. 300X.](image)
lysts appear to promote skeletal and hoppered crystals even at lower growth rates.

**Color**

Variations in temperature and pressure result in variations in color of the diamond produced. As the temperature is raised, the low temperature black is usually replaced by shades of yellow and green until colorless diamond is formed at the higher temperatures. If the color is caused by strains in the crystal lattice due to the insertion of interstitial foreign atoms, this change of color may be simply due to the inclusion of fewer foreign atoms as the temperature of the reaction is raised. However, even colorless diamonds may show x-ray patterns from the catalyst metal in the crystal. The color may be affected by the nature of the impurity in some cases and only by the amount of a given impurity in others. Selected conditions permit a wide variety of shades such as black, degrees of gray, amber, yellow, green, blue and colorless. The intensity of the color and the size of the crystal may make the diamond opaque or transparent.

**Twinning**

Twinning is very common in diamond. The macle or spinel twin is the most common form in natural diamond. We observe true twinning and random intergrowth in synthetic diamond. However, the macle twin can be grown in a range of thickness to length ratios. Interpenetrating cubes at random angles are also commonly observed. Diamond is predisposed toward twinning due to the relatively slight energy difference between the normal and twinned configuration.

**Inclusions**

It has not been possible so far to grow diamond without trace inclusions. This is true especially of the more rapidly grown diamond. In the more slowly grown crystals, the inclusions are frequently found to be oriented along the crystal axes and can be easily seen under the microscope.

Foreign inclusions in diamond including diamond in diamond (growth on a seed) are a source of strain. The strain patterns originating at the inclusion can be seen in the polariscope and such diamonds are easily fractured.

Foreign materials may be introduced into the growing process intentionally or otherwise and analysis of the diamond may show the presence of many of the light elements such as are found in natural diamond. Since the inclusions may be magnetic, the resulting diamond may exhibit weak magnetic properties. Garnet, which is found associated with and sometimes as an inclusion in natural diamond, is stable under some of the
conditions of our synthesis and garnet has been present as an intrusion in synthetic diamond. It does not act as a seeding agent, however.

Another mineral inclusion supposedly found in natural diamond is quartz. In attempts to introduce quartz into diamond, the quartz always changes to coesite. The quartz in all natural diamond so far examined is not totally enclosed by diamond but is found in cracks, fissures, or pockets. Under the quartz, one can often see (111) steps and trigons on the diamond surfaces. There is no evidence so far that natural diamond was grown at pressures and temperatures where quartz is stable.

Seed diamond can be used as a growth site for new diamond, which follows the same crystal orientation as the seed. However, the seed can always be seen if the new growth is transparent. Apparently, an interface of trapped impurity always makes the seed visible. This is also observed in natural diamond. There is little if any advantage in growing on seeds as opposed to not seeding as the conditions for good seed growth are the same as for new growth without seeds.

Conclusions

In synthetic diamond, we found a number of the forms and habit characteristics of natural diamond. Most of the growth variations in structure and habit have been duplicated with apparently some additional forms. The growing faces of a diamond crystal are usually, but not always, on the (111) crystallographic planes. Growth on the cube faces by a spiral growth mechanism sometimes occurs near minimal temperature conditions. Dendritic surface markings on synthetic diamond represent the imprint of the catalyst metal structure upon freezing.

The crystal habit is influenced by the physical conditions of formation and the growth rate. Dissolution apparently can take place to produce dodecahedral planes. Therefore, this growth habit is considered to be not a true growth form in synthetic diamond. Polycrystalline diamond is obtained when nucleation occurs at closely spaced intervals with relatively high growth rates.

The color of diamond is affected by impurity type and concentration and can be changed by varying the temperature at which the growth takes place.

References


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