

200 keV energy electron irradiation of single-crystal diamond: Quantification of vacancy and nitrogen-vacancy production

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Electron irradiation and annealing treatments are a method of color center/defect creation in diamond. The depth profile of defects created by low-energy 200 keV electrons in single-crystal high-purity (type II) electronic grade diamond grown via chemical vapor deposition has been investigated. The depth profile of monovacancies created was found, using photoluminescence (PL), to decay exponentially, with a decay length $12 \pm 1 \mu\text{m}$ and a production rate of $(1.1 \pm 0.2) \times 10^{-1} \text{ V/e}^-/\text{cm}$ at the surface. The depth distribution of the neutral and negatively charged nitrogen-vacancy ($\text{NV}^{0/1-}$) center, and the 733 nm zero phonon line defect formed during an isochronal annealing study, have also been investigated by PL. The observed NV profiles, which do not match the vacancy profiles, can be qualitatively explained in terms of a simple model that includes the formation of vacancy clusters and the nitrogen-divacancy (NV_2) defect. The production of ($\text{NV}^{0/-}$) has been assumed to be nitrogen-limited, but this paper has shown that this is not the case, with NVs lost to the production of NV_2 when the concentration of vacancies greatly exceeds that of substitutional nitrogen.

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I. INTRODUCTION

The nitrogen-vacancy (NV) center in diamond [1] is a point defect that has received significant interest in recent years. The negatively charged state of the center (NV^-) exhibits long spin coherence times, and due to its sensitivity to electric and magnetic fields [2] and intrinsic room-temperature optical spin initialization and readout, it has many potential applications, such as sensing [3–5], nanophotonics [6,7], quantum memory [8], and quantum information processing [9,10].

Both single NV centers and ensembles of centers have been utilized across these technology platforms and hence the reliable creation of NV centers on demand is an important research field [11–13].

The neutral NV^0 has an optical zero phonon line (ZPL) at 575 nm (2.156 eV). NV^0 can also accept an electron from donors in the diamond forming NV^- , which possesses an optical absorption and luminescence ZPL at 637 nm (1.945 eV). NV^- can be converted to NV^0 via photoionization using light [14–16]. However, at room temperature >95% of the total

absorption and emission of both centers is via the broad vibronic sideband.

The precise positioning of these functional defects, such as single NV^- centers, and the optimisation of NV^- ensembles, whilst minimising the concentration of unwanted defects that degrade the useful NV^- properties is desirable [17]. To achieve this it is important to understand diffusion in the lattice, and the formation/destruction kinetics of related defects. Intrinsic defects such as interstitials and vacancies are known to assist the diffusion of carbon atoms and impurities [18,19]. Therefore, the understanding of these intrinsic defects is key in the pursuit of deterministic defect creation.

In this work we analyze the depth profile of the damage created by low energy (200 keV) electron irradiation in high purity, “electronic grade” diamond (< 5 ppb nitrogen, < 1 ppb boron). An isochronal annealing study has been carried out to measure the depth profile of the defects created, focusing on $\text{NV}^{0/-}$ centers and a center with a zero phonon line (ZPL) at 733 nm believed to be a multivacancy complex [20]. It is an interesting finding that the peak of the NV emission is at a depth of 60 μm below the surface, where the vacancy emission peaks.

Electron irradiation in diamond

The most common method of vacancy and carbon interstitial creation is irradiation or ion implantation. Irradiation can be carried out using neutrons, protons, gamma rays and

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electrons, all which differ in the damage profiles they cause. Ion implantation of non carbon elements has the added effect of introducing impurities into the lattice, in the form of the ions used [21]. Irradiation in conjunction with annealing treatments can be used to investigate diffusion, along with the mechanisms through which vacancies and interstitials are lost [11,22,23]. Electron irradiation is particularly attractive because of the ability to control the vacancy production [17]. The quantification of the vacancy production efficiency of irradiation methods is therefore important for the formation of defects.

