DIFFERENCE IN NITROGEN CONCENTRATION & AGGREGATION AMONG (111) & (100) GROWTH SECTORS OF LARGE SYNTHETIC DIAMONDS

Shuichi SATOH, Hitoshi SUMIYA, Kazuwo TSUJI, and Shuji YAZU

Itami Research Laboratories, Sumitomo Electric Industries Ltd., 1-1-1 Koya Kita, Itami, Hyogo 664, Japan

Synthetic type Ib diamonds grown by the temperature gradient method contain isolated nitrogen atoms that influence the diamonds’ physical properties. The difference in nitrogen concentration among the (111) and (100) growth sectors is dependent upon the growth temperature. At low growth temperatures, the nitrogen concentration of the (100) growth sectors is stronger than that of the (111) growth sectors. As the growth temperature increases, the nitrogen concentration of the (100) growth sectors becomes weaker than that of the (111) growth sectors. A sharp peak due to nickel atom defects appears at 1332 cm\(^{-1}\) in the absorption spectrum of the (111) growth sectors. Through heat treatment under high pressure, 1b type diamonds are transformed into type IaA diamonds in which nitrogen atoms aggregate in pairs. Nitrogen atoms aggregate more easily in (111) growth sectors than in (100) growth sectors. Two suggestion are considered. One suggests that nitrogen atoms migrate easily and gather near one another on the (111) surface due to their higher diffusion coefficient on this surface as compared to that of the (100) growth surface. Another suggests that lattice defects due to nickel atoms in the (111) growth sectors accelerate nitrogen migration in the crystal.

1. Introduction

Large type 1b synthetic diamond crystals from 0.5 to 5 carats are produced by the temperature gradient method (Photo 1). Diamonds smaller than 2 carats are fabricated for commercial use as cutting tools, drawing dies and heat sinks. Synthetic type 1b diamonds contain isolated nitrogen atoms that influence the diamonds’ hardness\(^1\) and thermal conductivity\(^3\). The ultra precision market has recently grown, and high-quality diamonds with few defects and no inclusions are demanded for fabrication of turning tools. Therefore, it is important to measure the nitrogen distribution and defect patterns in synthetic diamonds. It is also interesting to consider how nitrogen atoms are contained and aggregated in a crystal. In order to investigate this, nitrogen distributions are measured under different growth conditions, and nitrogen atoms are aggregated by heat treatment under high pressure.

2. Experiment

Specimens were grown in a high-pressure and high-temperature vessel by the temperature gradient method using Fe–50 weight% Ni solvent under conditions of 5.5 GPa and 1350°C, 1370°C and 1400°C. In order to investigate the distribution of the nitrogen density, specimens were cut and polished into sheets about 1 mm thick, and absorption coefficients were measured at 1130 cm\(^{-1}\) by an FT-IR spectroscopy. Nitrogen concentrations were estimated by the following equation\(^3\):

\[
\text{(nitrogen concentration)} = 25 \times (\text{absorption coefficient}) \text{ ppm.}
\]

Photo 1. Synthetic 5 carats diamonds grown by the Temperature Gradient Method.

Using a Cassegrain-type focusing mirror, it was possible to measure the IR absorption spectrum of a 50° μm area in a specimen. In order to consider how nitrogen atoms are contained and aggregated in a crystal, specimens underwent nitrogen aggregation by heat treatment under high pressure (5.5 GPa, 1750°C & 2300°C). After that treatment the UV & visible absorption spectra of the specimen were measured at room temperature. Line defects in the specimens were investigated by the X-ray topographic method using an Mo target under conditions of 50 kV and 40 mA.

3. Results and discussion

Morphologies and growth sectors of synthetic diamonds grown by the temperature gradient method depend on the growth temperature. Schematic drawings of morphologies and growth sectors are shown in Fig. 1 for various growth temperatures. In the case of diamond grown at 1350°C, the morphology is almost a hexahedron and the (100) growth sectors occupy almost the whole structure of the crystal (Photo 2).

