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Change of absorption spectra in type-I*b* diamond with heavy neutron irradiation

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For type-I*b* diamond neutron irradiated and annealed at 900°C, it has been found that the nitrogen vacancy (NV) center is reduced in density with increasing irradiation in the dose range above a certain value, and instead the 575 and 594 nm centers appear abruptly. This fact is interpreted in terms of change in the charge state of defects correlated with large change in the Fermi level produced by heavy irradiation. Based on the present results, a model is proposed for the 575 nm center: $(\mathrm{NV})^0$, a defect released one electron from the NV center. It has been observed that the growth nature of the 594 nm center with irradiation is different between types I*a* and I*b*. This difference is explained by difference in the Fermi level of both types.

I. INTRODUCTION

Nitrogen is the most prominent impurity in diamond and nitrogen-contained diamonds are classified into types I*a* and I*b*. The former contains the nitrogen atoms in aggregate form and the latter is in singly substitutional form, respectively. In type I*b*, the charge state of nitrogen is neutral: N^0,[1,2] and its electronic level is located at 1.7 eV below the conduction band. The balance between neutral and negative vacancies was discussed in detail by Davies *et al.*[3] According to them, the concentration of neutral vacancy (V^0) always exceeds that of negative vacancy (V^-) in electron irradiated type I*a*. In type I*b* most of them become singly negative (V^-) because of an electron supplied from the single nitrogen atom (N^0) through charge compensation.[4] Therefore, the Fermi level of type I*b* (it may be located near the energy level of the isolated nitrogen) is higher than the V^- state. Although the Fermi level of type I*a* is not known experimentally, it must be lower than the V^- state.

When the position of the Fermi level is changed in any way, some defects are converted into their negative or positive charge states and correspondingly new absorption peaks will appear. There appear to be several methods to control the Fermi level or the quasi-Fermi level: (1) impurity doping, (2) sample heating, (3) photoexcitation, and so on. The change in the charge state of vacancy mentioned above is an example of item (1) and the photochromism of the *H*2 and *H*3 centers is item (3).[5,6] Irradiation gives the fourth method and it enables one to control the amount of charge compensation centers to some extent.

The author observed the drastic change in the absorption spectrum of neutron-irradiated and annealed type-I*b* diamonds under high neutron dose: decrease of the NV centers and simultaneously sudden appearance of the 575 and 594 nm centers. This paper presents these phenomena to be explained by change in the Fermi level as an example of the fourth method. In order to demonstrate the phenomena clearly, type-I*b* samples with a high density of nitrogen atoms are prepared and the neutron dose is varied in a wide range. The neutron irradiation is suitable to introduce the radiation defects much more compared to the electron irradiation.

Concerning the NV, 575, and 594 nm centers many authors reported the experimental works. The NV center whose zero phonon line (ZPL) is located at 638 nm is the most dominant defect in irradiated and annealed type-I*b* diamond and the structure of this center is a pair of a substitutional nitrogen and a vacancy.[7] From beautiful works of hole burning,[8–12] optically-detected spin locking,[13] nearly degenerate four-wave mixing,[14] electron nuclear double resonance (ENDOR),[15] optically detected magnetic resonance (ODMR),[16,17] and so on, it is established that the ground state is spin triplet, the ZPL absorption corresponds to $^3A \rightarrow {}^3E$ transition and the charge state of the center is singly negative $[(\mathrm{NV})^-]$.

The 575 nm center also contains a nitrogen atom and several authors showed the similarity between the NV center and the 575 nm center in many points.[18–24] The remarkable point of the 575 nm center is the absorption to be very weak or difficult to detect, especially in the case of highly nitrogen-contained type-I*b* diamond, in spite of its strong luminescence. This fact will be understood from the present explanation as shown later.

The 594 nm center is first reported by Dugdale.[25] This nonluminescent center is observed in irradiated and annealed types-I*a* and -I*b* diamonds.[26,27]

II. EXPERIMENT

Samples used are types-I*a* and -I*b* diamonds neutron irradiated and subsequently annealed at 900°C. Type-I*a* diamonds were natural and contained nitrogen atoms of approx. 350 to 700 ppm. Type-I*b* samples were synthesized by Sumitomo Electric Industries Ltd., and the isolated nitrogen concentration estimated from the infrared absorption coefficient is around 100 ppm. The neutron irradiation was carried out with doses of 0.7×10^{16} cm^{-2} to 2.8×10^{18} cm^{-2} at Kyoto University Research Reactor Institute (KURRI). The energy distribution of fast neutrons is spread from 0.1 to 7 MeV with its broad peak around 2.5 MeV. The irradiation was made at an ambient temperature about 100 °C. After radioactivity is decreased sufficiently, samples were annealed at 900°C for 1 h, and the absorption spectra were measured in the wavelength region of 300 to 900 nm by 0.5 nm in spectral resolution at 80 K.

