JOURNAL OF MATERIALS SCIENCE 8 (1973) 88–92

Internal structure of insulating and semiconducting synthetic diamonds

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From optical studies on polished cross sections of synthetic diamond crystals the diamond growth on three different crystallographic planes can be distinguished within the crystals. Diamond growth on the cubic, octahedral, and dodecahedral faces each have a characteristic abrasion resistance, colour, and inclusion content. The differences in abrasion resistance do not appear to be dependent on the content of dispersed nitrogen. The characteristic growth on each crystal face allows the relative growth history of the three faces to be reconstructed.

1. Introduction

It is well known that in grinding and polishing diamonds there are easy and hard directions within the crystals. This effect is generally explained by describing the abrasion process in terms of minute fragments cleaved from the surface [1]. It has been speculated that other variables, such as impurity content or dislocation densities, can cause major changes in the abrasion resistance of diamonds, but direct proof has been hindered by the difficulty in separating out the directional effects [2].

Recently it has been found that in cutting and polishing synthetic diamond crystals the abrasive resistance varied from one point to another within individual crystals, even though the abrasion direction was held constant with respect to the lattice. The synthetic crystals, therefore, allow the abrasion to be studied without regard to the directional effect, and they offer the possibility of identifying the chemical and structural features affecting the abrasion resistance of synthetic diamonds. This paper presents the results of optical studies on polished cross sections of the synthetic diamonds.

It is found that the diamond grown on the cubic {100}, octahedral {111}, or dodecahedral {110} faces each have a characteristic abrasion resistance, colour, and inclusion content. The differences in abrasion resistance are isotropic with respect to the crystal lattice and are not the result of crystallographic misalignment. In addition, the difference in abrasion resistance does not appear to be dependent on the content of the dispersed nitrogen. Finally, it is shown that through the polished cross sections of the crystals, the growth history of each crystal can be reconstructed.

2. Experimental

2.1. Regional abrasion resistance

The diamond crystals ground and polished were 35-40 mesh yellow cuboctahedral, yellow cubes, and black-hoppered cubes obtained from the Specialty Materials Department of the General Electric Company. In addition, some 40-60 mesh semiconducting diamonds were ground and polished. These latter crystals were obtained from General Electric's Magnetic Materials Business Section.

The diamonds were mounted in a ceramic-filled epoxy and surrounded by a hardened steel ring (0.25 in. o.d.). A high-speed (3600 rpm) cast iron wheel, with loose diamond abrasive mixed with olive oil both ground and polished the diamonds. For the crystals to be ground and polished on two sides, it was necessary to dissolve the epoxy and remount the crystals.

The external morphology and identification of the sets of crystallographic faces of a typical synthetic diamond crystal is given in Fig. 1, which has been designated a "3" shape by Litvin and Butuzov [3], typical of diamond growth at high supersaturations. On such cuboctahedral crystals, four sets of crystal faces can generally be identified; cubic {100}, octahedral {111},

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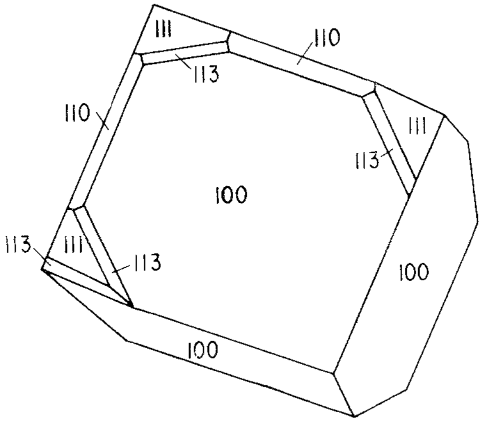

Figure 1 Prominent faces observed on a typical well-formed synthetic diamond crystal.

dodecahedral {1 1 0}, and the trisoctahedral {1 1 3}. A freezing metal dendrite pattern on each set of faces established them as growth faces [4].

Fig. 2 shows the polished cubic plane of a type "3" shape as viewed through a Nomarski objective. There is a characteristic pattern seen to greater or lesser extent in all such polished crystals, which is portrayed schematically in Fig. 3.

