Evidence for vacancy-interstitial pairs in Ib-type diamond

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Diamonds containing nitrogen in different forms have been irradiated by 3–MeV electrons or ^{60}Co gamma photons and characterized by optical absorption (OA) and electron spin resonance (ESR). An unusually low production rate of vacancies (V) and interstitials (I) was observed in gamma-irradiated Ib-type diamonds (those containing isolated nitrogen) and pure IIa-type diamonds as compared to Ia diamonds (containing nitrogen clusters). Postirradiation annealing at temperatures above 300 °C strongly increased the V and I concentrations in Ib diamond, but not in IIa diamond. These results are explained as gamma irradiation of diamond predominantly produces V–I complexes instead of individual V and I defects. Strong effect of charge state on V–I recombination is revealed: In Ib diamond, V–I complexes are negatively charged and dissociate upon annealing. On the contrary, V–I pairs are neutral in IIa diamond, and they annihilate during irradiation. The OA, ESR, and positron annihilation signatures of the V^-–I pairs are identified.

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I. INTRODUCTION

Defects produced by electron, neutron, or ion irradiation of diamond have been intensively studied for already about 100 years. Most results have been obtained using optical absorption (OA) and electron spin resonance (ESR) techniques, and can be summarized[1,2] as follows: Irradiation of pure (IIa-type) diamond predominantly produces neutral vacancies (V^0) and interstitials (I^0) with concentration ratio V^0/I^0 in the range of 3–10. With the OA technique, V^0 is identified as a tetrahedral center exhibiting a zero-phonon line at 1.673 eV and labeled GR1; it has spin $S=0$ and is thus ESR inactive. I^0 is associated with the OA line at 1.86 eV and a tetragonal $S=1$ ESR center named R1. Vacancies are immobile during irradiation and start migrating only at temperatures $T>600$ °C. The behavior of interstitials is more complex: They migrate during electron irradiation performed at $T>100$ K. However after irradiation, interstitials are stable at room temperature and start migrating only at $T>400$ °C.[1] Enhanced mobility of interstitials in pure diamond during irradiation results in partial V^0-I^0 recombination. As a result, the production rate of vacancies and interstitials is relatively low in IIa diamond (see also Table I).[2]

Nitrogen is a dominant impurity in diamond. In Ib-type diamond nitrogen is present as an isolated substitutional donor center N_S^0. It can be detected by ESR or OA, and tends to charge most other defects negatively, thus itself converting to N_S^+. Therefore, irradiation of Ib diamond predominantly produces negative rather than neutral vacancies. V^- was identified with the 3.15 eV OA center named ND1 and the tetrahedral $S=3/2$ ESR center S1/S2. Very few single interstitials are produced in irradiated Ib diamond. However, postirradiation annealing at $T\sim400$ °C strongly increases the I^0 concentration. This annealing also enhances N_S^0 signals.[2–4] Therefore, it was suggested that after electron irradiation most carbon interstitials are captured by the N_S^0 centers and released only upon further annealing. The associated N_S–I complexes have been tentatively ascribed to the 2.367 and 2.535 eV OA centers.[2–4]

The defects responsible for the 2.367 and 2.535 eV centers are the major subject of this study. On the basis of gamma irradiation results, we will demonstrate that they most probably involve a negative vacancy and a carbon interstitial, but not nitrogen. We will further associate those defects with the previously characterized $S=3/2$ W11 and W13 ESR centers and discuss their positron annihilation signatures.

Type-Ia diamond contains nitrogen mostly in the aggregated A ($2N_S^0$) and B ($4N_S-V^0$) forms. Those defects are rather inactive electrically, but they produce significant elastic strain in the diamond lattice. It was suggested[2] that this strain could assist separation of V–I pairs thereby enhancing the vacancy production rate in Ia diamond relatively to IIa diamond (see also Table I). Another possible reason for this enhancement could be the observed capture of interstitials by nitrogen complexes, which could suppress V–I recombination. Note that contrary to Ib diamond, the captured interstitials are not released upon annealing in Ia diamond.[2]

Previously, damage in diamond was mostly studied using irradiation by MeV electrons or neutrons. However, this paper focuses on the production and annealing of *dominant* irradiation-related defects in diamond after ^{60}Co gamma irradiation. The ^{60}Co radioisotope emits 1.17 and 1.33 MeV photons. They produce damage in the diamond lattice mostly[5] via Compton scattered electrons, whose average energy is only ~0.5 MeV. Note that the minimum electron

TABLE I. Maximal (versus annealing temperature, see Fig. 1) concentrations of defects observed in Ia, Ib, and IIa diamond irradiated by 10^{19} ^{60}Co gamma photons/cm^2 or 2×10^{18} 3–MeV electrons/cm^2. Concentrations are expressed either in parts per million (ppm) or as the integral under the zero-phonon line (in meV/cm). Accuracies are about 30%.

