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High pressure and high temperature annealing on nitrogen aggregation in lab-grown diamonds

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Abstracts Diamond single crystals were grown by a high-pressure high-temperature gradient method using a molten Fe–Ni catalyst in a split-sphere apparatus at a pressure of 5.5 GPa and a temperature of 1473–1873 K. The as-grown crystals, ranging in size from 0.2 to 0.6 g, were generally deep yellow in color because of intake of nitrogen impurity during the process. Two different annealing methods were used to change their color to light and vivid yellow. One method involved annealing at 5.5 GPa and 2193–2473 K within the split-sphere apparatus. The other involved annealing of E-beam irradiated crystals at 1773 K in a high-vacuum furnace at 10^{-6} Torr. Distribution of C-center nitrogen, single substitutional nitrogen, and A-center nitrogen defects, a pair of nearest-neighbor nitrogen, were thoroughly studied by FT–IR spectroscopy. Upon annealing, C-center nitrogen defects decreased by 10–60%, while A-center nitrogen defects increased by 5–70%. It was confirmed that the irradiation process and intake of nickel impurity enhanced the nitrogen aggregation rate, which followed the second order kinetics. Measured activation energies were in the range of 2.88–3.01 eV, which were not strongly affected by the irradiation process. The results indicate that the nitrogen aggregation rate was enhanced by vacancies and interstitials introduced by E-beam irradiation.

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Introduction

About 98% of mined diamonds contain nitrogen impurity between 30 and 3000 ppm. Such nitrogen-containing diamonds are called type I. There are also much rarer diamonds, called type II, which contain a much lower concentration of nitrogen impurity (<0.1 ppm). Type I diamonds, which appear as colorless and sometimes yellow or brown colored, are categorized into two subdivisions: type Ia and type Ib. In type Ib diamonds, most of the nitrogen impurities are present as single substitutional nitrogen atoms that are paramagnetic, which can be detected by infrared or electron paramagnetic resonance. These dispersed nitrogen atoms, called C-center nitrogen defects, show characteristic optical absorption in infrared, visible, and ultra-violet regions of spectrum. As a result, the color of Ib diamonds vary from canary yellow to deep orange depending on the C-center nitrogen amount. Most lab-grown diamonds belong to type Ib and have deep yellow to yellowish color depending on the concentration of nitrogen impurity. Type Ia diamonds are further separated into two small subdivisions, IaA and IaB, depending on whether they contain A or B centers of nitrogen. A-center nitrogen consists of a pair of nitrogen atoms on adjacent lattice sites, whereas B-center nitrogen consists of four nitrogen atoms surrounding a single vacancy. Type IaA and IaB diamonds are usually colorless or near colorless [1, 2]. Most natural diamonds are placed in these categories. It should be emphasized that from an HPHT processing standpoint, incorporation of high-nitrogen impurity is conducive to better quality and yield of diamond growth. However, since most consumer demand is for colorless and light yellow diamonds, color change of the as-grown crystals from deep yellow to light yellow (or colorless in future) is highly needed. It is found that irradiation reduces annealing temperature as well as pressure, which are both conducive for consistent process and cost reduction.

Chrenko et al. [3] was the first to change type Ib diamond (containing C-center nitrogen) to type IaA (containing A-center nitrogen or a nitrogen pair) in the laboratory using high-pressure and high-temperature (HPHT) annealing. The activation energy for the mitigation of nitrogen atoms was calculated as 2.4 eV, and the diffusion coefficient of nitrogen in the diamond was also estimated by assuming that nitrogen diffusion is the substitutional diffusion through vacancies. However, other researchers could not reproduce this result under the same experimental conditions. Kluyev et al. [4] and Kiflawi et al. [5] claimed that a higher temperature was required to reproduce Chrenko's result; the activation energies of those studies were 3.6 and 5.5 eV, respectively. Collins [6], on the other hand, found that the presence of irradiation-induced vacancies enhanced the nitrogen aggregation rate, and their activation energy was comparable with Chrenko's result. The sample were treated with E-beam at 2.0 MeV with 1×10^{18} electrons/cm^2. By observing the nitrogen-vacancy (N–V) pair at a relatively low temperature of 973–1173 K, it was proposed that the nitrogen-vacancy pair migrated in the diamond first before forming the nitrogen pair; this is called as vacancy-assisted diffusion mechanism. Evans and Qi [7] proposed the activation energy for a vacancy-assisted mechanism as 5 eV. Although irradiation should create vacancies and interstitials at the same time, the role of interstitials on nitrogen diffusion was ignored because no evidence was found about nitrogen interstitials related atomic structure and, furthermore, interstitials were believed to be mobile at very low temperature. Recently, Kiflawi et al. [8] found the characteristic peak of nitrogen interstitials in the infra-red region through nitrogen isotope experiments and proposed that nitrogen interstitials may play an important role in nitrogen aggregation. Mainwood [9] calculated activation energy theoretically and found that activation energies for the vacancy-assisted diffusion mechanism and the direct conversion of nitrogen atoms were 4.5 and 6.3 eV, respectively. In addition to the nitrogen diffusion mechanisms, the effect of metallic impurity on nitrogen aggregation has also been investigated [9–12]. It is found that most nickel or cobalt impurity atoms are incorporated in the {111} plane and are able to enhance nitrogen aggregation. Nevertheless, the reason why Ni and Co enhance nitrogen aggregation is not fully understood. It has been speculated that Ni or Co could create vacancies or interstitials when they are incorporated in diamonds.

