

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 in $K = A \exp(-E/kT)$ ($\text{ppm}^{-1} \text{min}^{-1}$) were 6.3×10^{60} 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 vacancy³⁾ 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.*⁶⁾ 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. Collins⁷⁾ 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.¹¹⁾ 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.

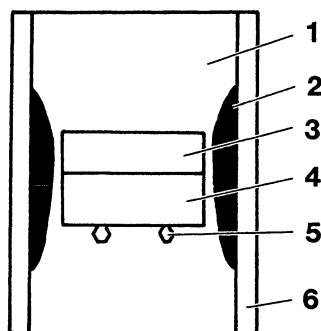


Fig. 1. Sample assembly for growth of diamonds. 1, NaCl pressure medium containing 6.5% MgO; 2, NaCl pressure medium melted during growth; 3, Graphite as a carbon source; 4, Cobalt metal as a solvent; 5, Diamond crystals as seeds and 6, Graphite heater 10 mm in diameter.

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, μ_{1280} and μ_{1130} , using the equations:

$$A_{1280}(\text{cm}^{-1}) = \mu_{1280} + 0.326 \mu_{1130} \quad (1)$$

and

$$A_{1130}(\text{cm}^{-1}) = \mu_{1130} + 0.171 \mu_{1280}. \quad (2)$$

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 1. Experimental results

RUN ^{a)}	Temp. ^{b)} (°C)	Time ^{b)} (h)	$A_A^c)$ (cm^{-1})	$A_C^c)$ (cm^{-1})	$N_A^c)$ (ppm)	$N_C^c)$ (ppm)	$N_A/N_A+N_C^c)$	$K^c)$ ($\text{ppm}^{-1} \text{min}^{-1}$)
2583A1	1430	18.0	2.66	8.2	0	205	0.00	0.00
2584A1	1445	18.0	4.1	7.48	58.6	179	0.25	1.28
2586A1	1500	10.0	7.92	7.09	198	151	0.57	6.25
" A2	"	"	9.04	5.43	256	103	0.71	11.5
2587A1	1500	13.0	5.65	8.47	102	199	0.34	2.18
" B1	"	"	3.71	8.40	34.3	205	0.14	0.89
" B2	"	"	5.61	8.20	104	192	0.35	2.35
2588A1	1460	15.8	4.41	8.81	54.3	213	0.20	1.00
" B1	"	"	5.59	7.83	107	182	0.37	2.15
" B2	"	"	5.74	10.25	84.6	245	0.26	1.11
" B3	"	"	4.92	11.75	38.6	275	0.12	0.48
" B4	"	"	4.97	11.51	43.0	282	0.13	0.95
2596A1	1390	17.2	1.94	5.61	4.0	140	0.03	0.19
2597A1	1430	16.2	1.95	6.64	0.0	167	0.00	0.00
2598A1	1420	17.2	2.34	7.22	0.0	180	0.00	0.00
" A2	"	"	2.46	7.38	2.0	184	0.01	0.06
2608A1	1450	12.4	4.49	8.00	66.3	191	0.26	1.81
" A2	"	"	4.47	8.05	65.3	193	0.25	1.75
2609A1	1445	13.3	3.12	7.42	24.6	182	0.12	0.83
2658A1	1420	16.0	3.14	9.41	2.7	235	0.01	0.06
2659A1	1450	16.5	4.30	10.87	26.6	268	0.09	0.34
2627A1	1430	18.0	2.78	8.33	2.3	208	0.01	0.04
" B1	"	"	2.88	8.84	0.0	221	0.00	0.00
" B2	"	"	3.07	9.23	2.3	230	0.01	0.03
" C1	"	"	3.17	9.32	4.7	232	0.02	0.08

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.

$$\text{and } N_A \text{ (ppm)} = 33.3 \mu_{1280} \text{ cm}^{-1} \quad (3)$$

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

where N_A and N_C are the concentrations of the A- and C-centers, respectively. In this calculation, we referred to Kaiser and Bond¹⁷⁾ 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°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

