Nonuniform Distributions of Color and Luminescence of Diamond Single Crystals

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The distributions of the color and luminescence of diamond are reviewed in relation to its growth mechanism. A wide variety of color and luminescence have been reported, which are caused by point defects such as impurities. The color and luminescence are not uniform inside a crystal; they vary depending on growth sectors and along growth directions. The slope of the growth surface and the propagation rate of growth steps affect the color and luminescence. Luminescence patterns related to strain are also observed.

1. Introduction

Diamond is intrinsically colorless, but a wide variety of color and luminescence such as yellow, green, and blue are commonly observed from natural and synthetic diamonds because of the presence of impurities and defects in the diamonds. The color and luminescence depend on the types of defects and impurities and their concentrations. When a diamond crystal is observed in detail, it is found that the color and luminescence are not uniformly distributed inside the crystal. In this article, the nonuniform distributions of color and luminescence are presented.

The impurities are incorporated during growth. Ion implantation is another technique for introducing impurities, but these impurities are out of the scope of this article. Optically active impurities that are incorporated during growth are limited. Nitrogen and boron are the major impurities, and additionally, hydrogen, silicon, phosphorus, nickel, and cobalt are also known to be present as optically active centers. However, visible color and luminescence are produced by only nitrogen, boron, nickel, cobalt, and hydrogen.

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To understand the origin of the distribution of the impurities incorporated during growth, it is inevitable to understand the growth process. In this article, therefore, the correlation between the incorporation of impurities and the growth mechanism is described. The effect of the irradiation of high-energy beams such as electrons and neutrons on the color and luminescence is not presented, although numerous optical centers are known to be created by such irradiation.\(^{(1)}\)

2. Growth of Diamond and Incorporation of Impurities

Diamond single crystals grow with two different mechanisms, i.e., solution growth and vapor growth. High-pressure synthetic diamond and natural diamond grow in solution, while chemical vapor deposition (CVD) diamond grows from vapor. In this article, we focus on the high-pressure synthetic diamond, although a brief description of the other diamond will be presented.

High-pressure diamond crystals grow from molten metals such as iron and nickel supersaturated with carbon at high pressure and temperature conditions of 5 GPa and 1500°C.\(^{(2)}\) Natural diamonds are found in solid rock, but the rock was in liquid form while the diamonds were growing. It has been confirmed that diamond grows from rock-forming minerals such as carbonates and hydroxides.\(^{(3)}\)

The diamond crystals grow in solution starting from a nucleus or a seed crystal. Figure 1 shows a schematic drawing of the cross section of a growth cell. The diamond was formed on a seed crystal in molten metal. Graphite or diamond placed on the upper side of the metal dissolves into the metal and the carbon atoms diffuse downward to the seed crystal followed by precipitation as diamond. The diamond on the seed crystal (Fig. 2) exhibits a polyhedral shape bounded by \{111\} and \{100\}, although \{110\}, \{113\}, and \{115\} surfaces also appear commonly on such crystals,\(^{(4,5)}\) whereas a round shape is common in natural diamond because of dissolution after growth.\(^{(6)}\)

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Fig. 1 (left). Schematic drawing of a cell for diamond growth by a temperature gradient method. 1: Carbon source; 2: metal solvent; 3: grown diamond; 4: seed crystal.

Fig. 2 (right). Diamond grown on a small seed crystal indicated by an arrow. The grown diamond is 2 mm wide.
On the other hand, CVD diamond is formed from the gas phase. Carbon containing gases such as methane and alcohol decompose in plasma and carbon atoms precipitate as diamond on a substrate. When a silicon wafer is used as the substrate, a polycrystalline film is usually formed on the substrate. The growth surface looks rough because the film is composed of polycrystalline aggregates, but each crystallite exhibits \{111\} and/or \{100\} surfaces. Single crystals can be synthesized, if a single-crystal diamond surface is used as the substrate.