Irradiation	Diamond type	I (ppm)	V^0 (ppm)	V^- (ppm)	V^- (meV/cm)	2.367 eV (meV/cm)	2.535 eV (meV/cm)
electron	Ia	3	16	3	250	<1	<1
gamma	Ia	0.03	0.14	0.03	2.5	<0.001	<0.001
electron	Ib	4	<0.1	16	1350	50	80
gamma	Ib	0.03	<0.001	0.16	14	2.1	2.3
electron	IIa	3	12	<0.1	<8	<1	<1
gamma	IIa	<0.003	0.004	<0.001	<0.1	<0.1	<0.1

energy required to displace a carbon atom in diamond lattice is ~0.2 MeV.[5] Therefore, the ^{60}Co Compton electrons produce little damage, as compared to MeV electrons or neutrons, and provide relatively little extra kinetic energy to the produced carbon interstitials.

II. EXPERIMENTAL DETAILS

Two similar sets of Ia, Ib, and IIa diamonds have been irradiated either by 2×10^{18} 3–MeV electron/cm^2 or by a 60 MGy dose (water) of ^{60}Co gamma photons, which is equivalent to 10^{19} photons/cm^2. The samples were mounted on a water-cooled (~10°C) block to minimize sample heating by the beam. The Ia diamonds were natural, but the Ib and IIa samples were grown using the high-pressure high-temperature technique. The Ib and Ia samples contained ~100 and ~500 ppm of nitrogen, respectively. The damage production rate in gamma-irradiated diamond is rather small.[5] Therefore, samples for which the absorption length was >5 mm have been used for most OA measurements on gamma-irradiated diamond. The OA spectra were recorded with a commercial Nicolet Avatar 360 Fourier-transform IR spectrometer in the range of 400–5000 cm^{-1} at room temperature and with a Perkin–Elmer Lambda 900 double-beam grating spectrometer in the range of 1.4–5.5 eV at 77 K. ESR measurements were performed at room temperature with a Bruker EMX X-band (~9.6 GHz) spectrometer. All of the reported results were reproduced on several samples.

III. EXPERIMENTAL RESULTS

The obtained results are summarized in Table I and Fig. 1. Table I lists the maximal concentrations of dominant defects encountered over the annealing temperature range of 0–600°C, while Fig. 1 presents their isochronal annealing curves for Ib diamonds. Note that due to the low production rate, the W11 and W13 ESR signals could not be reliably studied in gamma-irradiated diamonds and therefore are not shown in Fig. 1(b). As reported previously,[1,2] vacancies and interstitials in IIa and Ia diamond exhibit rather regular annealing curves, i.e., a plateau followed by a steplike decrease, which is therefore not shown either. On the contrary, Ib diamond exhibits rather interesting nonmonotonous annealing behavior, which will be the main subject of this paper.

A. Electron irradiation of Ib diamond

Most data of Fig. 1(a), in particular the annealing curves of the 2.367 eV, 2.535 eV, and I^0 defects in electron-irradiated Ib diamond, have already been reported and discussed previously.[2–4] There, it was suggested that irradiation of Ib diamond produces few interstitials because they are captured by N_S^0 centers. The resulting N_S^0–I defects exist in (at least) two configurations corresponding to the 2.367 and 2.535 eV centers. Those configurations interconvert upon annealing at $T\sim230$°C and disintegrate at $T\sim400$°C releasing the N_S^0 and I centers. Note that annealing out of I centers

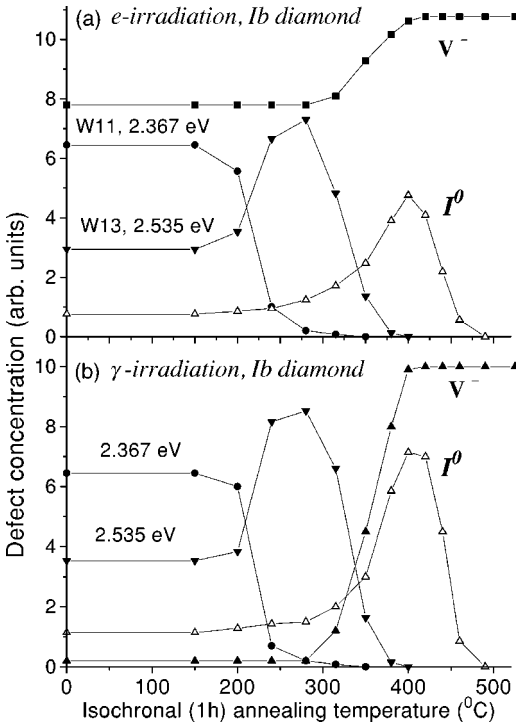

FIG. 1. Isochronal (1 h) annealing curves for dominant defects in electron- (a) and gamma- (b) irradiated Ib-type diamond. Both absolute and relative intensities are arbitrary.

at $T \sim 500\,^{\circ}\mathrm{C}$ is not unique to Ib diamond; it occurs in Ia and IIa diamond as well.[1,2]