A major challenge in conducting HPHT annealing experiments is precise control and measurement of temperature. In fact, as pointed out by Lawson and Kanda [12], precise control and measurement of temperature in a high-pressure chamber may be impossible due to difficulty of locating thermocouples and the large temperature gradient in the diamond growth core. These authors indicate that the definition of the annealing temperature, which determines the activation energy, is ambiguous between previous researches. Thus, comparing previous researches to understand the influence of irradiation on nitrogen aggregation may not be accurate. In order to address some of these uncertainties in this study, the same metallic catalyst (Fe–Ni) was selected for diamond growth, and annealing experiments were conducted for identical crystals, and the influence of irradiation was determined by direct comparison of irradiated and non-irradiated samples. Moreover, other studies have found that irradiation can also induce different color centers such as dull yellow or green if too many vacancies are created [5]. Thus, a relatively weak irradiation condition was selected to prevent oversupply of vacancies and to test color change efficiency.

Experiments

Diamond crystals were grown by the HPHT method [13–15] in a ceramic core which contained a carbon source, molten metal solvent, and diamond seed as schematically shown in Fig. 1a. The driving force of diamond growth is the carbon solubility difference resulting from about 15 to 30° temperature difference between the carbon source and the seed area. Diamond crystals were grown at 1873 K and 5.5 GPa with varying C-center nitrogen impurity (69–161 ppm). A high-purity Fe–Ni alloy was used as a solvent for most of the crystals. However, a few experiments were conducted using a high-purity Fe catalyst to test the effect of nickel on the nitrogen aggregation process.

For high-temperature (2193–2493 K) and high-pressure (5.5 GPa) annealing, ZrO_2 powder was packed around the diamond in the ceramic core in Fig. 1b. The annealing temperature was measured by B type (Pt-30%Rh and Pt-6%Rh) thermocouples, inserted at three different locations as shown in Fig. 1b. The relation of supplied power and measured temperature up to 1873 K was determined using thermocouples. The temperature data were calibrated using the stability region for diamond and graphite growth at lower temperatures, and were subsequently extrapolated to higher temperatures. It should be noted that absolute calibration of temperature was challenging, so that a constant power input for the same nominal temperature runs was used to represent equal temperatures. Annealing temperature was regarded as the temperature measured from TC 2,

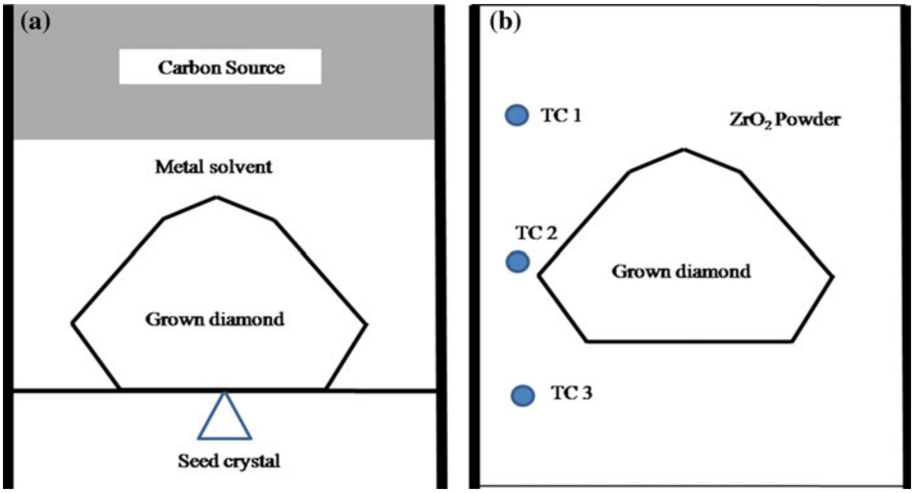

Fig. 1 Schematic of diamond growth core (**a**) and HPHT annealing (**b**)

which is the thermocouple placed at the middle of the core. Through multiple measurements at TC 2, it was found that temperature variation was ±37 K at the same power input. The temperature at TC1 and TC3, which were 6 mm apart from TC2, were observed to be 100° and 108° below TC2, respectively. However, it is believed that, owing to high-thermal conductivity of diamonds and their relatively large size, 0.2–0.6 g, the temperature gradient within diamond itself where annealing is taking place is much less than those measured within the ceramic.

For irradiation and high-temperature annealing in a high vacuum, diamond samples were irradiated with an E-beam with intensity and dose of 5 MeV and 1×10^{17} electrons/cm^2, respectively. These diamonds were heat-treated at 973 K for 3 h in a conventional vacuum furnace at roughly 1×10^{-3} Torr. For higher temperature treatment, some of these samples were heat-treated to 1773 K at 1×10^{-6} Torr using ultra-high-vacuum furnace. After the desired duration of annealing, samples were taken out from hot zone rapidly to avoid graphitization. For irradiation and HPHT annealing, samples were irradiated under the same condition as above and pre-heated at 973 K for 3 h. Then, samples were loaded in the HPHT annealing core as described previously.

After annealing treatments, infrared measurements in the defect-induced one phonon region were taken using a Fourier transform infrared machine (Nicolet 950 of 'Thermo Scientific'). Amounts of C-center nitrogen and A-center nitrogen were determined by decomposing the spectra, and determining the absorption coefficients for peaks at 1130 and 1280 cm^{-1}, respectively. Non-destructive tests of bulk diamonds were performed using the diffusive mode in the FT–IR instrument. By repeating the same sample, it was found that variation of nitrogen concentration in the diffusive mode was ±3 ppm. This error range is allowable in the case that initial nitrogen amounts are very high.

