FORMATION OF NITROGEN PAIRS IN SYNTHETIC DIAMOND DURING GROWTH

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Considerable numbers of nitrogen pairs, A-centers, were found in crystals grown from molten cobalt at various temperatures between 1400–1500°C under 6 GPa. The concentration of A-centers increases with increasing growth temperature. The largest amount of A-centers achieved in this study was about 70% of total nitrogen. Assuming that nitrogen was converted to A-centers from its singly substitutional form, C-centers, by annealing during growth, the conversion rate, \( K \), was calculated using a second order diffusion kinetics formula. \( A \) and \( E \ln K = A \exp(-E/kT) \) (ppm\(^{-1}\) min\(^{-1}\)) were 6.3 \times 10\(^{10}\) and 21 eV, respectively, which are quite a bit larger than those reported previously.

1. Introduction

Nitrogen and boron are major impurities of diamonds, and diamonds are classified into type I and II on the basis of the concentration and structure of these impurities.

Type I, which contains nitrogen, is further classified into IaA, IaB and Ib. IaA diamonds contain nitrogen in a paired form (A-centers),\(^1\) the IaB type is suggested to contain an aggregate consisting of four nitrogen atoms and a vacancy (B-centers)\(^2\) and Ib diamonds contain singly substitutional nitrogen atoms (C-centers). Other impurity centers of nitrogen have been reported, for example, N3 consisting of three nitrogens and a vacancy\(^3\) and platelets, a structural model of which has been proposed to be a planar aggregate of nitrogen or a cluster of interstitial carbon\(^4\)\(^,\)\(^5\).

Most natural diamonds contain nitrogen in the aggregated forms, i.e. IaA, IaB, N3 and platelets. On the other hand, nitrogen in synthetic diamond is present in the form of C-centers, but it has been established that the aggregated forms are obtained in the laboratory if a synthetic crystal is heated.\(^6\)\(^-\)\(^10\)

Chrenko et al.\(^9\) reported A-centers are formed when a crystal containing C-centers is heated above 1700°C. Evans et al.\(^8\),\(^10\) heated crystals up to 2700°C and detected B-centers and platelets in addition to A-centers. Collins\(^7\) reported vacancies produced by irradiation enhanced the aggregation.

In the course of diamond growth, a considerably high content of A-centers in addition to C-centers was found in some as-grown crystals. A paper has reported that crystals synthesized at higher temperatures contain A-centers.\(^1\) Thus, in the present study, the effect of growth temperature on the formation of A-centers was investigated.

2. Experimental

2.1 Assembly for growth of diamond

Diamonds were grown by the temperature gradient method in an assembly as shown in Fig. 1. They grew on 3 seed crystals placed at the bottom of cobalt metal, by the deposition of carbon atoms supplied from graphite at the top of the metal.

Fig. 1. Sample assembly for growth of diamonds. 1, NaCl pressure medium containing 6.5% MgO; 2, NaCl pressure medium melted during growth; 3, Graphite as a carbon source; 4, Cobalt metal as a solvent; 5, Diamond crystals as seeds and 6, Graphite heater 10 mm in diameter.

Details of the assembly have been reported in previous papers.\textsuperscript{12,13}

Growth experiments were performed at 1350–1500°C and 6 GPa for 10–18 h.

As the growth temperature is important in the present study, it was determined as follows. We did not assemble a thermocouple in the growth cell in every growth experiment, but instead measured the inner diameter of a melt region of the NaCl pressure medium, as shown in Fig. 1, in order to determine the growth temperature. The NaCl melt region was easily detected when the growth assembly was recovered from the high pressure cell, and the inner diameter of the region, which decreased with increasing growth temperature, had a one-to-one relation with the growth temperature in the range between 1350 and 1460°C, although it could not be measured above 1460°C. The diameter was calibrated by a Pt6%Rh–Pt30%Rh thermocouple in several runs.

Temperature is commonly determined from the electric power input calibrated by a thermocouple, but this method occasionally gives large errors because of the scattered size and quality of parts assembled in the growth cell. Therefore, the method employed in this study has an advantage over the common method. Of course, the common method was also considered.