The growth environment is different between solution growth and vapor growth, but both growth processes may be the same, namely, carbon atoms migrate in the growth medium and deposit on the diamond surface. The manner of impurity incorporation, therefore, would be the same in both solution growth and vapor growth. The impurities are supplied from the growth media and precipitate on the growing surface, and then are incorporated into the diamond lattice. In the process, the behavior of the incorporation of impurity atoms would be affected by the atomic arrangement of the growth surface and growth kinetics, although factors determining macroscopic growth conditions such as temperature are important parameters related to the incorporation of impurities.

The crystal structure of the surface differs depending on crystal orientation. It is readily understood that the difference in atomic arrangement of the diamond surface results in a difference in the precipitation behavior of the impurities on the growing surface. For example, it is observed that impurities on \{111\} growth surfaces differ markedly from those on \{100\} growth surfaces. In addition, if we observe a surface in detail, we detect nonuniformity even on a surface.

Real growth surfaces are not perfectly flat, but some slopes and steps are commonly observed on the surface. For example, vicinal slopes indexed to be \{1, 1, 1 \+ \delta \} (\delta \ll 1) are seen on \{111\} surfaces. The atomic arrangement of the vicinal slope is different from that on an ideal \{111\} surface, resulting in different impurity incorporation behaviors.

The kinetics of growth is another parameter that affects the incorporation of the impurities. It would be reasonably assumed that the incorporation of impurities would change with growth rates. The growth rates may mean a rate normal to the growth surface, but we can consider the propagation rate of growth layers parallel to the growth surface as well.

In the following sections, the author presents the dependences of impurity incorporation on 1) the orientation of the growth surface, 2) the vicinal surface, 3) the growth rate normal to the growth layer, and 4) the propagation rate of the growth layer. The effect of plastic deformation formed after growth on the luminescence properties is also briefly described.

3. Growth Sector Dependence of Impurity Incorporation

3.1 Nitrogen

Nitrogen impurities are incorporated with different concentrations depending on the orientation of growth surfaces. The orientation dependence is clearly seen in cross sections of a high-pressure-high-temperature (HPHT) synthetic diamond single crystal grown from molten metal. A schematic drawing of the cross section of a crystal grown
by the temperature gradient method(12) is shown in Fig. 3.

Figure 4 shows a cross section of a type Ib crystal bounded by {111} and {113} surfaces, which was grown from a cobalt solvent/catalyst. This has been polished parallel to the {110} dodecahedral plane so as to expose regions that are formed by the stacking of individual growth layers. The region is called a growth sector. As seen in Fig. 4, there are yellow and colorless regions in the crystals, and it is easily identified from the observation of their morphology that the yellow and colorless regions are {111} and {113} growth sectors, respectively. The yellow color is caused by single substitutional nitrogen impurities, and its concentration is 100 ppm according to microscopic FTIR measurement. On the other hand, the concentration of nitrogen in the {113} sectors is lower than 1 ppm. The low concentration indicates that the {113} growth sectors are classified as type Iia, although the overall properties of the crystal may show that the crystal is of type Ib.

Such an inhomogeneous color distribution is observed in other diamonds having {100}, {110}, and {115} sectors in addition to {111} and {113}. The sector dependence of the nitrogen concentrations is in the order of {111}>{100}>{113}={110}={115}.(13) {111} and {100} sectors contain nitrogen impurities whose concentrations are high enough to produce yellow color, while the nitrogen concentrations are always low in {113}, {110}, and {115}. Commericially available HPHT synthetic diamond usually shows yellow color, which is due to {111} and {100} growth sectors, which appear dominantly. When the depths of the yellow color are compared between {111} and {100} sectors, {111} sectors are usually deeper in color than {100}, but there is a condition in which {100} sectors become deeper in color than {111}. Satoh et al.(14) have found that {100} sectors give a deeper yellow color than {111} in diamonds grown at the lowest limit of growth temperature.

A clear sector dependence is observed in cathodoluminescence and photoluminescence images.(11) Nitrogen-related luminescence bands such as the N3 and H3 bands are observed.(15) It is noted, in particular, that the H3 center is commonly observed even in {100} growth sectors of as-grown HPHT diamonds, although the center is known to be a radiation damage product.(1) The center consists of two nitrogen atoms and a vacancy, and the presence of the H3 center in the {100} growth sectors suggests that vacancies are
incorporated even in a normal growth process, although its concentration is really low. The H3 center is observed only in luminescence but not in absorption because of low concentrations.