Results

Figure 2a exhibits growth planes of an as-grown stone. The major plane is octahedral plane {111} with minor planes such as dodecahedral {110} and trapezohedral {113}. The as-grown diamonds, which contained total nitrogen impurity in the range of 119–187 ppm, had the characteristic deep yellow to orange color depending on the nitrogen content. One example, which contains 130 ppm of C-center nitrogen, is shown in Fig. 2b. The color became deeper yellow (or orange) with increased nitrogen content. Most of the lab-grown diamonds had an absorption spectrum in infra-red region as shown in Figs. 3 and 4. Before heat treatment, the most prominent feature of the spectrum for C-center nitrogen was the peak at 1344 cm^{-1} for local mode single nitrogen vibration and the broad band with a maximum peak at 1130 cm^{-1}. By measuring absorbance intensity at either of these locations, the concentration of single substitutional nitrogen, C-center, can be determined. However, the peak at 1130 cm^{-1} is often used because the peak at 1344 cm^{-1} can be undetectable in low nitrogen concentrations. These diamonds also contained A-center nitrogen as evidenced by the peak at 1280 cm^{-1}. The A-center nitrogen content was in the range of 17–29 ppm, as summarized in Table 1. The C-center concentration, N_C, is related to the absorption factor at 1130 cm^{-1} using the following relation [3]:

$$N_\mathrm{c} = 25\,\alpha_{1130}\,\mathrm{ppm}, \tag{1}$$

where α_{1130} is absorbance at 1130 cm^{-1}. Similarly, the A-center nitrogen concentration represented by 1280 cm^{-1} peak, N_A, can be measured

$$N_\mathrm{c} = 33\,\alpha_{1280}\,\mathrm{ppm}, \tag{2}$$

where $\alpha_{1280}$is absorbance at 1280 cm^{-1} and the absorption factor is 33 [3]. It should be noted that there is another peak at 1175 cm^{-1}, known as the B-center nitrogen center, and

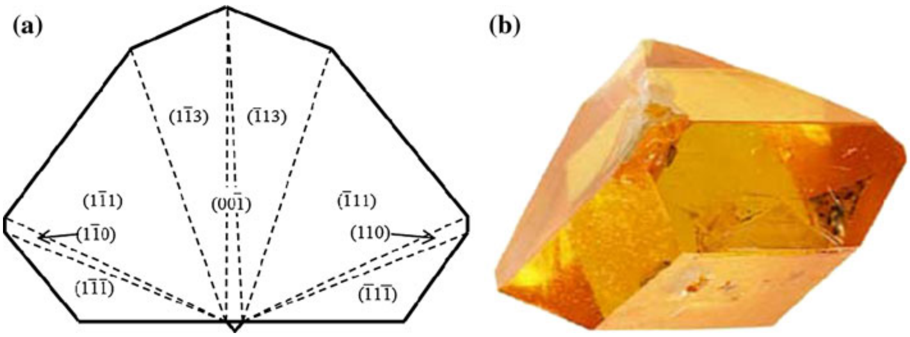

Fig. 2 **a** Schematic of growth planes in a lab-grown diamond exhibits major octahedral {111} plane with minor dodecahedral {110} and trapezohedral {113} planes. **b** As-grown deep *yellow* (or *orange*) diamond (Color figure online)

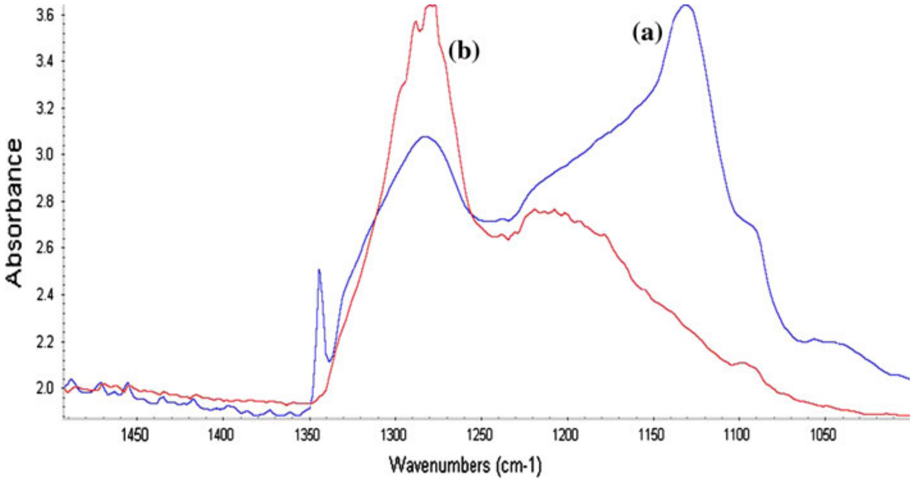

Fig. 3 Infrared absorption spectra in one-phonon region for **a** as-grown diamond and **b** after HPHT treatment at 2173 K and 5.5 GPa for 1200 min