2.2 General characteristics of grown crystals

Grown crystals of 1.5–2.5 mm diameter most predominantly exhibit [111] faces accompanied by small [100] and [113] faces but rarely [110] faces. They are yellow in color but their depth is not homogeneous; the [111] sectors are yellow whereas the [113] and [100] areas are colorless. No diamond grew below 1350°C, because of the low temperature at which the solvent did not melt. Crystals grown at 1390°C were clusters of small crystals with wavy surfaces, a kind of parallel intergrowth. This feature is consistent with descriptions of clusters grown at low temperatures.\textsuperscript{14}

2.3 Measurement of infrared absorption spectra

A DIGLAB FTS-60 infrared absorption spectrometer was used for the measurement. Spectra were taken under the absorbance mode, and absorbance is considered to be zero around 1500 cm\textsuperscript{-1}. In order to determine the absorption coefficient in the one phonon region, absorbance at 2000 cm\textsuperscript{-1} was used as a standard whose intensity is 1.23 mm\textsuperscript{-1}.\textsuperscript{15}

A crystal was set in the holder in such a way that the infrared beam passed the as-grown [111] surfaces. The influence of the inhomogeneous distribution of nitrogen atoms was neglected, and this might make the results of the measurements scattered.

3. Results and discussion

3.1 Typical absorption spectra in the infrared one-phonon region

Impurity-induced absorption is observed between 1400 and 1000 cm\textsuperscript{-1}. The C-center spectrum is characterized by a highest peak at 1130 cm\textsuperscript{-1} and a sharp peak at 1344 cm\textsuperscript{-1}. The A-center spectrum consists of two peaks, the higher one of which is at 1280 cm\textsuperscript{-1}.\textsuperscript{15}

As shown in Fig. 2, the absorption spectra measured showed the pure C-center shape or a mixture of A-centers and C-centers, but no peak of pure A-centers was observed.

The concentrations of the A- and C-centers were

![Absorbance vs. Wave number](image-url)

Fig. 2. Typical examples of absorption spectra in the infrared one-phonon region. 1–3 are spectra of crystals grown at 1500, 1460 and 1420°C, respectively. The A- and C-centers are characterized by peaks at 1280 and 1130 cm\textsuperscript{-1}, respectively.
calculated from the absorption coefficients at 1280 and 1130 cm\(^{-1}\).

3.2 Concentration of A- and C-centers

In Table 1, the absorption coefficients measured at 1280 and 1130 cm\(^{-1}\) of 17 crystals grown in 13 growth experiments are listed together with growth temperatures and growth times. Spectroscopic measurements were repeated for a few crystals. As seen in Table 1, crystals grown in the same run do not always show the same spectra, and when measurement was repeated for the same crystal, the spectra were not exactly the same. These scattered measurement results may be due to (1) crystals not always growing at the same temperature as each other even in the same cell, because of the presence of a temperature gradient in the cell, (2) the inhomogeneous distribution of nitrogen in a crystal or (3) errors in spectroscopic measurements.

To obtain the relationship between the concentration of the A- and C-centers and the growth temperatures, nitrogen concentrations were calculated as follows; the results are also listed in Table 1.

1. The absorption coefficients measured, \(A_{1280}\) and \(A_{1130}\), were decomposed to those of the A- and C-centers, \(\mu_{1280}\) and \(\mu_{1130}\), using the equations:

\[
A_{1280}(\text{cm}^{-1}) = \mu_{1280} + 0.326 \mu_{1130} \tag{1}
\]

and

\[
A_{1130}(\text{cm}^{-1}) = \mu_{1130} + 0.171 \mu_{1280}. \tag{2}
\]

These equations were derived from the shapes of absorption spectra shown by Clark and Davy.\(^{16}\)