3.2 Boron

The growth sector dependence of the incorporation of boron has been reported. The dependence is readily detected from the depth of blue color. However, the concentration of boron impurities is not simply judged from the depth of blue color, because the presence of nitrogen impurities also affects the coloration. The nitrogen impurities compensate the activity of boron to produce the blue color. Only uncompensated boron contributes the blue color, namely, the depth of blue color is proportional to [boron impurity] – [nitrogen impurity]. Therefore, inhomogeneous coloration is observed as follows.

Figure 5 shows two examples of blue coloration. A crystal shown in Fig. 5(a) consists of {111} sectors with a dark blue color and {113} with a light blue color, suggesting that the boron impurities are more readily incorporated in {111} than in {113}. However, another crystal has an unusual feature. As shown in Fig. 5(b), the crystal exhibits yellow and blue regions. {111} sectors are yellow, while {113} sectors are blue. The coexistence of the blue and yellow colors is reasonably understood if we assume that the concentrations of both nitrogen and boron are high in the {111} sectors, but the nitrogen concentrations exceed the boron concentrations resulting in yellow color. As for the {113} sectors, the concentrations of boron and nitrogen are low, but the boron concentrations exceed the nitrogen concentrations, and the {113} sectors are blue.

Figure 6 shows other examples of color distribution, in which two types of distribution are found, namely, {111} sectors have a deeper blue color than {110} sectors in Fig. 6(a), and the relation is opposite in Fig. 6(b). These examples are also understandable if we consider the concentrations of both nitrogen and boron.

Sector dependence is also observed in luminescence from boron-doped diamond. The color is bluish green but its color tint and intensity is different. Several broad luminescence bands have been observed from different growth sectors.

3.3 Nickel and cobalt

Nickel impurities are incorporated in diamond when nickel-containing alloy is used as a solvent/catalyst, and produce a number of absorption bands. The diamonds show a brownish yellow, green or brown color depending on the concentrations of nitrogen impurities coexisting with nickel. The colors have a clear sector dependence.

Figure 7 shows a transmission optical micrograph of nickel-containing diamond after being polished to a thin disk. It is definitely found that the brown color is localized only in {111} sectors. The restriction to {111} sectors has been reported by local area absorption spectroscopy. In addition, the restriction has been confirmed by microscopic electron-spin resonance (ESR) and X-ray fluorescence techniques. The microscopic ESR technique can be used to detect the location of Ni impurities in {111} sectors. Both Ni and Co impurities have been detected by X-ray fluorescence spectroscopy using synchrotron radiation.
Fig. 4. Cross section of a type Ib synthetic diamond grown by the temperature gradient method under HPHT conditions. This specimen was prepared by polishing a crystal along the \{110\} plane.

(a) (b)

Fig. 5. Two types of boron-doped diamonds in which nitrogen is (a) absent and (b) contained.

(a) (b)

Fig. 6. Sector dependence of blue coloration of two types of diamond. (110) sectors are (a) brighter and (b) deeper than the adjacent \{111\} sectors.
Regarding cobalt impurities, the location is not visible in the color distribution, because the optical absorption due to cobalt is very weak. However, the location is clearly found in luminescence images. Cobalt impurities produce yellow luminescence as shown in Fig. 8. The yellow luminescence is observed only in \{111\} growth sectors, giving evidence that cobalt impurities are located in \{111\} sectors.

### 3.4 Other Impurities

It has been established that phosphorus doping gives rise to n-type semiconducting properties for CVD diamond. The incorporation also depends on the orientation of the growth surface. n-Type properties were successfully realized in homoepitaxially grown diamond film, when a \{111\} substrate was used for the first time. Recently, phosphorus doping has been achieved in the \{100\} growth layer using a \{100\} substrate, but a large amount of phosphorus additive is required in a CVD growth system.

Hydrogen impurities are readily detected by means of FTIR. The hydrogen impurities are commonly found in natural diamond, although it is difficult to find the hydrogen-related absorption peak in HPHT synthetic diamond. Some natural diamonds are found to exhibit hydrogen-rich \{100\} sectors.