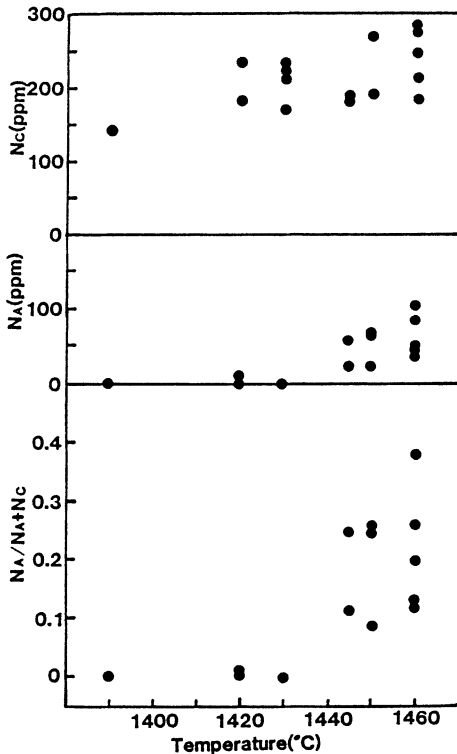


Fig. 3. Concentrations of the A- and C-centers and the ratio of the A-centers to total nitrogen against growth temperatures.

crystal grown at a temperature higher than 1460°C, probably about 1500°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°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 Qi¹⁰⁾ calculated the conversion rate, assuming it obeyed second-order kinetics with the formulae:

$$Kt = 1/N_C - 1/N_{C_0}, \quad (5)$$

and

$$K = A \exp(-E/kT) \quad (6)$$

where K is the rate constant, t is time of heat treatment, N_{C_0} and N_C 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),7),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°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

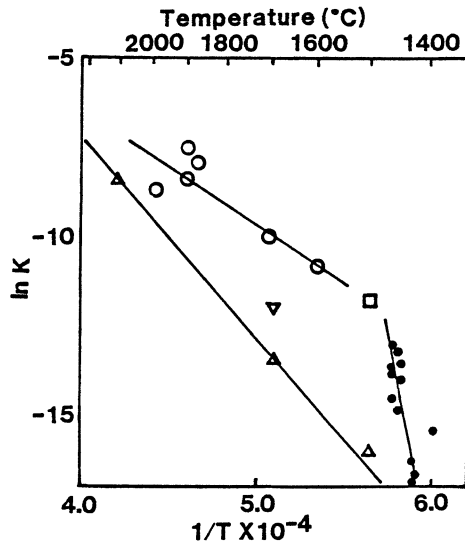


Fig. 4. Arrhenius plot of conversion rate of nitrogen from the C- to A-centers. ●, the present work; ○ and △, heat treatment under high pressure by Chrenko *et al.*⁶⁾ and Evans and Qi,¹⁰⁾ respectively; ▽, at 1 atm by Evans and Qi¹⁰⁾ and □, heat treatment of crystals irradiated by electron (Collins⁷⁾).

Table 2. A and E in the conversion rate, K ($\text{ppm}^{-1} \text{min}^{-1}$) = $A \exp(-E/kT)$

A ($\text{ppm}^{-1} \text{min}^{-1}$)	E (eV)	
6.3×10^{60}	21	This work
8.1×10^2	2.6	Chrenko <i>et al.</i> ⁶⁾
3.3×10^6	5	Evans and Qi ¹⁰⁾

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 Qi¹⁰⁾ 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 Chrenko⁶⁾ or Evans and Qi¹⁰⁾ 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 ($\text{ppm}^{-1} \text{min}^{-1}$) = $A \exp(-E/kT)$, are 6.3×10^{60} and 21 eV, respectively, which are quite a bit larger than the values reported previously.

Acknowledgements. The authors thank Dr. A. T. Collins for pointing out the presence of the A-center in absorption spectra we measured, which induced us to start this work, and also thank Drs. G. S. Woods and H. Monma for help with spectroscopic measurements.

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