2. A- and C-center concentrations were calculated using the equations:

<table>
<thead>
<tr>
<th>RUN(^{a})</th>
<th>Temp(^{b}) (°C)</th>
<th>Time(^{b}) (h)</th>
<th>(A_{A}^{c}) (cm(^{-1}))</th>
<th>(A_{C}^{c}) (cm(^{-1}))</th>
<th>(N_{A}^{c}) (ppm)</th>
<th>(N_{C}^{c}) (ppm)</th>
<th>(N_{A}/N_{A}+N_{C}^{c})</th>
<th>(K^{c}) (ppm(^{-1}) min(^{-1}))</th>
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<tr>
<td>2583A1</td>
<td>1430</td>
<td>18.0</td>
<td>2.66</td>
<td>8.2</td>
<td>0</td>
<td>205</td>
<td>0.00</td>
<td>0.00</td>
</tr>
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<td>18.0</td>
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<td>58.6</td>
<td>179</td>
<td>0.25</td>
<td>1.28</td>
</tr>
<tr>
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<td>10.0</td>
<td>7.92</td>
<td>7.09</td>
<td>198</td>
<td>151</td>
<td>0.57</td>
<td>6.25</td>
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<td>&quot; A2</td>
<td>&quot;</td>
<td>&quot;</td>
<td>9.04</td>
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<td>256</td>
<td>103</td>
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<tr>
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<td>1500</td>
<td>13.0</td>
<td>5.65</td>
<td>8.47</td>
<td>102</td>
<td>199</td>
<td>0.34</td>
<td>2.18</td>
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<tr>
<td>&quot; B1</td>
<td>&quot;</td>
<td>&quot;</td>
<td>3.71</td>
<td>8.40</td>
<td>34.3</td>
<td>205</td>
<td>0.14</td>
<td>0.89</td>
</tr>
<tr>
<td>&quot; B2</td>
<td>&quot;</td>
<td>&quot;</td>
<td>5.61</td>
<td>8.20</td>
<td>104</td>
<td>192</td>
<td>0.35</td>
<td>2.35</td>
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<td>4.41</td>
<td>8.81</td>
<td>54.3</td>
<td>213</td>
<td>0.20</td>
<td>1.00</td>
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<tr>
<td>&quot; B1</td>
<td>&quot;</td>
<td>&quot;</td>
<td>5.59</td>
<td>7.83</td>
<td>107</td>
<td>182</td>
<td>0.37</td>
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<td>&quot; B2</td>
<td>&quot;</td>
<td>&quot;</td>
<td>5.74</td>
<td>10.25</td>
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<td>&quot;</td>
<td>4.92</td>
<td>11.75</td>
<td>38.6</td>
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<td>&quot; B4</td>
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<td>4.97</td>
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<td>&quot;</td>
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<td>0.01</td>
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<td>12.4</td>
<td>4.49</td>
<td>8.00</td>
<td>66.3</td>
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<td>1.81</td>
</tr>
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<td>&quot;</td>
<td>&quot;</td>
<td>4.47</td>
<td>8.05</td>
<td>65.3</td>
<td>193</td>
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<td>1445</td>
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<td>3.12</td>
<td>7.42</td>
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<td>9.41</td>
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<tr>
<td>2659A1</td>
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<td>16.5</td>
<td>4.30</td>
<td>10.87</td>
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<td>&quot; B1</td>
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<td>&quot;</td>
<td>2.88</td>
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<td>221</td>
<td>0.00</td>
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<tr>
<td>&quot; B2</td>
<td>&quot;</td>
<td>&quot;</td>
<td>3.07</td>
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<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>&quot; C1</td>
<td>&quot;</td>
<td>&quot;</td>
<td>3.17</td>
<td>9.32</td>
<td>4.7</td>
<td>232</td>
<td>0.02</td>
<td>0.08</td>
</tr>
</tbody>
</table>

a) For example, 2583 means the run number of a growth experiment, and A, B or C means different crystals grown in the same run. B1 and B2 means measurement was repeated.

b) Temp. and Time are growth temperature and growth time, respectively.

c) See text.
\[ N_A \text{ (ppm)} = 33.3 \mu_{1280} \text{ cm}^{-1} \] (3)

\[ N_C \text{ (ppm)} = 25 \mu_{1130} \text{ cm}^{-1} \] (4)

where \( N_A \) and \( N_C \) are the concentrations of the A- and C-centers, respectively. In this calculation, we referred to Kaiser and Bond\(^{17}\) for the A-center data and Chrenko et al.\(^6\) for the C-center data. The A- and C-center concentrations calculated in this way and the relative A-center content are plotted against growth temperatures in Fig. 3. The figure shows that the A-center concentration rapidly increases with increasing growth temperature, whereas the C-center concentration does not change distinctly, and further shows that the relative A-center content rapidly increases with increasing growth temperature around 1450\(^\circ\)C, as shown in Fig. 3(c) and that the total nitrogen content increases with increasing temperature.

The largest A-center content achieved was about 70\% of total nitrogen, which was contained in a crystal grown at a temperature higher than 1460\(^\circ\)C, probably about 1500\(^\circ\)C estimated from the electric power input.

The A-centers found in this study may be formed by heat treatment during growth after nitrogen was deposited as C-centers, but the A-center presence in crystals grown below 1500\(^\circ\)C seems not to be consistent with previous reports on heat treatment\(^6,^{10}\). In order to compare these results more quantitatively, the conversion rate was calculated in the same way as in the previous reports\(^6,^{10}\) in the following section.