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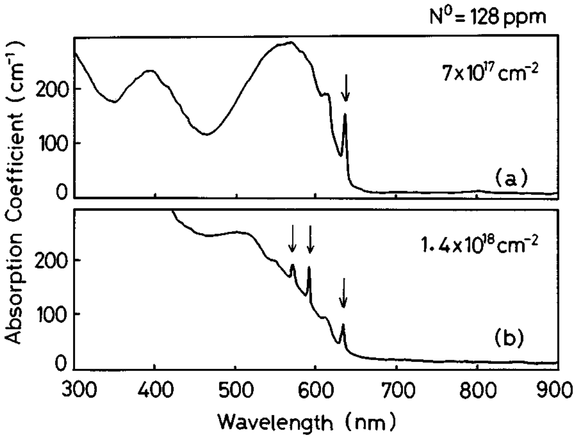

FIG. 1. Drastic change in the absorption spectrum of the same sample of type I*b* induced by twice the neutron dose. Nitrogen concentration is 128 ppm (2.25×10^{19} cm^{-3}) and the measurements were performed at 80 K. (a) Annealing at 900 °C followed a neutron dose of 7×10^{17} cm^{-2}. The dominant absorption is of the NV center which exhibits a zero phonon line (ZPL) at 638 nm. (b) After twice the same treatment with (a). The 575 and 594 nm centers are observed distinctly instead of decreasing NV center.

III. RESULTS

For type-I*b* diamond with the above treatment, usually the most dominant defect is the NV center, but heavy neutron irradiation makes this situation change drastically, as shown in Fig. 1. Figure 1(a) denotes the absorption spectrum of a sample containing 128 ppm single nitrogen atoms and annealed at 900°C after a neutron dose of 7×10^{17} cm^{-2} measured at 80 K. The spectrum exhibits the ZPL of the NV center at 638 nm, but the peaks at 594 nm and especially 575 nm are hardly detected. Figure 1(b) is of the same sample irradiated twice the same amount of neutrons additionally followed by annealing. Consequently the total dose is 1.4×10^{18} cm^{-2}. This denotes a decrease of the 638 nm peak height and a remarkable appearance of the 575 and 594 nm peaks.

Figure 2 shows the relation of the integrated zero phonon absorption intensities of the NV (full circles), 575 nm (open circles), and 594 nm (triangles) centers to the neutron dose. The absorption intensity of NV center increases linearly with the neutron dose in the low dose range up to 1×10^{18} cm^{-2}. Below, we call the dose regions below and above 1×10^{18} cm^{-1} the low dose and the high dose region, respectively. In the high dose range the absorption intensity of NV centers decreases, and at the same time, new absorption peaks of 575 and 594 nm centers appear.

In order to compare this growth nature of the 575 and 594 nm centers between types I*b* and I*a*, the absorption spectrum of type-I*a* diamond is shown in Fig. 3. In contrast to type I*b* [Fig. 1(a)], the 594 nm peak is seen clearly, but the 575 nm peak cannot be found. The latter fact is explained from the fact that the type-I*a* diamond used contains scarcely the nitrogen atoms in a single form. Another remarkable peak at 503 nm is the ZPL of the *H*3 center which is characteristic of type-I*a* diamond.[28]