The threshold energy of electrons required to create damage in diamond has been measured to be 145 ± 15 keV for a (100) incident direction, consistent with a displacement energy for a lattice carbon atom of 30 ± 4 eV [22]. Monte Carlo simulations have been used to predict the number of vacancies created per micrometer per depth created for 1, 2, and 5 MeV over a depth of 8000 μm and the resultant profiles demonstrated constant vacancy production profiles with sharp cut offs at a maximum depth [24]. Casino simulations of the depth profile of lower energy electrons (200 keV) have predicted a gradual decrease in vacancy production over a depth of 38 μm , beyond which the incident electrons are no longer able to generate vacancies [25]. Previous experimental measurements of the depth profiles of vacancies created by 300 keV electrons using a transmission electron microscope have been observed to decrease gradually to a depth of 140 μm [26].

II. EXPERIMENTAL DETAIL

A. Sample preparation

The sample studied here is an (001) oriented $2.09 \times 2.09 \times 0.52$ mm electronic grade plate grown via chemical vapor deposition (CVD) by Element Six [27]. It is specified to contain <1 ppb boron and <5 ppb nitrogen impurities.

The sample was irradiated using a “PCT Ebeam and Integration” CE60120 Ebeam lamp. 200 keV electrons were used with an estimated dose of 10^{19} e^-/cm^2 perpendicular to the 2.09×2.09 mm face. The electrons traveled through air before arrival at the sample surface, however the path length was minimized to reduce energy loss (approx. 32 mm). A comparison of the depth profile with that of an irradiation carried out in a vacuum by a 200 keV transmission electron microscope indicated that the energy loss was negligible. After irradiation the 2.09×0.52 mm laser cut sides were polished to allow photoluminescence (PL) measurements of the depth profile of luminescent defects from the polished sides.

B. Methods

Optical absorption measurements were made postirradiation, using a Perkin Elmer Lambda 1050 spectrometer through the large face in the same direction as irradiation, with the sample held at 77 K.

The sample was annealed in an Elite Thermal Systems tube furnace at atmospheric pressure in a nitrogen atmosphere for an hour at 400, 600, 800, 1000, and 1200 $^{\circ}\text{C}$. A traceable calibrated thermocouple was used to measure the furnace temperature at the sample position to ensure the quoted

annealing temperature was achieved. The sample was held in a ceramic crucible and buried in a sacrificial layer of diamond grit to prevent surface graphitization. At each annealing stage the sample was loaded at the stated annealing temperature, a process that takes approximately 15 minutes to minimize thermal strain on the crucible. At higher temperatures, the change in concentration of defects can be significant even for short loading times.

Confocal PL line scans were taken both at room temperature and at 77 K in a liquid nitrogen cryostat across the 2.09×0.52 mm side to measure the depth profile of the defects after each annealing stage. Spectra were taken using 660, 514, and 488 nm excitation on two different spectrometers—a Horiba LabRam HR Evolution and a Renishaw inVia Raman Microscope.

III. RESULTS

A. Vacancy damage profile

After irradiation, absorption measurements were performed to quantify the irradiation damage. Only the neutral charge state of the vacancy V^0 , was visible in the absorption spectra with a ZPL at 741 nm (known as the GR1 peak). No signal was observed from the negatively charged vacancy V^- in absorption, which has a ZPL at 393.5 nm (ND1). Given the sample contains $< 5\text{ppbN}_s$ the majority of the vacancies are expected to be in the neutral charge state after irradiation [28]. The average number of vacancies per unit volume was measured to be $(2.5 \pm 0.5) \times 10^{15}$ V/cm^3 across the whole diamond thickness of 0.52 mm, equivalent to 14 ± 3 ppb, if the vacancies were homogeneously distributed through depth. A calibration constant of $(1.2 \pm 3) \times 10^{-16}$ meV cm^2 [29] was used to convert the area under the GR1 ZPL to a concentration.

To determine the depth profile of the V^0 PL after irradiation, a line scan of the GR1 sideband at room temperature was taken across the polished side of the sample with a 2 μm step size [30], as indicated in Fig. 1(e). The laser was focused 10 μm below the surface of the side. The measured depth profile is a convolution between the actual defect concentration profile and the spatial point spread function of the Raman spectrometer. To analyze the data some assumptions have been made. An exponential decay has been assumed for the V^0 concentration as a function of depth from the irradiated surface, $h(x)$, supported by results reported in previous studies [26] and a Gaussian function with a width of 2.1 μm was used to model the spectrometer spatial response function. The resultant convolution, detailed in the supporting information [31], was fit to the GR1 depth profile [Fig. 1(a)], allowing the exponential decay constant to be determined as $t_0 = 12 \pm 1$ μm .