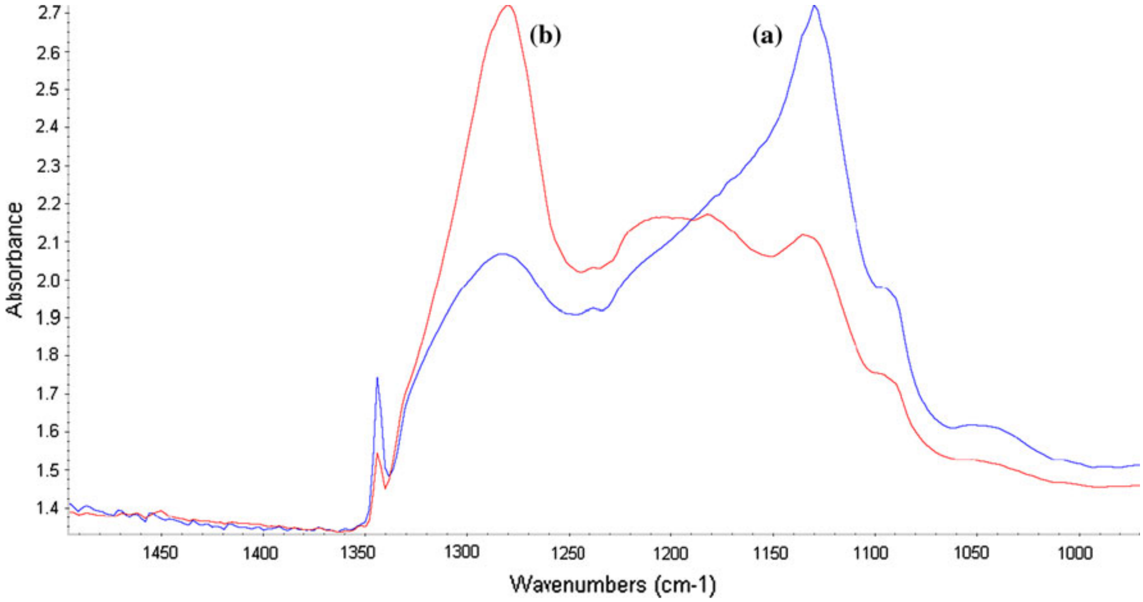

Fig. 4 Infrared absorption spectra in one-phonon region for **a** as-grown diamond and **b** after irradiation and HPHT annealing at 1773 K and 5.5 GPa for 20 min

at 1365 cm^{-1}, known as a 'platelet' defects. However, in this study, these peaks were negligible and did not change significantly upon annealing. The ratio of the C-center nitrogen atoms to those in the A-center was found to be approximately 2/1–4/1. In this respect, the distribution of nitrogen in the laboratory grown Ib diamonds is

Table 1 Rate constants and nitrogen concentration change according to annealing times

Sample #	*P*	*T* (K)	*t* (min)	**N_C (Before) (ppm)	***N_A (Before) (ppm)	N_C (after) (ppm)	N_A (after) (ppm)	10^5 k (min^{-1} ppm^{-1})	Absorbance at 1332 cm^{-1}
HPHT #1	5.5 GPa	2173	300	161.4	26.4	59.9	90.9	3.7	0.07
HPHT #2	5.5 GPa	2173	300	131.7	17.2	59.4	79.3	3.1	0.04
HPHT #3	5.5 GPa	2173	45	91.6	21.9	50.7	62.2	7.1	0.09
HPHT #4	5.5 GPa	2173	1200	109.2	25.0	23.7	76.5	2.8	0.03
*HPHT #5	5.5 GPa	2173	536	106.7	25.9	51.5	106.5	1.9	<0.01
HPHT #6	5.5 GPa	2473	25	137.0	28.0	66	83	41.9	0.04
	5.5 GPa	2473	60	66.0	83.0	36	101		
HPHT #7	5.5 GPa	2373	120	94.0	25.0	47	96	8.8	0.03
IrrHT #1	10^{-6} Torr	1773	8	101	19	84	36	25.4	0.04
	10^{-6} Torr	1773	60	84	36	37	74		
IrrHPHT #1	5.5 GPa	1773	20	112.0	16.0	91.0	29.0	6.1	0.02
	5.5 GPa	1773	60	91.0	29.0	60.3	61.0		
IrrHPHT #2	5.5 GPa	1973	112	69	9	24	52	23.2	0.02

* HPHT #5 sample was produced by using pure Fe catalyst

** N_C is the C-center nitrogen concentration and *** N_A is A-center nitrogen concentration

considerably different than for natural type Ia diamonds. The latter mostly have total nitrogen impurity in the range of 10–3000 ppm, but most of them are present in the aggregated form of pairs, trios, quartets, or even platelets ranging in size from a few nano meters to microns [16].

After heat treatment of all samples, the deep yellow (or orange) color of Ib diamonds changed to light yellow, similar to that of type IaA natural diamonds. The red line, marked as (b) in Fig. 3, signifies absorption spectrum after HPHT annealing at 2173 K and 5.5 GPa. It can be seen that the peak at 1280 cm^{-1} increased substantially upon annealing with concomitant reduction but was still detectable at 1130 cm^{-1}. It is also observed that 1344 cm^{-1} becomes invisible after annealing.

Figure 4 shows the spectrum change by HPHT annealing with irradiation at 1773 K and 5.5 GPa for 60 min after pre-heating at 973 K for 3 h. Similar to Fig. 3, absorption of nitrogen at the A-center now dominates at 1280 cm^{-1}, and absorption at 1130 cm^{-1} is reduced significantly. Compared to non-irradiated diamonds, additional continuum absorption is evident in 1300–1200 cm^{-1}.