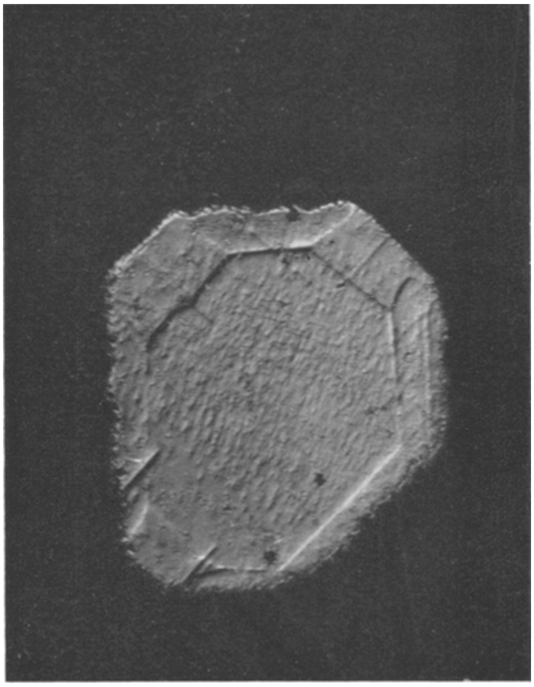

Figure 2 Polished cube plane of a cuboctahedral synthetic diamond crystal as viewed through a Nomarski interference contrast objective (magnification × 110).

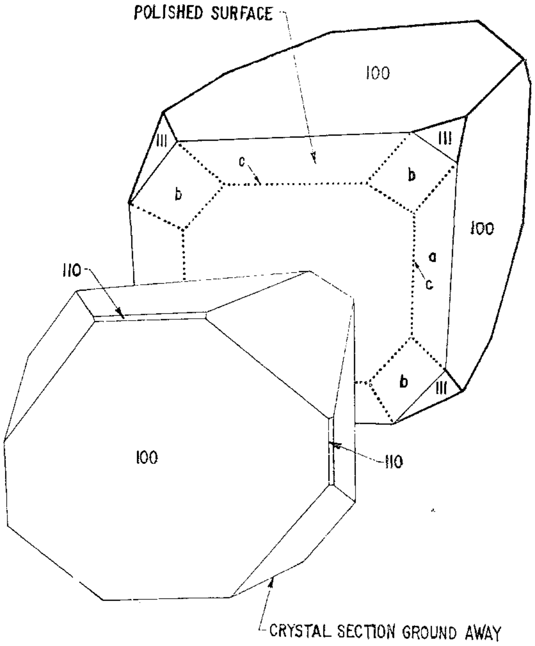

Figure 3 Schematic representation of the positioning of the polished cube plane in a cuboctahedral synthetic diamond crystal.

The regions "a" extending to cubic faces were measured interferometrically to be approximately 500Å below the regions "b" extending to octahedral faces. There are small elevated regions "c" connecting the "b" regions which may be interpreted as extending to dodecahedral faces. The polished surface patterns indicate that the material in the "b" and "c" regions, when ground approximately on a cube plane, are more abrasive resistant than the material in the "a" regions when ground on the cube plane.

Fig. 4 shows the polished octahedral plane of a cuboctahedral crystal. The characteristic pattern seen on this surface is shown in Fig. 5. Again, the polished surface can be divided into either "b" regions extending to and apparently formed from the growth on the octahedral faces, and "a" regions that extends to and apparently grown on the cubic faces. The position of the narrow region "c" connecting the various "b" regions has apparently been formed by the growth on the dodecahedral faces.

Finally, Fig. 6 shows a polished cube plane of a semiconducting diamond, the "a", "b" and "c" regions are found in exactly the same position and with similar differences in abrasion resistances as found in typical insulating cuboctahedral crystals.