Having determined the decay constant of the GR1 PL depth profile, we can now use the PL in conjunction with the absorption measurements to calculate the spatial distribution of vacancies per unit volume with depth (assuming the PL intensity of the GR1 sideband is proportional to V^0 concentration). By integrating over the distribution measured using PL and normalising the area to the absorption data, the

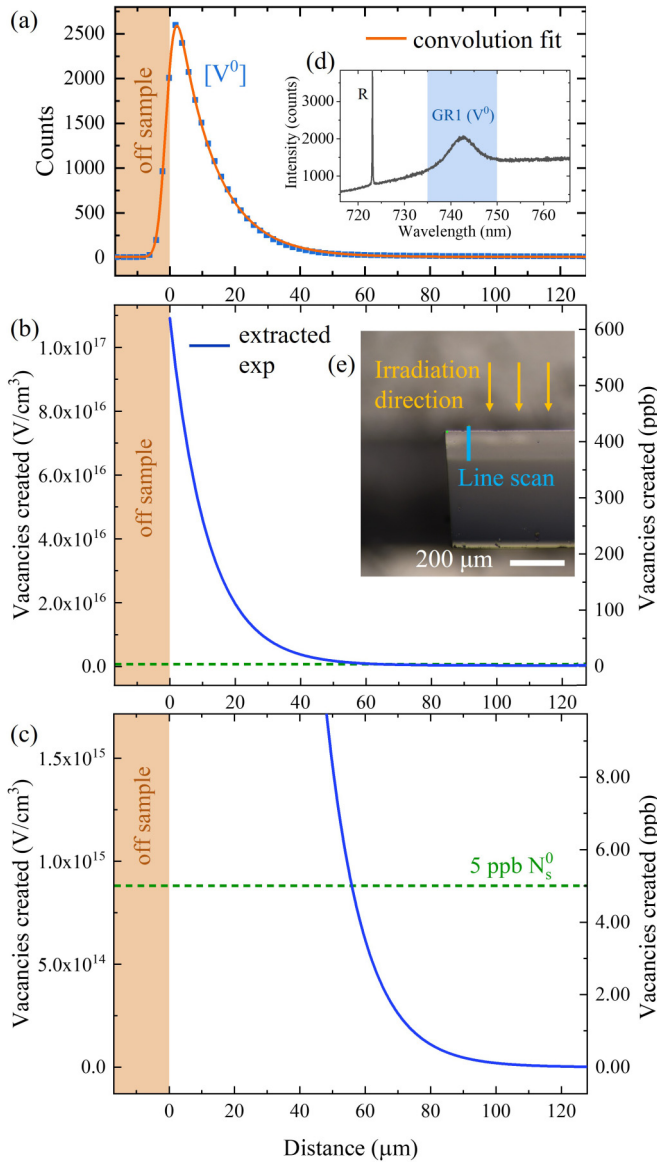


FIG. 1. (a) Room-temperature PL line scan showing the spatial depth profile of GR1 sideband as irradiated, fit with a convolution of a Gaussian and peak and an exponential decay. 660 nm excitation used with a 0.9 NA $\times 100$ objective, resulting in a 1 μ m spot size. (b) Plot of the exponential extracted from the convolution fit in (a). Area under the exponential has been normalized to the concentration determined by absorption measurements to calculate V^0 concentration with depth. Dotted line shows estimated nitrogen concentration present in the sample. (c) Magnified region of (b). (d) Example room-temperature GR1 spectra. Shaded region indicates integrated area. (e) White light image of the location of the line scan marked in blue.

PL depth profile can be converted into a quantitative vacancy depth profile, as shown in Fig. 1(b).