The reciprocal of C-center nitrogen concentration of the as-grown samples before and after annealing at 5.5 GPa are plotted in Fig. 5. All crystals were grown using Fe–Ni catalyst except sample HPHT #5 which was grown in a pure Fe catalyst. This sample shows the slowest nitrogen aggregation rate at 2173 K annealing. For these samples, as listed in Table 1, the initial C-center concentration varied from 91 to 161 ppm, which changed from 24 to 60 ppm after annealing. In comparison, Fig. 6 shows the change in the reciprocal of C-center nitrogen concentration using irradiation before and after annealing. For comparison, HPHT #6, which was annealed at 2493 K and 5.5 GPa without irradiation, is included in this figure as well. Here, the IrrHT #1 sample shows a fast aggregation rate even at the relatively low temperature of 1773 K. It is also found that aggregation rates are comparable between IrrHT #1, IrrHPHT #2, and HPHT #6 of which aggregation rate constants are 25.1 × 10^{-5}, 23.2 × 10^{-5}, and 41.8 × 10^{-5} min^{-1} ppm^{-1}, respectively, as discussed later. By considering the annealing temperature, it is evident that irradiation process accelerated nitrogen aggregation efficiently even at much lower temperatures relative to HPHT annealing. Furthermore, even between

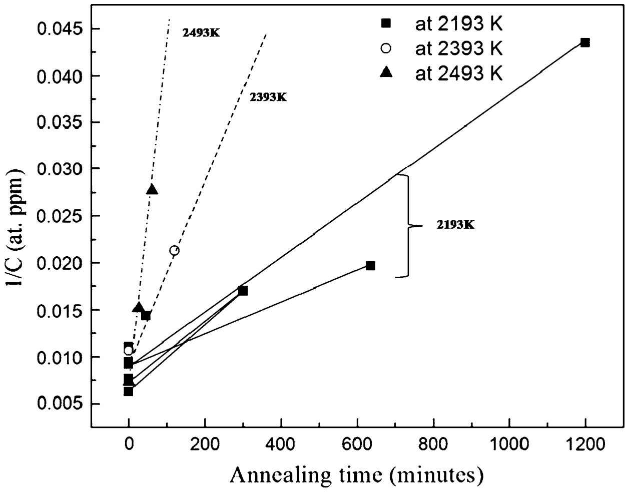

Fig. 5 Change of inverse nitrogen concentration at C-center during annealing at different temperatures: *solid squares* at 2193 K + 5.5 GPa, *hollow circles* at 2373 K + 5.5 GPa, and *solid triangle dots* at 2473 K + 5.5 GPa

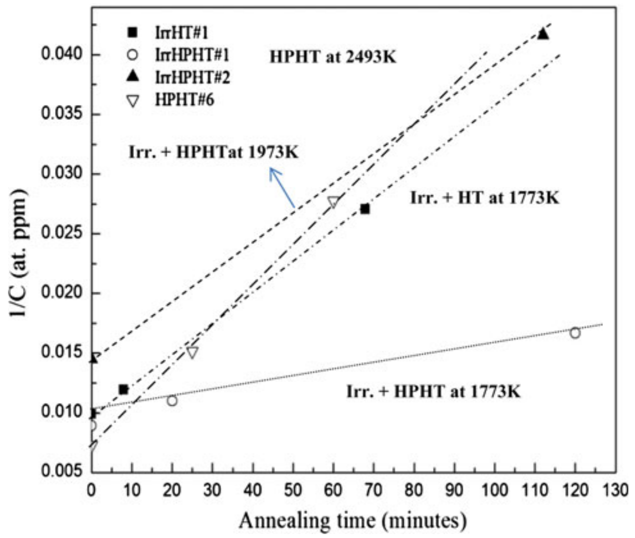

Fig. 6 Inverse of nitrogen concentration at C-center versus annealing time at various experimental condition described in the text and summarized in Table 1

irradiated samples, the aggregation rate was faster when the samples were treated in a high vacuum rather than in high pressure. By assuming that the nitrogen aggregation process follows second order kinetics (Eq. 3 in discussion) as proposed by Chrenko et al. [3], the average aggregation rate constant of sample HPHT #1 to HPHT #4 at 2173 K was found as 4.18 × 10^{-5} min^{-1} ppm^{-1}. As shown in Table 1, sample HPHT #3 showed a high-aggregation rate constant of 7.1 × 10^{-5} min^{-1} ppm^{-1} at 2173 K of the annealing temperature; at the same time, absorbance at 1332 cm^{-1} in the infra-red region is relatively high compared to samples annealed under the same condition. Large variation of aggregation rates was observed even with using same metallic catalyst, growth rate, and annealing temperature. At 2373 K, the aggregation rate constant was 8.8 × 10^{-5} min^{-1} ppm^{-1}, and increased to 41.9 × 10^{-5} min^{-1} ppm^{-1} at 2473 K. The same sample was treated twice at 2493 K and 5.5 GPa. The first run held for 25 min and, subsequently, the second run was performed for 60 min after FT–IR measurement.

Discussion

The aggregation rate constant, *k,* varied from 1.9 to 7.1 × 10^{-5} min^{-1} ppm^{-1} under the same annealing conditions of 2173 K and 5.5 GPa. Based on collision theory, it can be expected that the nitrogen atoms will aggregate faster in samples that contain a higher-nitrogen concentration. As shown in Table 1, the initial C-center nitrogen concentration of samples HPHT #1 and #3 were 161 and 91 ppm, respectively. However, the aggregation rate was much faster for HPHT #3. It is also seen that aggregation rate of HPHT #5 was slower than for HPHT #3 although HPHT #5 has more C-center nitrogen amount. The only difference between the two samples was that HPHT #3 was grown with the Fe–Ni catalyst, while HPHT #5 was grown with the pure Fe. Thus, the difference could not be attributed to the errors in measuring temperatures as both samples were treated using the same power setting and cores. As such, the potential difference between the two is the difference in the nickel impurity content of the samples. It has been reported that Ni can accelerate the nitrogen aggregation rate by two to four times because Ni can create another vacancy or interstitial sources when incorporated in the diamond lattice. The presence of Ni can be detected in the infra-red region by an absorption at 1332 cm^{-1} [8, 10]. In Figs. 3 and 4, this peak is not clear, because the absorption of Ni defect in a diamond is relatively small. The absorption at 1332 cm^{-1} can be noticeable using peak analysis software. Furthermore, it needs to be noted that the absorbance at 1332 cm^{-1} is only detectable in a high nitrogen concentration (>50 ppm). For nitrogen concentrations less than 50 ppm, the Ni atom can be detected by electron-spin-resonance (ESR) [12, 17]. These ESR study show, the absorbance at 1332 cm^{-1} is associated with Ni^{-} with effective spin of $s = \frac{3}{2}$ It has been shown that single substitutional nitrogen acts as a stronger donor element in the diamond, leaving Ni and the vacancy center in a negatively charged state. All the samples in this study had much higher than 50 ppm of nitrogen contents, so Ni amount can be quantified with 1332 cm^{-1} peak in the infra-red region as summarized in Table 1.