It was tentatively proposed[3,4] that the 2.367 and 2.535 eV OA centers correspond to some of the ESR centers W11–14,[6] which are the dominant irradiation-induced ESR signals in Ib diamond. The current results corroborate this as indeed, Fig. 1(a) reveals a very similar annealing behavior of the W11 and 2.367 eV, as well as of the W13 and 2.535 eV centers, thus suggesting that they pairwise originate from the same defects. This conclusion for the W11 and 2.367 eV centers is further supported by the observation that they both correspond to excited states at ~2 meV above the ground state.[7,8]

B. Gamma irradiation

In this study, some remarkable results have been obtained from gamma-irradiated diamonds. Table I reveals that 10^{19} photons/cm^2 ^{60}Co gamma irradiation is about 100 times less efficient than 2×10^{18} 3–MeV electron/cm^2 irradiation in producing lattice damage in Ia and Ib diamond. However, the relative defect production rates in Ia and Ib diamond are rather similar. Also similar in electron- and gamma-irradiated diamond are the isochronal annealing curves for the vacancies and interstitials in Ia and IIa diamond (not shown), as well as for the I^0, 2.367, and 2.535 eV centers in Ib diamond (see Fig. 1). By contrast, the vacancy production rate in IIa diamond is ~3000 times weaker for gamma irradiation than for electron irradiation (Table I). Note that similar results were previously obtained by Newton *et al.*[9] However, the most important result of this study, presented in Table I and Fig. 1, is that in contrast with electron irradiation, the dominant defects produced by gamma irradiation in Ib diamond are not negative vacancies, but the 2.367 and 2.535 eV centers; annealing at $T \sim 400\,^{\circ}\mathrm{C}$ destroys those centers and increases the V^- concentration ~50 times.

IV. DISCUSSION AND CONCLUSIONS

The unusual results of the previous paragraph can be logically explained by the following model: Gamma irradiation of Ib diamond predominantly produces not individual vacancies and interstitials but V^-–I^0 complexes. Those complexes exist in different configurations, which interconvert upon annealing at $T \sim 230\,^{\circ}\mathrm{C}$. One configuration can be associated with the 2.367 eV OA center and the $S=3/2$ W11 center of triclinic symmetry. Another configuration is probably responsible for the 2.535 eV OA center and $S=3/2$ W13 center of monoclinic-I symmetry.[6] The V^- part of those complexes is responsible for the $S=3/2$ spin and for the characteristic value of spin-spin interaction, which was previously attributed[6] to a perturbation of V^- by a nearby species (I^0 in our model). Annealing at $T \sim 400\,^{\circ}\mathrm{C}$ destroys those complexes releasing V^- and I^0 defects.

Our data strongly suggest that, contrary to the previous tentative model,[2–4] nitrogen is not involved in those V^-–I^0 pairs. Indeed, no nitrogen hyperfine splitting (<0.1 mT) could be detected for the W11–14 centers in the present and previous[6] ESR studies. Moreover, considering that close V^-–I^0 pairs are the dominant defects produced by gamma irradiation of Ib diamond, it is hard to imagine how could they migrate to the N_S centers during irradiation. Note, that the changes with annealing in the N_S^0 and N_S^+ concentrations, which were previously considered as evidence for nitrogen involvement,[2–4] could simply originate from a charge transfer between the N_S and *V–I* complexes.

The discussed V^-–I^0 complexes have been recently characterized by positron annihilation studies on gamma-irradiated Ib diamond.[10] They exhibit a lifetime of 130 ps and unusually large positron trapping rate. The latter parameter strongly suggests involvement of V^- in the trapping center thus further supporting the proposed model.

As mentioned in the last paragraph of the Introduction, the formation of *V–I* complexes, instead of individual vacancies and interstitials, in gamma-irradiated diamond can be attributed to the mild nature of gamma irradiation. Contrary to conventional MeV electron beams, the Compton scattered electrons produced by ^{60}Co gamma source supply only a relatively small amount of kinetic energy to the displaced carbon atoms, which could be insufficient to separate the *V–I* pairs.

A significant finding of this work is that *V–I* pairs have been identified in gamma-irradiated Ib diamond, but not in IIa diamond. It probably demonstrates the effect of charge state on the recombination of *V–I* pairs as follows: In Ib diamond, *V–I* complexes are negatively charged and dissociate upon annealing. On the contrary, *V–I* pairs are neutral in IIa diamond and they recombine, either during gamma irradiation or upon annealing of electron-irradiated diamond.[2] Note, that neutral *V–2I* complexes have been previously identified by ESR in electron-irradiated IIa diamond.[11] Similar to the neutral *V–I* pairs, they recombine rather than dissociate upon annealing. The thus revealed effect of the charge state on the *V–I* recombination clearly requires further theoretical modeling.

Finally, the reported here results appear important for practical applications concerning radiation hardness of diamond electronic devices. In particular, the present study demonstrates the importance of diamond purity for its stability against gamma irradiation—Table I reveals that damage production in pure diamond is ~40 times smaller than in nitrogen containing diamond.

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