The V^0 profile shown in Fig. 1(b) is given by

$$[V^0] = (1.1 \pm 0.2 \times 10^{17}) \exp\left(-\frac{x}{12 \pm 1}\right) / \text{cm}^{-3}. \quad (1)$$

Equation (1) can be used to derive the V^0 concentration at the surface: $(1.1 \pm 0.2) \times 10^{17} \text{ V/cm}^3$ or 600 ± 100 ppb.

To study the annealing of vacancies as a function of temperature, line scans of the GR1 PL depth profile from the polished side of the sample were measured at each stage of an isochronal annealing study. Measurements made during the annealing study were carried out at liquid nitrogen temperatures, and therefore the defect ZPLs were fitted instead of the sidebands. Due to the cryostat used, measurements were made using a $\times 50$ long working distance objective with a numerical aperture of 0.5, as opposed to the $\times 100$ objective used to measure the profile in Fig. 1. The spectrometer response function of these measurements is therefore different; further discussion of this is given in [32]. No change was observed to the V^0 GR1 PL intensity depth profile after the 400 and 600 $^\circ\text{C}$ anneals. The V^0 PL depth profile is decreased by the same factor across the entire depth profile by the 800 $^\circ\text{C}$ anneal, shown in Fig. 2(a). This suggests that the fractional vacancy concentration loss is uniform throughout the sample. After the 1000 $^\circ\text{C}$ anneal however, the profile has changed shape, Fig. 2(b), with the highest V^0 concentration shifting to a depth of $49 \pm 2 \mu\text{m}$. There was no GR1 visible after the anneal at 1200 $^\circ\text{C}$, indicating the vacancies have formed complexes, recombined with interstitials, or lost to extended defects or surfaces.

B. Nitrogen-vacancy creation

Emission from NV^0/NV^- centers is detectable after the 800 $^\circ\text{C}$ anneal (Fig. 3). Measurements of the NV^0 and NV^- ZPL PL depth profiles were made using both 488 nm and a 514 nm laser excitation. The 488 nm excitation causes partial photoionisation $NV^- \rightarrow NV^0$, whereas the 514 nm laser allows the difference in the distribution of the NV^0 and NV^- charge states to be probed without significant perturbation of the charge state distribution.

After the 800 $^\circ\text{C}$ anneal the distribution of NV^0 was observed to be approximately Gaussian, assuming ZPL PL is proportional to concentration, with a peak position at a depth of $30 \pm 5 \mu\text{m}$ below the irradiation surface, Fig. 3(b). After the 1000 $^\circ\text{C}$ anneal an increase in NV^0 centers is observed across the whole depth profile, as seen with the 488 nm laser, and the peak of the depth profile is shifted to $48 \pm 5 \mu\text{m}$ [Fig. 3(a)]. The measurements taken with the 514 nm laser show a distinct difference in the profiles of the NV^0 and NV^- centers [Fig. 3(c)]. It is seen that the NV^- centers are present deeper into the diamond, with a profile that peaks at $64 \pm 5 \mu\text{m}$, as opposed to the NV^0 profile which peaks at $54 \pm 5 \mu\text{m}$.

After the 1200 $^\circ\text{C}$ anneal, another increase in both NV^0 and NV^- PL across the whole depth profile is observed with both lasers, however the shape of the NV^0 profile changes significantly, developing a shoulder in the shallow depth region. Signal from NV^- centers is also visible with the 488 nm laser, where previously it was not. The NV^0 profile measured with 488 nm excitation peaks at $49 \pm 5 \mu\text{m}$, while the NV^- profile peaks at $51 \pm 5 \mu\text{m}$. The NV^0 profile measured with 514 nm excitation peaks at $55 \pm 5 \mu\text{m}$, while the NV^- profile peaks at $60 \pm 5 \mu\text{m}$.