### 4. Vicinal Face Dependence

The incorporation of impurities depends on the vicinal slope on the growing surface, because the atomic arrangement on the vicinal surface is not the same as that on the ideal facet surface. The inhomogeneous distribution of impurities is observed in CL images of the growth surface.

Figure 9 shows an example of a CL image of a diamond \{111\} surface grown from phosphorus melt. CL contrast with a radial pattern is due to the vicinal surface. The surface of the crystal has a growth hillock with slopes surrounding a top that corresponds to the center of the radial pattern. The radial pattern exhibits three fold symmetry, which corresponds to the symmetry of the vicinal surface. On the vicinal surface, the atomic arrangement is the same on three vicinal surfaces, \((1+\delta, 1, 1), (1, 1+\delta, 1), \) and \((1, 1, 1+\delta)\) \((\delta \ll 1)\), which extend to three directions from the top of the vicinal surface, because the atomic arrangement of \{111\} surfaces has threefold symmetry.

This type of image is observed on the growth surface of diamond grown from the conventional metal solvent-catalyst. The CL patterns also have threefold symmetry on \{111\} surfaces. Such patterns related to vicinal surfaces were found for the first time on the \{100\} growth sector. In this case, the pattern has fourfold symmetry because of the symmetry of the atomic arrangement of its surface.

The effect of the slope of the vicinal surface on the impurity incorporation has been observed on CVD diamond as well. The CVD diamond grown at high rates, i.e., 0.1 mm/h, exhibits undulation on its grown surface. The undulation consists of vicinal surfaces with different tilt angles, leading to a variation in atomic arrangement. The variation causes nonuniform CL contrast as shown in Fig. 10. This picture is a CL image of a growth surface of a CVD diamond homoepitaxially grown on a \{100\} diamond surface.
Fig. 7 (left). Nickel-containing diamond exhibiting brown color only in \{111\} sectors.
Fig. 8 (right). Yellow luminescence from cobalt-containing diamond.

Fig. 11. Color changes of diamonds at epochs of temperature change that occurred while they were growing. The color change is indicated by arrows. Color changes related to (a) nitrogen, (b) boron, and (c) nickel. Figure 11(a) is displayed in black and white color in order to make the change of depth of yellow color clear. The black triangle in the center of the image is due to metallic inclusion.

Fig. 12 (left). Nonuniform distribution of blue coloration.
Fig. 13 (right). Nonuniform distribution of yellow coloration. Paler yellow is seen near sector boundaries as indicated by arrows.
5. Growth Striations

Striations like annual rings of trees are commonly observed in crystals. The striations are lines appearing in a cross section due to a nonuniform distribution of impurities and/or defects caused by fluctuations of growth conditions during the growth process. High-pressure synthetic diamond exhibits the striations as well as natural diamond, although they may not be obvious. The striations become clear, when growth temperature is intentionally changed.\(^{(29)}\)

Examples are shown in Fig. 11. Growth temperature was intentionally changed during growth.

Figures 11(a)–11(c) show changes of color related to nitrogen, boron, and nickel impurities, respectively. The pictures are cross sections of crystals, and lines parallel to growth surfaces are seen at points when the growth temperature was changed during growth.

In Fig. 11(a), it is seen that the depth of yellow color increases during the growth process. This crystal was grown at a high temperature in the first stage and the temperature was decreased by 50°C, at which temperature the crystal growth was continued. The change in depth of yellow color indicates that the nitrogen concentration increases as temperature decreases.

In Fig. 11(b), color changes from blue to yellow, and then to blue again during the growth process. This crystal was grown at a high temperature in the first stage, then at a lower temperature, and at a high temperature again. The color change indicates that blue color was produced at higher temperatures and yellow color at lower temperatures. As for this temperature effect, there are two possibilities on the change of impurities; boron concentrations increase or nitrogen concentrations decrease, when growth temperature increases. The latter possibility is probable, because it has been found that the change of blue color is not evident in nitrogen-free crystals even if growth temperature is changed.\(^{(29)}\)
In Fig. 11(c), dark lines, where nickel concentrations are higher, are formed at positions when the growth temperature was dropped two times during growth. It is noted that the dark lines are formed only when the temperature was decreasing. The result suggests that the depth of the color is affected by the differential of temperature rather than temperature itself. While the growth temperature decreases, the supersaturation level of carbon in the molten metal increases temporarily, resulting in higher growth rates. In conclusion, the concentrations of nickel increase with increasing growth rates.