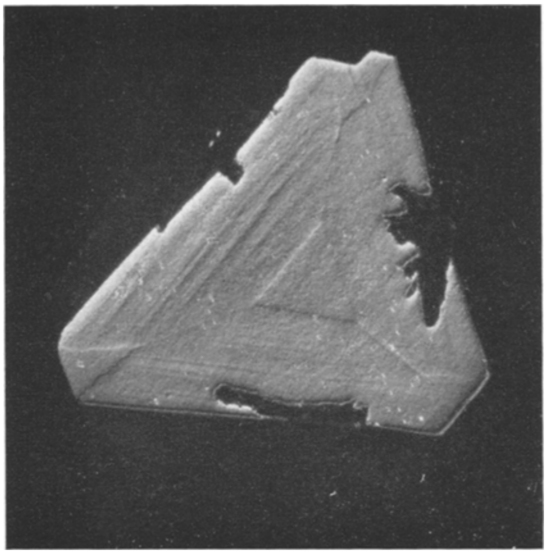

Figure 4 Polished octahedral plane of a cuboctahedral synthetic diamond crystal as viewed through a Nomarski interference contrast objective (magnification × 110).

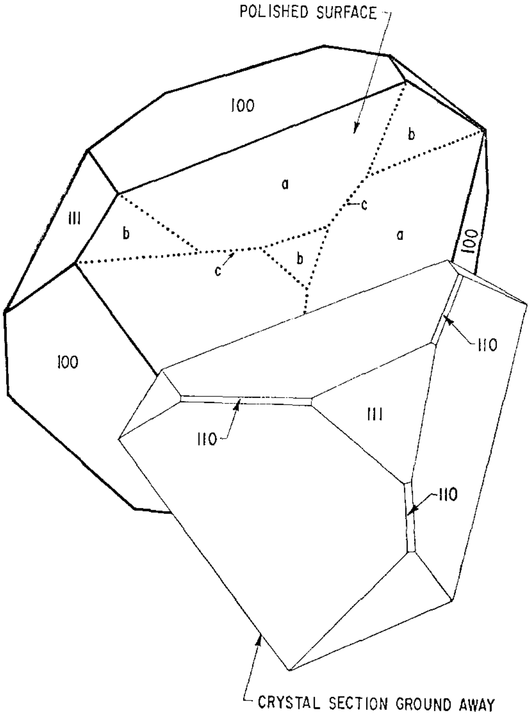

Figure 5 Schematic representation of the positioning of the polished octahedral plane in a cuboctahedral synthetic diamond crystal.

In all the polishing of the synthetic crystals the plane of polishing only approximated either the cubic or octahedral planes and often missed it by 10°. However, the "b" and "c" regions always appear more abrasion resistant than the "a" regions. It should also be noted that back-reflection Laue patterns show no evidence for high-angle twinning or misalignment in these crystals. These two facts combine to eliminate any possibility that the abrasion differences in the crystals are due to crystallographic misalignment between the regions. It must be concluded that the differences in abrasion resistance are isotropic within the crystal. Therefore, the regions grown on the cubic faces have lower abrasion resistance than the material grown on the octahedral faces.

2.2. Regional impurity content

The variation in the diamond abrasion resistance indicates there is a difference in the energy required to nucleate or propagate fractures. This energy, in turn, is controlled by the level or levels of defects within the lattice, which must differ in some manner from one region to another. The cut and polished sections of the synthetic diamond crystals allowed the various regions to be viewed separately and to make some preliminary conclusions about the differences in the concentrations of impurities.

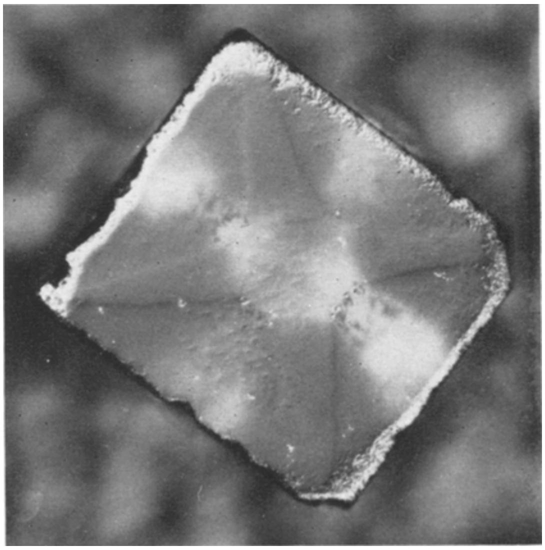

Figure 6 Polished cube plane of a synthetic semiconducting diamond crystal as viewed through a Nomarski interference contrast objective (magnification × 110).