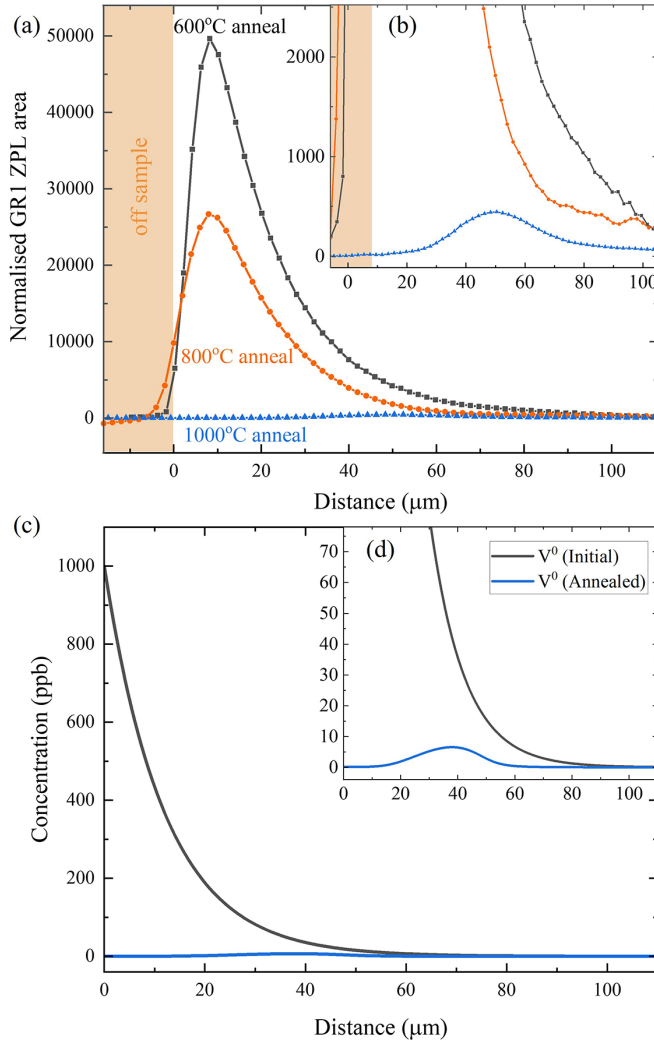


FIG. 2. (a) Cold PL line scans showing the spatial depth profile of GR1 ZPL after a 1 h anneal at 600, 800, and 1000 °C. Spectra were taken at 77 K and have been normalized by the Raman line. 660 nm excitation used with a 0.5 NA $\times$ 50LWD objective. Units are counts nm. (b) Magnified region of (a) for clarity. (c) Simulated vacancy concentration before and after a 1 h anneal at $T_1 = 1000^\circ\text{C}$. (d) Magnified region of (c).

C. The 733 nm ZPL center

The 733 nm ZPL has in recent years been attributed to a center consisting of multiple vacancies [33–35]. It has been observed in high-purity type IIa diamond irradiated and annealed to temperatures above 700 °C [20,26,33–35].

In this work it is observed to anneal in after the 1000 °C anneal and can be excited with the 488, 514, and 660 nm lasers, though it is strongest with 660 nm excitation. The 733 nm PL anneals in with a depth profile the same as the initial GR1 PL profile, shown in Fig. 4(a). After the 1200 °C anneal, it can be seen to drop in intensity across the entire profile, but keeps the same profile shape and is not detectable after the 1200 °C anneal. An example spectra of the feature is displayed in Fig. 4(b).