### 3.3 Conversion of C-centers to A-centers

Chrenko et al.\(^6\) and Evans and Qi\(^10\) calculated the conversion rate, assuming it obeyed second-order kinetics with the formulae:

\[ Kt = 1/N_C - 1/N_{C_0} \] (5)

and

\[ K = A \exp(-E/kT) \] (6)

where \( K \) is the rate constant, \( t \) is time of heat treatment, \( N_C \) and \( N_{C_0} \) are the concentrations of the C-centers before and after heat treatment, \( A \) is a constant, \( E \) is the activation energy, \( k \) is the Boltzmann constant and \( T \) is the absolute temperature.

We calculated the conversion rate of the results described in the preceding section using the above formulae and compared it with previous reports.\(^6,^{10}\) We roughly estimated that the time of heat treatment, \( t \), is the same as the growing time to simplify the calculation, although \( t \) should be shorter than the growing time. \( N_{C_0} \) is equal to the total nitrogen concentration, \( N_A + N_C \).

Results of the calculation are plotted in Fig. 4 together with those reported previously.\(^6,^{17},^{10}\) As seen from the figure, the conversion rate of the present work has the values of \( K=8 \times 10^{-5} \text{ ppm}^{-1} \text{ min}^{-1} \) at 1450\(^\circ\)C, and \( A \) and \( E \) in Eq. (6) are \( 6.3 \times 10^{60} \text{ (ppm}^{-1} \text{ min}^{-1}) \) and 21 (eV), respectively.

As shown in Fig. 4 and Table 2, compared with the conversion rates reported previously, it is clearly seen that the rate constant, \( K \), of the present results is not consistent with the others and that the coefficient of the rate constant \( A \) and the activation energy \( E \) of this study are very much
Fig. 4. Arrhenius plot of conversion rate of nitrogen from the C- to A-centers. •, the present work; ○ and △, heat treatment under high pressure by Chrenko et al.\(^6\) and Evans and Qi\(^{10}\) respectively; ▽, at 1 atm by Evans and Qi\(^{10}\) and □, heat treatment of crystals irradiated by electron (Collins\(^7\)).

<table>
<thead>
<tr>
<th>A (ppm⁻¹ min⁻¹)</th>
<th>E(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3×10⁶</td>
<td>21</td>
</tr>
<tr>
<td>8.1×10⁷</td>
<td>2.6</td>
</tr>
<tr>
<td>3.3×10⁸</td>
<td>5</td>
</tr>
</tbody>
</table>

larger than the values used by others. The conversion rate at 1500°C of this study is comparable to that enhanced by the vacancy induced by electron irradiation.\(^7\)

Collins,\(^7\) and Evans and Qi\(^{10}\) employed 45 instead of 25 as the coefficient in Eq. (4). Even if the coefficient is modified, a large discrepancy still remains between their results and this study.

In order to fit the present results to the previous reports of Chrenko\(^6\) or Evans and Qi\(^{10}\) in Fig. 4, we have to modify the values of the conversion rate \(K\) or temperature \(T\). There are several factors which could cause errors in \(K\) in the process of conversion from spectral data to \(K\). However, it is easily concluded that it is difficult to modify the \(K\) values enough account for the discrepancy, because the previous reports do not show the peak at 1280 cm⁻¹ so obviously as the present study around 1450°C. If we want to modify the temperatures, we have to expand the temperature scale by about 200°C. Temperatures determined in the present study may be reasonable because of the evidence: (1) the eutectic temperature of the Co–C system determined in this study was about 1350°C, and (2) temperature determined by thermocouple had a linear relationship with the electric power input for heating the growth cell. Therefore, it is difficult to modify the temperature by about 200°C.

According to the above discussion, it is a realistic estimation that the formation mechanism of A-centers in the present study is different from the C-center aggregation by heat treatment, rather than accepting that errors in experiments or calculation cause the discrepancy shown in Fig. 4. We have to consider another formation mechanism for the A-centers: that nitrogen may deposit in the paired form during growth.

4. Conclusion

(1) Nitrogen pairs, A-centers, were found in as-grown crystals grown from molten cobalt metal.

(2) The A-center content rapidly increases with increasing growth temperature above 1450°C.

(3) As a result of calculation of the conversion rate \(K\), assuming that nitrogen was converted to A-centers by heat treatment, \(A\) and \(E\) in \(K\) (ppm⁻¹ min⁻¹) = \(A\exp(-E/kT)\), are 6.3×10⁶⁰ and 21 eV, respectively, which are quite a bit larger than the values reported previously.

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