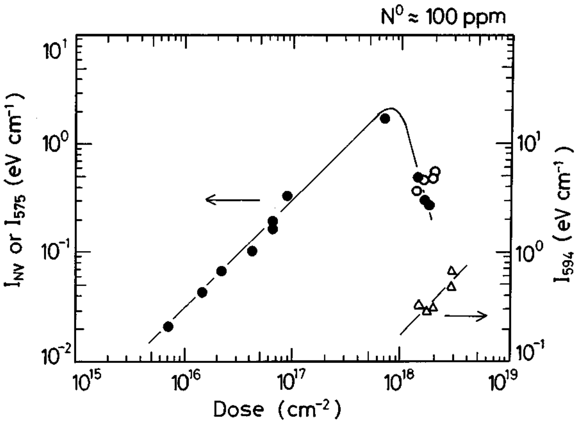

FIG. 2. Growth of the NV (full circles), 575 nm (open circles), and 594 nm (triangles) centers in type-I*b* diamond as a function of neutron dose. The NV center increases linearly with a dose up to 7×10^{17} cm^{-2} and then begins to decrease. The 575 and 594 nm centers appear abruptly around a dose of 1.4×10^{18} cm^{-2}. Samples used are different but their nitrogen concentrations are arranged to be approx. 100 ppm. All the measurements were performed at 80 K.

Figure 4 presents comparison on the dose dependence of the zero phonon absorption intensity of the 594 nm center between types I*b* (circles) and I*a* (triangles). There is a noticeable difference; in type I*a*, the 594 nm peak is observed over the whole range from the low dose, while in type I*b* it is observed only in the high dose range above 1×10^{18} cm^{-2} where the NV center is decreasing. In both types, the density of the 594 nm centers shows a linear increase with the neutron dose and the absorption intensity is quantitatively in a fairly well agreement.

IV. DISCUSSION

We discuss that the abrupt appearance of the 575 and 594 nm centers in the high dose range for type I*b* is ascribed to change in the charge state of defects arising from change in the Fermi level. The two centers are discussed separately. Figure 5 shows the qualitative energy level scheme to interpret the experimental results.

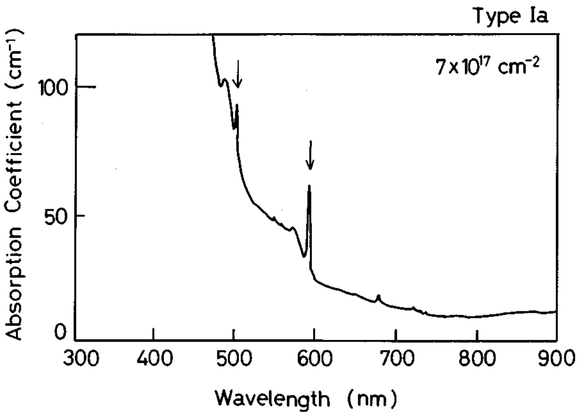

FIG. 3. 80 K absorption spectrum of type-I*a* diamond with similar treatment. Neutron dose is 7×10^{17} cm^{-2}. In contrast to type I*b* [Fig. 1(a)], the 594 nm peak is observed remarkably. Another peak at 503 nm is the ZPL of the *H*3 center.

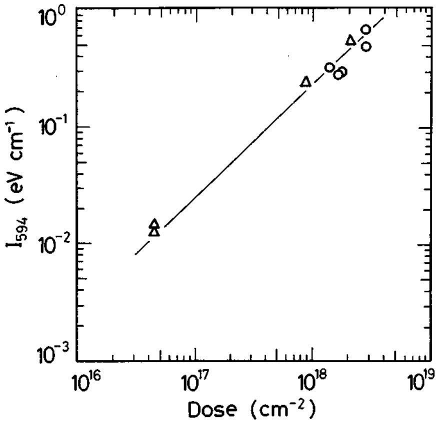

FIG. 4. Comparison of the dependence of the 594 nm center on the neutron dose between types I*a* (triangles) and I*b* (circles) at 80 K. The nitrogen concentration of the latter is around 100 ppm. Experimental points for both types stand in the same linear line but there is a noticeable difference: for type I*a* this center is observed from the low dose range, while for I*b* it bring out itself only in the high dose range where the NV begins to decrease (above 1×10^{18} cm^{-2}).

A. The 575 nm center

We describe the proposal for a model that the 575 nm center has the same structure with the NV, but is removed one electron from it. Among the NV center and the 575 nm, several common features are pointed out as follows. (1) They contain one nitrogen atom from two independent experiments of the ^{15}N isotope effect of the phonon replica,[23] and the linear growth with increasing number of implanted nitrogen ions,[21] (2) the symmetry is C_{3V} from the absorption measurement under the uniaxial stress[19] and external electric field,[20] and (3) both of them contain a vacancy.[21]