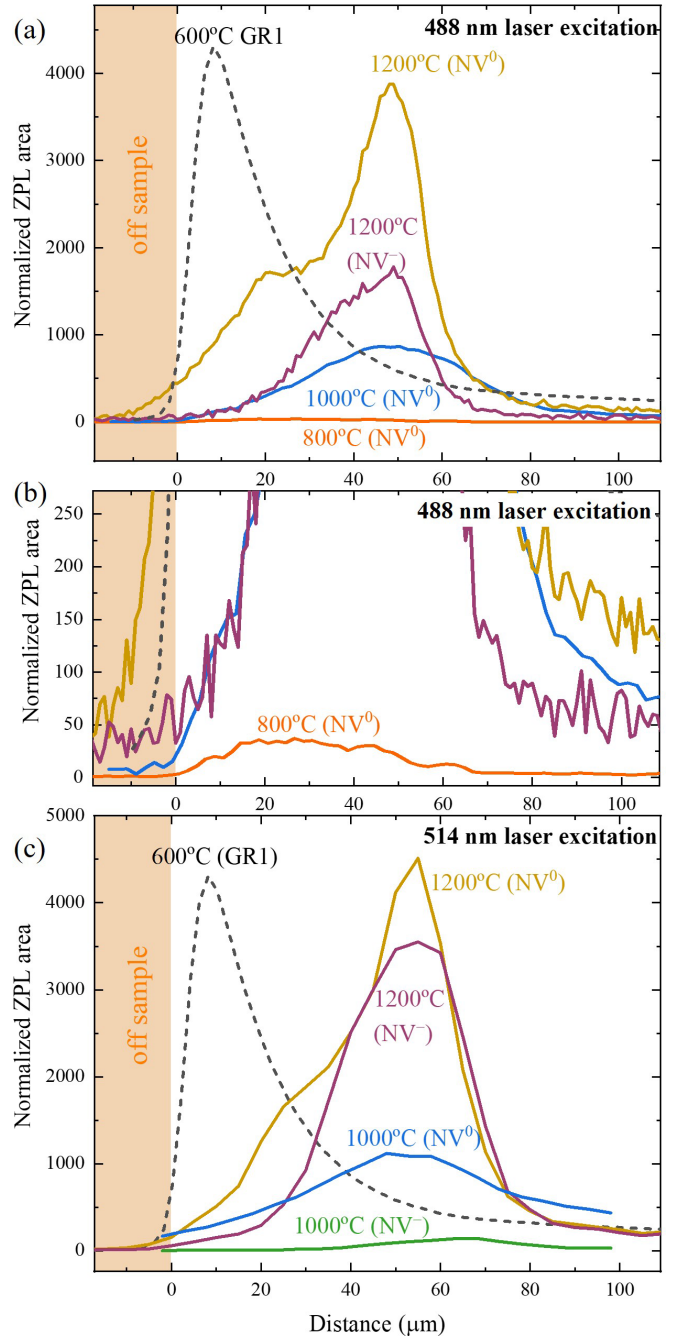


FIG. 3. PL line scans at 77 K showing the spatial depth profile of the area of the NV^0 and NV^- ZPL after a 1 h anneal at each temperature. Units are counts nm. (a) Line scans taken with 488 nm laser excitation normalized to the Raman line. (b) Magnified region of (a) for clarity. (c) Line scans taken with 514 nm laser excitation normalized to the second-order Raman line.

This work indicates there is a very narrow temperature window in which the 733 nm center is detectable; between 1000 and 1200 °C. Its depth profile at both annealing stages distinctly matches that of the initial irradiation corroborating its dependence on a high vacancy concentration for formation.

A number of other spectral features were measured during the annealing process and a list is given in [32].

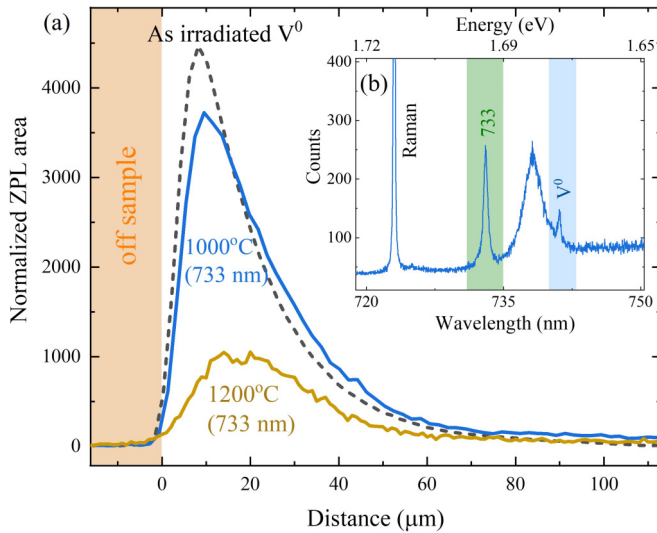


FIG. 4. (a) PL line scans taken at 77 K showing the spatial depth profile of the area of the 733 nm ZPL multivacancy defect. Dotted line shows scaled V^0 for comparison. 660 nm laser excitation used. Units are counts nm. (b) Example spectra of the 733 nm ZPL and sideband, taken at 77 K, taken after the 1000 °C anneal.