Figure 7 shows that the Ni content can enhance the nitrogen aggregation rate. The aggregation rate is the slowest in sample HPHT #5, which was grown using the pure Fe catalyst. Although a few researches reported Ni-free

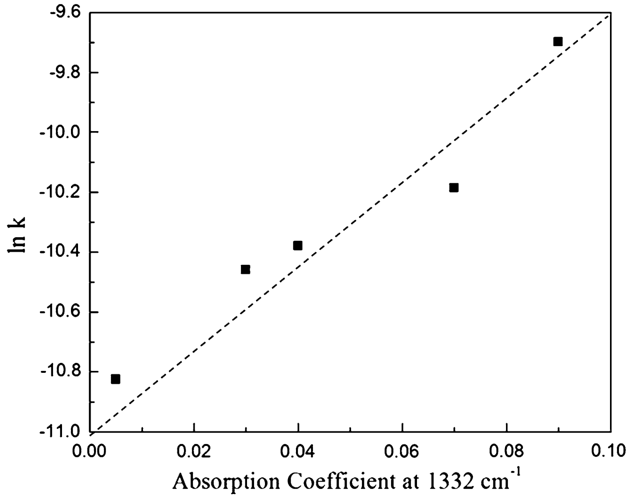

Fig. 7 Relationship between absorption coefficient at 1332 cm^{-1} and ln(*k*) min^{-1} ppm^{-1} for as-grown diamonds after annealing at 5.5 GPa and 2173 K

diamonds with a negligible aggregation rate, a considerable amount of nitrogen was still aggregated in this study. This may indicate that Ni can enhance the nitrogen aggregation process but Ni is not the root cause of aggregation. In addition, it has been shown that Ni atoms can be incorporated easily in the {111} plane of the diamond. In {100} and {110}, however, Ni incorporations are insignificant even when diamond is grown in a pure Ni catalyst [8]. At the same time, it is well known that the diamond shape depends on its growth temperature with the same metallic catalyst [14]. In the Fe–Ni catalyst, as shown in Fig. 2, the {111} plane is dominant at high-temperature growth conditions. As the growth temperature decreases, {113} and {110} planes appear, and their surface area becomes more prominent. When diamond is produced near melting temperatures of Fe–Ni catalyst, the {100} plane becomes dominant [14, 15]. Although {100} growth plane is rarely seen, in this study, variation of the {113} plane size can suggest that there may have been some temperature difference during sample diamond growth. Since Ni can be incorporated in easily {111} relative to {113} and {100}, it can be thought that sample HPHT#3, which shows the fastest aggregation rates at 2173 K annealing, was grown at a relatively high temperature.

Mathematically, Chrenko et al. [3] determined that the nitrogen diffusion process obeyed second order kinetics.

$$\frac{1}{C_0} - \frac{1}{C_t} = kt, \tag{3}$$

where C_0 is the initial concentration of nitrogen at the C-center and C_t is C-center concentration at time t, k is the aggregation rate constant (min^{-1} ppm^{-1}), and t is the annealing time in minutes. The aggregation rates calculated using the above equation are given in Table 1. Kluyev et al. [4] claimed that their measurement followed an exponential relationship:

$$\frac{C_0}{C_t} = \exp(k' t^n), \tag{4}$$

where n is experimental constant and chosen to 3/2. Using this equation, the average aggregation rate constant, k', of HPHT#1–5 was calculated as 3.77×10^{-5} min$^{-3/2}$ at 2173 K.

Figure 8 shows the nitrogen concentration change at the C-center after annealing at time t using Eqs. 3 and 4. Two initial C-center nitrogen concentrations were selected arbitrarily at 90 and 160 ppm, because the range of initial C-center nitrogen concentrations is from 91 ppm (HPHT #3) to 161 ppm (HPHT #1), respectively. As can be seen, the present measurements show better agreement with the second order kinetics in considering the initial nitrogen concentration of each sample. It needs to be noted that the difference of these two models can be recognizable between about 600 and 5000 min annealing. Even after such long annealing, the C-center concentrations become very close regardless of the initial nitrogen concentration, making it difficult to differentiate between the two models again.