Proportionally as the growth temperature increases, the morphology changes to a hexa-octahedron and finally becomes nearly octahedral in shape. In the same way, the (111) growth sectors increase with the number of (100) growth sectors.

Finally, the (111) growth sectors occupy the whole crystal.

It is found that the nitrogen concentration of the (111) growth sectors differs from those of the (100) growth sectors. The difference in nitrogen concentration of those growth sectors also depends on the growth temperature. The results of the FT-IR absorption measurement is shown in Table 1. At the lowest growth temperature, the nitrogen concentration of the (100) growth sectors is stronger than that of the (111) growth sectors. As the growth temperature increases, the nitrogen concentration of the (111) growth sector becomes stronger than that of (111) growth sectors. The nitrogen concentration of the (111) growth sectors grown at

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Temperature</th>
<th>Morphology</th>
<th>Schematic drawing of morphology &amp; growth sectors</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5 GPa</td>
<td>1350 °C</td>
<td>Hexahedron</td>
<td>Seed</td>
</tr>
<tr>
<td></td>
<td>1370 °C</td>
<td>Hexa-octahedron</td>
<td>Seed</td>
</tr>
<tr>
<td></td>
<td>1400 °C</td>
<td>Octahedron</td>
<td>Seed</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic drawings of morphologies and sectors on (110) cross sections. A shaded portion indicates a (100) growth sector and a white portion indicates a (111) growth sector.
Table 1. Estimated nitrogen concentrations & absorption coefficient at 1130 cm\(^{-1}\) of the (111) & (100) growth sectors in different growth conditions.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Absorption Coefficient at 1130cm(^{-1})</th>
<th>Estimated Nitrogen Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(111) growth sector</td>
<td>(100) growth sector</td>
</tr>
<tr>
<td>1350°C</td>
<td>5.3 cm(^{-1})</td>
<td>6.9 cm(^{-1})</td>
</tr>
<tr>
<td>1370°C</td>
<td>3.68 cm(^{-1})</td>
<td>3.88 cm(^{-1})</td>
</tr>
<tr>
<td>1400°C</td>
<td>4.22 cm(^{-1}) (upper part)</td>
<td>0.88 cm(^{-1}) (upper part)</td>
</tr>
</tbody>
</table>

1350°C is weaker than that of the (100) growth sectors (Photo 2). The darker part has a higher density of nitrogen in Photo 2. However, the nitrogen concentration of the (111) growth sectors grown at 1370°C is the same as that of the (100) growth sectors. Finally, the nitrogen concentration of the upper part in the (111) growth sectors grown at 1400°C is stronger than that of the (100) growth sectors.

On the other hand, the nitrogen concentration of the lower part in the (100) growth sectors is almost equal to that of the (111) growth sectors. It is considered that nitrogen concentration relates to the growth rate of each growth sector. For example, the (111) growth sectors grow faster at 1350°C than the (100) growth sectors (Fig. 1 and Photo 2). Therefore, nitrogen atoms would be contained more easily in (100) growth sectors than (111) growth sectors.

Significant features of the IR absorption spectrum of synthetic 1b type diamond are a sharp peak at 1344 cm\(^{-1}\) and a broad peak at 1130 cm\(^{-1}\) (Fig. 2); all absorption spectra of the specimens have these two significant peaks. A sharp new peak appears at 1332 cm\(^{-1}\) in the absorption spectrum of a (111) growth sector grown at 1350°C in addition to the two peaks (Fig. 2), but this sharp line cannot be observed in the absorption spectrum of a (100) growth sector grown at 1350°C (Fig. 2). This peak appears only in the absorption spectrum of a (111) sector and depends on the growth temperature, as it fades proportionally as the growth temperature increases. This peak corresponds to the Raman frequency, and it is suggested that it is associated with the incorporation of nickel in diamond. The same sharp peak also appears by electron irradiation. The infrared absorption spectrum of type 1b diamond subjected to various doses of 2 MeV is shown in Fig. 3. The previous sharp peak due to the nickel atom defects corresponds to the peak irradiated by a dose of 10\(^{18}\) electrons/cm\(^2\). It is considered that many
nitrogen atoms remain at 1334 cm\(^{-1}\) & 1130 cm\(^{-1}\) in the (100) growth sector. This result demonstrates that nitrogen atoms aggregate more easily in (111) growth sectors than in (100) growth sectors; we consider the following reasons why (Fig. 5):