In particular, the concentration of paramagnetic nitrogen (the dominant form of nitrogen in synthetic diamonds) can be measured by the intensity of the yellow colour [5]. Visual examination of the cubic, octahedral and dodecahedral regions leads to the conclusion that the paramagnetic nitrogen content was the same in the cubic and octahedral regions but lower in the dodecahedral regions. This is in contrast with the abrasion resistance, which shows a difference between the cubic and octahedral regions but not between the octahedral and dodecahedral regions. The differences in abrasion resistance between regions, therefore, do not seem dependent on the concentration of paramagnetic nitrogen. (This does not exclude a possible correlation between paramagnetic nitrogen and hardness within a region; for example, see the following section on Inclusions.)

However, the other important impurity found in synthetic diamonds, the boron or boron-aluminium acceptor state [6, 7], does show some correlation with the regional differences in diamond abrasion resistance. In a series of semiconducting synthetic diamonds, the same type of regionalization of the abrasion resistance as in the insulating yellow cuboctahedral was found (see Fig. 6), and the electrically active states occur almost exclusively in the more abrasion resistant "b" regions. (The dodecahedral and trisoctahedral regions could not be identified as separate regions within these crystals.) Whether the concentration of boron or boron-aluminium in an electrically inactive state correlates with the abrasion resistance differences in the insulating yellow cuboctahedral has not yet been answered.

2.3. Inclusions

Other features shown in the polished cross section of the cuboctahedral crystals are the sections of metallic inclusions which appear as discontinuities and re-entrants in the growth surface, particularly on the cubic or octahedral surfaces (Fig. 5). These inclusions generally lie in a plane parallel to the cubic or octahedral face, are magnetic, and appear to be an encapsulation of the metal solvent, from which the crystal has grown. Also seen in the polished cross sections of the crystals are the fluctuations in the abrasion resistance that form bands parallel to the growth face within the material grown on the cubic face. The bands appear along the ⟨100⟩ directions only and tend to disappear in the vicinity of the larger metallic inclusions. This banding of the abrasion resistance is generally accompanied by a banding in the yellow colour (paramagnetic nitrogen). Furthermore, the colour on paramagnetic nitrogen tends to decrease in the vicinity of the larger metal inclusions.

Careful examination of the banding in the colour and the abrasion resistance shows that where the intensity of the colour increased, the abrasion resistance decreased. Therefore, in at least the cubic material, the presence of paramagnetic nitrogen either lowers the abrasion resistance or is associated with an impurity or defect that does. The fact that the paramagnetic nitrogen does not correlate with the differences in abrasion resistance between the crystallographic regions means that the nitrogen is probably only a secondary factor in determining the abrasion resistance within the diamond.

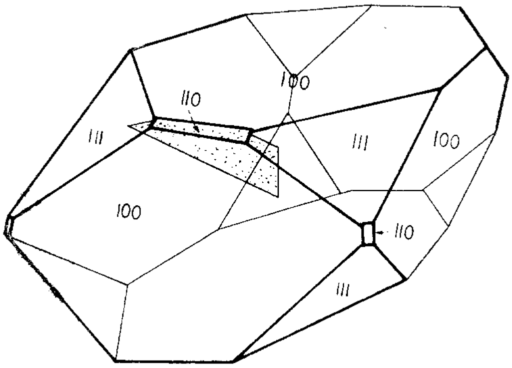

Figure 7 Schematic representation of the positioning of a region of fine inclusions extending to one dodecahedral face in a cuboctahedral synthetic diamond crystal.

It has been mentioned that in a few of the polished crystals, material extending to and apparently grown on the dodecahedral face can be viewed separately, and it was found to be colourless. However, the colour of most of the material grown on the dodecahedral faces was difficult to observe due to the high concentration of very fine (1 μm) opaque inclusions that do not appear to be ferromagnetic. Within the crystals, these fine inclusions lie in a thin region 3 to 4 μm thick extending to the dodecahedral faces. Fig. 7 gives, schematically the positioning of one of these regions within the crystals.