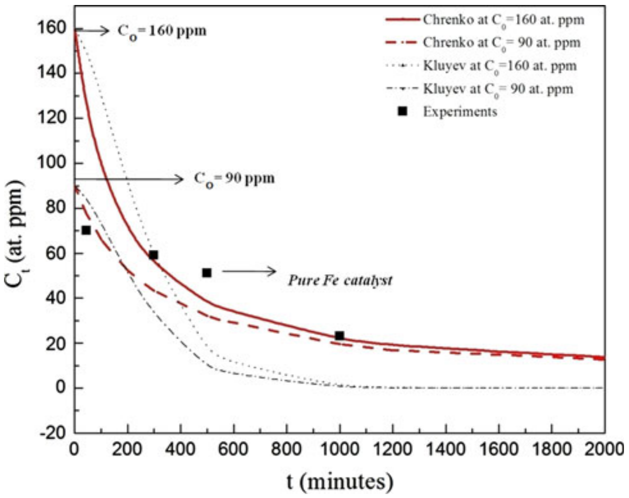

Fig. 8 Nitrogen concentration at C center, C_t, change versus annealing time at 5.5 GPa and 2173 K

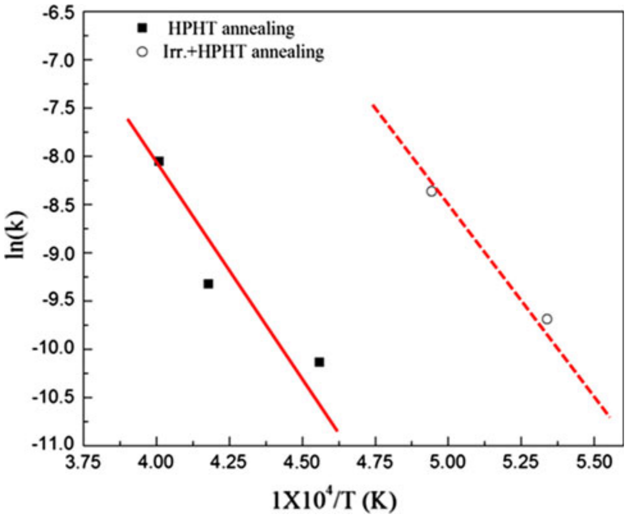

Fig. 9 Relationship between ln(k) versus inverse temperature for diamonds after HPHT annealing and irradiation + HPHT annealing

As shown in Fig. 9, the activation energy of non-irradiated and irradiated samples were calculated as 3.01 ± 0.4 eV (=69.51 kcal/mol) and 2.88 ± 0.4 eV (=67.30 kcal/mol), respectively, using rate constants from second order kinetics as shown in Eq. 3. Both calculated activation energies are within the error range. From the Arrhenius equation, $k = A\exp\left(-Q/_{kT}\right)$, where A is the pre-exponential factor, Q is the activation energy, and k in the Arrhenius equation is the gas constant, it can be found that nitrogen diffusion mechanism for its aggregation is the same and the difference of aggregation rate constant, *k*, is solely caused by the pre-exponential factor, *A*. The difference in the pre-exponential factor should be attributed to the irradiation process, which introduces more vacancies or interstitials in the diamond lattice.

Although it is clear that nitrogen aggregation follows the second order kinetics and the activation energy is very close regardless of the presence of irradiation process, it is still important to delineate the atomic mechanism or mechanisms for the aggregation of nitrogen atoms. The most probable second order reactions in diamond can be enumerated as follows:

$$\mathrm{N} + \mathrm{N} = (\mathrm{N}-\mathrm{N}) \tag{5}$$

$$(\mathrm{N}-\mathrm{V}) + \mathrm{N} = (\mathrm{N}-\mathrm{N}) + \mathrm{V} \tag{6}$$

Equation 5 is the second order kinetics involving nitrogen at interstitial sites ($\mathrm{N_i}$) and nitrogen at substitutional sites (N). Kiflawi et al. [8] claimed that nickel or irradiation can create carbon interstitials which can couple with nitrogen atoms, $\mathrm{C_i}$(–N), and exchange positions creating nitrogen interstitials, $\mathrm{N_i}$(–C). These nitrogen interstitials are believed to migrate and react with substitutional nitrogen according to Eq. 5. This mechanism can be called as interstitial-assisted diffusion. Since both nitrogen atoms at the nitrogen pair (A-center) are at substitutional sites, nitrogen interstitials coupled with carbon ($\mathrm{N_i}$–C) must return to nitrogen at substitutional sites ($\mathrm{C_i}$–N) to form nitrogen pairs. A possible reaction sequence can be then summarized as follows:

$$\mathrm{C_i} + \mathrm{N} \longrightarrow \mathrm{C_i}-\mathrm{N} \longrightarrow \mathrm{N_i}-\mathrm{C} + \mathrm{N} \longrightarrow (\mathrm{N}-\mathrm{N}) + \mathrm{C_i} \tag{7}$$

According to Mainwood et al. [9], the calculated dissociation energy of $\mathrm{N_i}$–C to N–$\mathrm{C_i}$ is 2.5 eV. Kiflawi et al. [8] also offered a characteristic peak at 1450 $\mathrm{cm^{-1}}$ as evidence for the presence of $\mathrm{N_i}$, but such a peak was not observed in this study. It is possible that the $\mathrm{N_i}$ concentration is low ($[\mathrm{N_i}] < 5$ ppm), which is below the detection limit of the analytical instrument (FT–IR).