Since the charge state of the NV is $(NV)^-$, the 575 nm is assigned to $(NV)^0$. In Fig. 5 the energy level of the neutral nitrogen N^0 is situated at 1.7 eV below the conduction band, based on the photoconductivity measurement.[1] We assume the Fermi level of type I*b*, $E_F(Ib)$, is located near at the energy level of the nitrogen atom. The level of the $(NV)^-$ is deduced to be at the position lower than 2 eV from the conduction band for the following reason. If the excited state of the NV center comes into the conduction band, its ZPL would not be so sharp due to the resonance interaction. Hence the energy difference between the ground state and the conduction band must be larger than the zero phonon energy (1.945 eV). Similarly the ground state of the 575 nm center should be located at least 2.2 eV below the conduction band. In Fig. 5 the position of the ground state of the 575 nm center is expressed only qualitatively except for its position lower than the $(NV)^-$ state.

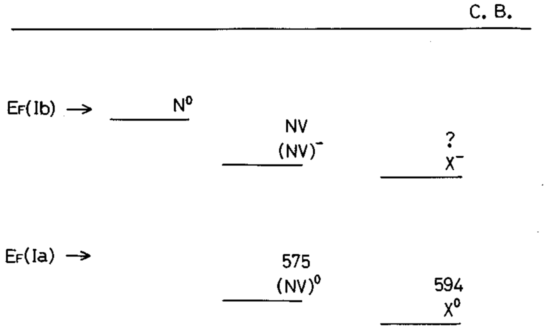

FIG. 5. Proposal for the qualitative energy level scheme of the NV, 575, and 594 nm centers. Level of the neutral state of nitrogen impurity N^0 is based on the result of Ref. 1. The so-called NV center corresponds to $(NV)^-$ in the charge state and the 575 nm does to $(NV)^0$ with the same atomic configuration. The charge state of the 594 nm center is assumed tentatively to be neutral (X^0) and its singly negative charge state (X^-) has not been observed. Notations, $E_F(Ia)$ and $E_F(Ib)$ represent the position of the Fermi level of types I*a* and I*b*, respectively.

The neutron irradiation produces Frenkel pairs and a vacancy migrates above 650 °C to combine with a nitrogen atom to form an NV center,[7] i.e., an $(NV)^-$ state. These two step reactions are summarized by an equation:

$$2N^0+V^0\rightarrow(NV)^-+N^+. \quad (1)$$

The formation of one NV center wastes two isolated neutral nitrogen atoms and consequently the Fermi level shifts towards a lower energy. This process gives an explanation for the linear growth of the NV centers with the dose, as shown in Fig. 2. The reaction (1) will continue till the Fermi level reaches the energy level of the $(NV)^-$ state, and all of the nitrogen atoms are ionized. The Fermi level in the low dose range is varied between $E_F(Ib)$ and the energy level of $(NV)^-$.

In the high dose range starting from about a 1×10^{18} cm^{-2} dose, the vacancies introduced will not be able to form the NV center any more if all neutral nitrogen atoms are converted into N^+ or $(NV)^-$ according to Eq. (1). Further lowering in the Fermi level with increasing the vacancy concentration may be produced, for example, by the following reactions:

$$2(NV)^-+V^0\rightarrow(NV)^0+(NV_2)^-, \quad (2)$$

$$(NV)^-+2V^0\rightarrow(NV)^0+(V_2)^-, \quad (3)$$

under the condition for the levels of $(NV)^-$ and $(V_2)^-$ to exist lower than that of $(NV)^-$. Unfortunately, existence of the negatively charged nitrogen-divacancy complex $(NV_2)^-$ or the negatively charged divacancy $(V_2)^-$ has not been found experimentally. However, the conversion of $(NV)^-$ into $(NV)^0$ may occur from the common viewpoint that introduction of the radiation defects makes the Fermi level go down. Therefore the appearance of the 575 nm center and the decrease of the NV center will occur suddenly and just at the same time, as shown in Fig. 2. The above discussion entirely neglects the contribution of interstitial atoms since there is no detailed information about their behaviors. However the situation remains qualitatively unchanged so long as the interstitial atoms and their related complexes are deep centers with the level lower than the $(NV)^-$ state. From the above discussion, the turning point from the low dose ranges to the high is predicted generally to depend on the nitrogen concentration: the more nitrogen concentration will shift the turning point to the higher dose. This explains the experimental fact that the detection of the 575 nm absorption is difficult in particular for type I*b* with a large density of single nitrogen under light dose.