It is the inclusion of these fine opaque inclusions that give the black-hoppered cubes and cuboctahedral their dominant colour. A series of such black-hoppered cubes (Fig. 8) were cut and polished and it was found that the most growth is along the ⟨110⟩, with the branches in the

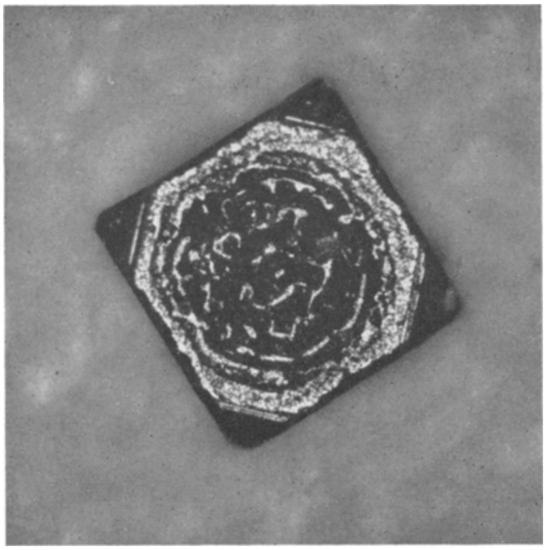

Figure 8 A black-hoppered cuboctahedral synthetic crystal with the dominant growth along the ⟨110⟩ and ⟨113⟩ (magnification × 110).

⟨100⟩ planes. In the black cuboctahedral crystals, ⟨113⟩ dendrites are also seen.

3. Discussion

The fact that the diamond growth on each major face can be characterized by inclusion content, colour, and abrasion resistance allows the relative growth history of the major faces to be reconstructed. Starting with the diamond growth typical of the coldest conditions [3], the black-hoppered cubes are found to be almost exclusively ⟨100⟩ and ⟨113⟩ dendrites. Their characteristic colour comes from the high concentration of fine opaque particles incorporated in the dodecahedral growth.

At higher temperatures (lower supersaturation) regular polyhedral (cuboctahedral) are formed, but the dodecahedral and trisoctahedral faces are still apparent. The positioning of the large metal inclusions in the centre of the cubic or octahedral faces, however, suggest that growths on these faces are nucleated at their edges, where the dodecahedral and trisoctahedral faces are located.

A reconstruction of the growth process of the regular polyhedral might be made as follows. The growth on the dodecahedral and trisoctahedral faces nucleate the growth across the cube and octahedral faces, which sweeps toward the faces' centres, expelling impurities in front of the growth edge. The impurities tend to accumulate in the solvent film at the centre of each face. This would hinder further diffusion of carbon and nitrogen to the growing surfaces. First, the amount of nitrogen being incorporated in the diamond drops off (the diamond growth is lighter), and then the carbon stops depositing. Further growth from the edge builds up and would eventually fill over the halted crystal surface and its film of metal.

Grinding and polishing synthetic diamond crystals have shown that other factors besides lattice orientation play an important role in determining the abrasion resistance in synthetic crystals. A more detailed chemical analysis should be undertaken in order to determine what is the underlaying mechanism for these abrasion differences within the crystals. At this point in the research, all that can be said is that the most obvious impurity, dispersed nitrogen, probably plays only a secondary role in determining the abrasion resistance of synthetic diamond.

Natural diamonds are generally more homogeneous in their abrasion resistance than the synthetic crystals shown in this report. This might be explained by the fact that natural crystals generally grow on only one set of crystal faces, the octahedral. It is rare to find natural cubes or cuboctahedral and, even then, it is difficult to tell whether they are growth or etch faces. The synthetic diamond crystals, which show at least four different sets of growth faces, offer the unique opportunity to measure directly the relative abrasion resistance of the crystal growth on the various faces and, in turn, the crystal quality.

References

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Received 17 April and accepted 19 May 1972.