IV. DISCUSSION

A. Intrinsic radiation damage

Models considering the displacement of carbon atoms by high-energy electrons have been proposed, [24,25] however the vacancy profile predicted for 200 keV electron irradiation [Fig. 1(d) of Ref. [25]], does not match that measured in our (see Fig. 1) or other experimental results [36]. For 200 keV incident electrons, the probability that an ejected carbon atom has sufficient energy to displace further carbon atoms is negligible and hence secondary cascade processes for vacancy and interstitial production can be ignored. During room-temperature electron irradiation, interstitial complexes are produced [37–40], indicating that at least one form of self-interstitial is mobile [41]. The annealing of interstitial atoms under conditions during electron irradiation is different to the thermally activated annealing of the $\langle 001 \rangle$ -split self-interstitial ($C_{i(001)}$); under electron irradiation a highly mobile interstitial is produced by charge transfer or electronic excitation [41].

The data in Fig. 1 show that the maximum depth at which significant concentrations of vacancies are detected is consistent with energy loss due to electronic excitation; after propagating approximately 38 μm in diamond [42], the energy of a 200 keV incident electron has decreased below the displacement threshold. The estimated 200 keV electron dose was $10^{19} \text{ e}^-/\text{cm}^2$ and comparison of the vacancy distribution profile determined from photoluminescence and bulk optical absorption measurements enabled the vacancy production to be determined (Sec. III A). At the surface the maximum vacancy concentration was $(1.1 \pm 0.2) \times 10^{17} \text{ V}/\text{cm}^3$ equating to a production rate of 0.01 $\text{V}/\text{e}^- \text{cm}$. This is 50 times less than recent modeling predicts [43]. Thus either the experimental electron dose has been overestimated, or the modeling of vacancy production is incorrect. Even if the quantitative discrepancy in vacancy production could be in part explained

by overestimation of the electron dose, theory does not produce the observed vacancy production profile. To bring theory and experiment into agreement for vacancy production by low-energy electron irradiation, it is suggested that the modeling must include the contribution of electronic excitation to interstitial migration [41], and related changes to the barrier between vacancy-interstitial recombination must be considered to account for the measured profile.

Thermal annealing at 400 and 600 °C for 1 h did not change the concentration of vacancies produced by 200 keV electron irradiation or the profile (Fig. 2), as measured by the PL of the GR1 ZPL and sideband. The former is surprising since absorption studies on diamond samples irradiated with 1–2 MeV electrons at room temperature and below, show that when the $C_{i(001)}$ is annealed out there is a corresponding reduction in vacancies [44]. The same study showed absorption using the area under the GR1 ZPL underestimated the V^0 concentration by approximately 25% due to the presence of strained vacancies (i.e., those with a nearby interstitial). The study showed once these close $V-C_{i(001)}$ pairs annealed out such underestimation was no longer a problem.

We have not been able to measure the $C_{i(001)}$ concentration in this sample, but the lack of change of the vacancy PL after annealing at 600 °C suggests that either the $C_{i(001)}$ concentration is much lower than that of vacancies, or the vacancies close to interstitials (presumably the first to anneal out) do not luminesce. Energy transfer between close $V-C_{i(001)}$ pairs is entirely possible, and $C_{i(001)}$ does not luminesce, so such energy transfer is followed by nonradiative deexcitation [43]. Alternatively, the lower (than predicted by theory) vacancy production measured may be accounted for by higher than expected vacancy-interstitial recombination, with fewer close vacancy interstitial pairs surviving, during low-energy electron irradiation. If this is accompanied by higher production rates of stable interstitial aggregates, then indeed the production of isolated interstitials may be less for low-energy electron irradiation. This warrants further experimental study to see if the production efficiency of isolated interstitials relative to vacancies varies with electron irradiation energy or vacancies in close $V-C_{i(001)}$ pairs do not luminesce.