As for the cobalt impurities, the same behavior has been observed in a luminescence image. A yellow luminescence line was formed while growth temperature was being reduced. Cobalt does not produce any specific color, and the characteristic lines are observed only in the luminescence image.

Nitrogen impurities in high-pressure synthetic diamond are usually in a single substitutional form, but some crystals contain nitrogen pairs, when they are grown at relatively high temperatures. The nitrogen pairs tend to be present in inner regions of the grown crystal, which formed in an early stage of growth. The nitrogen atoms incorporated as a single form have enough time for aggregation to nitrogen pairs in the inner region, which forms in the early stage of growth, before the growth run ends.

6. Effect of Propagation Rates of Growth Layer

Nonuniform coloration is sometimes observed in a growth sector in addition to the nonuniformity described above. Figure 12 shows an example observed from a boron-doped diamond. The blue color characteristic of boron-doped diamond is weak in a region surrounding a metal inclusion located in the center of a growth sector, suggesting that the boron concentrations tend to be lower in the center of a sector. Another example is shown in Fig. 13, in which regions near sector boundaries are paler in their yellow color than the other regions far from the sector boundaries. According to FTIR measurement, the paler yellow is not due to lower concentrations of nitrogen, but due to the higher degree of aggregation of nitrogen atoms, suggesting that aggregation rates were higher near the sector boundaries because of higher concentrations of defects that accelerate the aggregation. The nonuniformity has been observed earlier by Woods and Lang. In the pictures presented in Woods and Lang’s paper, the CL intensity is weaker, and absorption is stronger near the sector boundaries inside {100} sectors.

These types of nonuniformity may be understandable, if we assume that the propagation rate of each growth layer is not constant on a given growth surface as follows.

Diamond grows with the stacking of growth layers. Each growth layer starts at corners and edges of a polyhedral crystal toward the center of a surface as shown in Fig. 14. The propagation rate of the growth layer is higher near the corner and edges, then decreases toward the center of the surface, because the degree of supersaturation is higher at corners and edges of polyhedral crystals in solution growth. This growth process has been generally accepted in the research field of crystal growth, when the degree of supersaturation is relatively high. If we assume that boron concentrations are higher with a higher propagation rate of the growth layer, the boron concentrations are higher around the edges and lower in the center of the growth surface as shown in Fig. 12. The
lower propagation rates of the growth layer in the center of the growth surface result in the formation of a metallic inclusion. As for Fig. 13, the higher defect concentrations that enhance the aggregation of nitrogen are related to the higher propagation rates of the growth layer near the edge of growth surfaces.

7. Effect of Strain on Luminescence

Luminescence patterns related to strain are often observed in diamonds. It is known since early days that type II natural diamond exhibits a mosaic pattern in CL images (Fig. 15) that is produced by strain.\(^{(33)}\) Evidence of plastic deformation can be seen in polarized microscopic images. On the other hand, HPHT synthetic type II diamonds do not show such a mosaic pattern, but the mosaic pattern is formed with an HPHT treatment that introduces strain in the crystal.\(^{(34)}\)

Linear luminescence lines are also commonly observed in cross sections of diamond; they are related to cracks from type I synthetic diamond.\(^{(23)}\) An example is shown in Fig. 16. This type of linear luminescence lines has been produced by an indenter on a diamond surface.\(^{(35)}\)

8. Conclusion

Diamond has potential applications in electronics and optics. For these applications, control of defects is important, and the uniformity of the defects is also important. However, it is usually difficult to produce crystals in which defects are uniformly distributed. When diamond samples are characterized, we have to consider that properties related to defects are not uniform in order to avoid drawing the wrong conclusions.
References