The introduction rate of vacancy is able to estimate based on the assumptions that all the vacancies are captured at a neutral nitrogen atom by annealing at 900°C and a neutral vacancy wastes two neutral nitrogen atoms according to Eq. (1): about $1\times10^{19}\ \mathrm{cm}^{-3}$ (half of nitrogen concentration) vacancies are introduced by the neutron dose of $1\times10^{18}\ \mathrm{cm}^{-2}$. Therefore the introduction rate of negative vacancies under present irradiation conditions is estimated about 10 cm^{-1}. Next, let us discuss the ZPL absorption intensities of an NV center and a 575 nm center. From above discussion the maximum density of the NV center is $1\times10^{19}\ \mathrm{cm}^{-3}$, and it corresponds about 2 $\mathrm{eV\,cm}^{-1}$ ZPL absorption (see Fig. 2). Therefore the ZPL intensity per NV center (f_{NV}) is $2\times10^{-19}\ \mathrm{eV\,cm}^2$. On the other hand, if all the reduced NV centers in the high dose region are converted to the 575 nm centers $(\mathrm{NV})^0$ only, the decrease density of the NV center is equal to the density of the 575 nm center. In the case of $1.4\times10^{17}\ \mathrm{cm}^{-2}$ neutron dose, the decrease of the NV center from the maximum value is estimated at $0.6\times10^{19}\ \mathrm{cm}^{-3}$ by using the data of Fig. 2 and the relation $f_{\mathrm{NV}}=2\times10^{-19}\ \mathrm{eV\,cm}^2$. Therefore the ZPL intensity per 575 nm center (f_{575}) and the ratio f_{NV}/f_{575} are obtained as $0.7\times10^{-19}\ \mathrm{eV\,cm}^2$ and about 3, respectively. Finally, according to the present model, the 575 nm center should be paramagnetic. Now the author is trying to detect it by ESR measurement.

B. The 594 nm center

Let us discuss the present result that the 594 nm center appears only in the high dose range for type I*b* but in the whole dose range for type I*a*. Since the structure of this center is not known, we denote it X. It is assumed that the optical absorption of the ZPL at 594 nm arises from the charge state X^0 and its energy level is located sufficiently below that of the $(\mathrm{NV})^-$, as shown in Fig. 5. Further its negatively charged state, X^-, is assumed to be near the $(\mathrm{NV})^-$ state, but not to be detected optically. When lowering of the Fermi level with increasing dose occurs in the manner discussed above, the abrupt appearance of the 594 nm center in the high dose range of type I*b* can be also understood by the change in the charge state of the 594 nm center from X^- to X^0. On the other hand, since the Fermi level for type I*a*, $E_F(\mathrm{I}a)$, is thought to be located much lower than that for type I*b*, it is explained that the X^0 state and hence the 594 nm center may be generated even in the low dose range.

In Fig. 4, the linear growth of the 594 nm center with dose is clear. The present observation reveals that the 594 nm center begins to appear around the annealing temperature of 300°C, which is much below at the temperature of vacancy migration. Furthermore it is mentioned more directly by Davies and Nazare that there is no relationship between the growth of this center and the destruction of the vacancy.[27] Therefore, it seems that the 594 nm center is an interstitial related center. In addition there is a report for the symmetry to be D_{3d}.[20] In diamond structure, for example, an interstitial atom located at the hexagonal or the bond center site satisfies this symmetry,[29] but the stability of interstitial atom to a high temperature such as 900 °C is unlikely. Further study is necessary to determine the structure.

V. SUMMARY

For type-I*b* diamond with a high dose of neutron and subsequent annealing, the drastic change in the absorption spectrum was observed: sudden decrease of the NV center and simultaneous appearance of the 575 and 594 nm centers. This phenomena were explained in terms of the lowering of the Fermi level induced by heavy irradiation. A model was proposed for the 575 nm center to be the neutral charge state of the NV, since the NV was established to the charge state, $(\mathrm{NV})^-$. The fact that the 575 nm is usually too weak to detect especially for type I*b* with high concentration of nitrogen can be understood by the fact that the high position of the Fermi level makes the charge state $(\mathrm{NV})^-$ exist mainly, but scarcely $(\mathrm{NV})^0$. Contrary to type I*b*, type I*a* with similar treatment showed the formation of the 594 nm in the low dose. This is ascribed to a difference in the Fermi level between the two types.

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