By assuming vacancy as a catalyst, Eq. 6 can be another second order kinetics. The reaction steps can be summarized as:

$$\mathrm{N} + \mathrm{V} \longrightarrow (\mathrm{N}-\mathrm{V}) + \mathrm{N} \longrightarrow (\mathrm{N}-\mathrm{N}) + \mathrm{V} \tag{8}$$

Collins [5] observed the N–V pair formation at 973–1173 K and claimed that these pairs migrate in diamonds to meet other substitutional nitrogen atoms, resulting in the (N–N) pair formation as shown in Eq. 8. Based on the calculation by Mainwood et al. [9], the dissociation energy of N–V to N and V in Eq. 8 is the largest, 4.5 eV, in this series of reaction. Thus, Eq. 6 was claimed as the rate liming step and 4.5 eV could be the activation energy for vacancy-assisted mechanism of nitrogen diffusion. As pointed out by other researchers, the irradiation process should create vacancies and interstitials at the same time. Recently, it was reported that A-centers can trap vacancies by forming an H3 center (N–V–N) and expel carbon interstitials due to strain field created around A-centers [17, 18]. In this regards, both vacancies and interstitials can initially enhance nitrogen aggregation rate. Once some of nitrogen pairs are formed, interstitials may play a larger role in nitrogen mitigation, because vacancies cannot escape from the nitrogen pair. As a result, the measured activation energy of 2.88–3.01 eV, which is closer to interstitial-assisted mechanism rather than vacancy-assisted mechanism, appears to be reasonable N.

For practical application of annealing, it is necessary to know the relative time-dependent importance of various processing conditions (e.g., irradiation, high-pressure annealing, Ni catalyst, and pressurized annealing) on the aggregation of nitrogen atoms. This can be realized easily with the aid of Fig. (10). The curves in this figure shows the calculated nitrogen concentration change at the C-center at 1973 K for an arbitrarily chosen initial nitrogen concentration of 120 ppm using second order kinetics. The dotted line shows the nitrogen concentration change when a

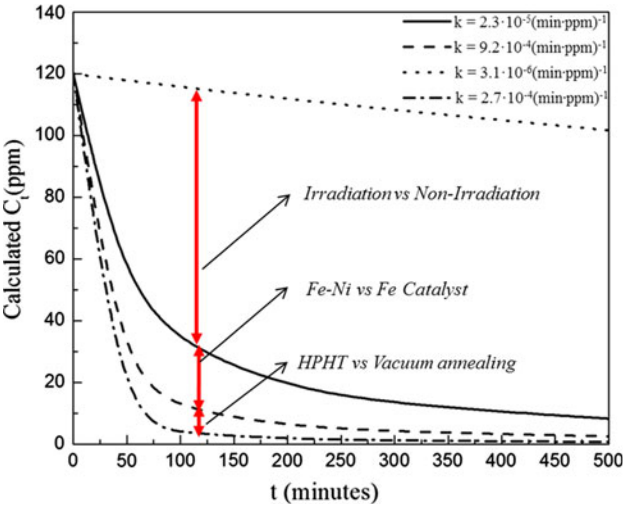

Fig. 10 Calculated nitrogen concentration change at C-center, C_t, versus annealing time at 5.5 GPa and 1973 K: The *dotted line* shows the calculated C-center nitrogen change using HPHT annealing without an irradiation process when a sample diamond is grown in Fe–Ni catalyst, the *solid line* shows the calculated C-center nitrogen change using HPHT annealing with an irradiation process when a sample diamond is grown in pure Fe catalyst, the *dashed line* shows the calculated C-center nitrogen change using HPHT annealing with an irradiation process when a sample diamond is grown in Fe–Ni as a catalyst, and the *dash-dotted line* shows the calculated C-center nitrogen change using vacuum annealing with an irradiation process when a sample diamond is grown in Fe–Ni as a catalyst

sample is heat treated at 1973 K and 5.5 GPa without irradiation. The rate constant used for the calculations at 1973 K was obtained by extrapolating the measured values at 2173, 2473, and 2473 K. The solid line is the calculated C-center concentration at 1973 K and 5.5 GPa with irradiation using rate constant using pure Fe catalyst. This curve excludes the effect of nickel on nitrogen aggregation. This rate constant was estimated from the measured one at 1773 K. The dashed line was drawn by using the measured rate constant of Fe–Ni catalyst. Finally, the dashed and dotted line is the C-center nitrogen concentration change when the sample is annealed at 1973 K and 10^{-6} torr of vacuum. As shown, nitrogen aggregation rate is enhanced by using irradiation, even with relatively weak irradiation conditions, and Ni catalyst. This enhancement is more pronounced at within 75–150 min of annealing. Beyond this time, their benefits seem to diminish. Annealing in a vacuum, rather than at high pressures, also enhances nitrogen aggregation. It has been speculated that nitrogen diffusivity may decrease in high pressure. However, vacuum annealing is still limited because extensive graphitization will take place for extended annealing times or temperatures. This graphitization was found to be severe near metallic catalyst inclusions, since the molten metal also catalyzes the reverse reaction from diamond to graphite. However, the problem of diamond to graphite transformation can be suppressed using high-quality stones and by controlling exposure-time and-temperature.

Conclusion

Lab-grown diamonds were annealed to change color from deep yellow to light yellow using two different methods. One method involved annealing at 5.5 GPa and 2193–2473 K and the other involved annealing of E-beam irradiated crystals at 1773–1973 K. Both methods showed that, upon annealing, C-center nitrogen defects decreased by 10–60% while A-center nitrogen defects increased by 5–70%. It has been shown that the irradiation and high-nickel catalyst enhanced nitrogen aggregation even with a relatively low dose of E-beam. Nitrogen aggregation in this study obeyed second order kinetics, and activation energies were very close regardless of the presence of irradiation. It is believed that the enhancement of nitrogen aggregation results from the addition of vacancies or interstitials. Although the nitrogen aggregation mechanism is still on debate, the measured activation energy is closer to interstitial-assisted nitrogen aggregation mechanism. This is reasonable since the nitrogen pair can entrap vacancies and expel carbon interstitials.

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