(Supposition 1) Since a (111) surface is the most condensed surface, the diffusion coefficient of carbon atoms on the (111) surface is high. A nitrogen atom on a (111) surface is exchanged for a carbon atom or moves with one. So nitrogen atoms also move easily and gather with one another.

(Supposition 2) Nitrogen atoms migrate easily in a (111) growth sector by the high density of lattice defects due to nickel atoms. It is well known that lattice defects accelerate nitrogen aggregation.\(^{5,6}\)

The specimens undergo nitrogen aggregation at higher growth temperatures (5.5 GPa, 2300°C) without electron irradiation. An N3 color center appears strongly in the (100) growth sector (Fig. 6); that color center consists of one center carbon atom and three surrounding nitrogen atoms.

Line defects spread out in the ⟨001⟩ and ⟨112⟩ directions from the surface of the seed crystal; regardless of the crystal's morphology (Ex hexahedron, hexa-octahedron and octahedron), they spread out in the same directions. An X-ray topograph of the specimen grown at 1350°C is shown in Photo 3. The black lines indicate line defects that are bundled and spread out in the same directions. This synthetic diamond is very bulky and has no line defects or inclusions (Photo 3).

![Figure 3. Infrared absorption spectrum of type Ib diamond irradiated by various doses of 2MeV.](image)

Defects are contained in a (111) growth sector.

In order to investigate the way in which nickel atoms are contained in diamond, the specimens underwent nitrogen aggregation by heat treatment under high pressure (5.5 GPa, 1750°C) after electron irradiation of a 2 MeV dose of \(10^{18}\) electrons/cm\(^2\) to accelerate nitrogen aggregation. Ib type nitrogen atoms isolated in the crystal are transformed into IaA type nitrogen atoms that aggregate in pairs. The IR absorption spectra of the (111) and (100) growth sectors after heat treatment are shown in Fig. 4. A broad peak due to IaA type nitrogen atoms appears at 1280 cm\(^{-1}\) in each growth sector, and significant peaks of Ib type nitrogen atoms remain at 1334 cm\(^{-1}\) & 1130 cm\(^{-1}\) in the (100) growth sector. This result demonstrates that nitrogen atoms aggregate more easily in (111) growth sectors than in (100) growth sectors; we consider the following reasons why (Fig. 5):

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![Figure 4. IR absorption spectra of the (111) & the (100) growth sector in the same specimen after nitrogen aggregation treatment.](image)

![Figure 5. Models of nitrogen aggregation.](image)
Since it is easy to discover suitable parts of crystals, synthetic diamonds are available for fabrication into turning tools.

4. Conclusion

1) The difference in nitrogen concentration among (111) & (100) growth sectors is dependent on growth temperature as in the following relations. N.C. indicates nitrogen concentration.
   a) [N.C. of (100) growth sectors]>[N.C. of (111) growth sectors] (at 1350°C).
   b) [N.C. of (100) growth sectors]=[N.C. of (111) growth sectors] (at 1370°C).
   c) [N.C. of (100) growth sectors]<[N.C. of (111) growth sectors] (upper part at 1400°C).
   d) [N.C. of (100) growth sectors]=[N.C. of (111) growth sectors] (lower part at 1400°C).
2) A sharp peak due to nickel atom lattice defects appears in the (111) growth sectors.
3) Nitrogen atoms aggregate in paris more easily in (111) growth sectors than in (100) growth sectors.

REFERENCES