B. Vacancy clusters

At 800 °C, in the absence of impurities, vacancies are lost to multivacancy complexes, also termed vacancy clusters. The structure, electron and optical properties of multivacancy point defects in diamond have been considered both experimentally and theoretically. Early experimental work was interpreted as the existence of a family of $\{110\}$ oriented vacancy chains [45], but more recent theoretical studies indicated that $\{110\}$ planar vacancy chains larger than three vacancies are not energetically the most stable structures. Exceptionally stable clusters are composed of 6 (atoms in a chair configuration are removed to form an ideal hexa-vacancy cluster), 10 and 14 vacancies are predicted, but this stability was not attributed to rebonding as was the case in silicon [46]. The $\{111\}$ π -bonded vacancy disk (a double $\{111\}$ plane of carbon atoms removed) has a much lower in formation energy per vacancy than any of the multivacancy point defects [46,47]. Thus if a large quantity of vacancies is introduced

by irradiation damage, then upon annealing at temperatures where vacancies are mobile, but the clusters stable, we would expect the formation of a variety of vacancy clusters. The smaller clusters (e.g., V_2 and V_3) will in turn be lost as they trap mobile vacancies to make larger clusters and ultimately vacancy discs.

In silicon for the $[111]$ divacancy to reorient the two vacancies have to separate by one lattice spacing and then reunite but with a differently oriented axis [48]. The fact that this occurs with no loss of di-vacancies shows that there is a substantial binding energy between the two vacancies and demonstrates that in silicon the divacancy can reorientate and diffuse without permanently dissociating. Such a reorientation of divacancies in diamond has not, to the best of our knowledge, been measured. The neutral nearest neighbor divacancy (V_2) in diamond [29], anneals in as the isolated vacancy anneals out, but does not persist as the temperature is increased and itself anneals out rapidly at temperatures above about 900 °C [49]. The 733 nm center also anneals in as the isolated vacancy anneals out and anneals out at temperatures above about 1200 °C. This defect has been previously attributed to a divacancy defect in diamond [20], but the structure has not been determined.

C. Nitrogen-vacancy (NV) and nitrogen-divacancy (NV_2) defects

If present, it is well known that the substitutional nitrogen defect is an effective trap for the vacancy, producing the NV defect. Above 1400 °C the NV defects readily migrate and can be trapped by remaining substitutional nitrogen defect to produce N_2V . The energy required to completely break a NV defect (i.e., for the vacancy to escape Coulombic attraction and the nitrogen-induced strain field) is greater than that required for a sequence of local vacancy emission and retrapping steps [50]. In this process the vacancy interchanges place with a neighboring carbon, and then either returns to reform the original NV or moves further away into the third nearest neighbor site of the nitrogen. From this position it does not escape but returns to the nitrogen; however, in doing so could take an alternate route and produce a differently oriented NV defect. NV reorientation has been observed at temperatures as low as 1050 °C [51], but for NV diffusion the nitrogen and vacancy must additionally swap places. Significant numbers of NV defects survive annealing at 1200 °C and this annealing temperature is often used in an effort to remove divacancy defects and optimize NV production.

In recent work using ion implantation, the relative production efficiencies of NV and V_2 defects have been investigated [52]. Additionally, when the concentration of vacancies is high it is necessary to consider the production of NV_2 since NV is also a trap for vacancies. The most likely structure of NV_2 is a divacancy with one of the six carbon neighbors replaced with a nitrogen [53]. The consequence of this is that NV production is reduced in the presence of excess vacancies.

V. MODELING OF VACANCY ANNEALING

A. Chemical kinetics

To explain/investigate the vacancy aggregation pathways a simple chemical kinetics model of the vacancy annealing

was implemented. In the simple model described here, it is assumed that small vacancy clusters (V_2 , V_3 , V_4) anneal in by vacancy aggregation, but are not themselves mobile and V_2 and V_3 are lost at higher temperatures by dissociation. V_4 is assumed to be stable at the annealing temperatures studied. The simulation could be extended to include diffusion of the multivacancy aggregates, and formation of larger clusters of vacancies, but there are insufficient data against which to constrain or confirm the former, and the latter would not change our interpretation of the data for isolated vacancies and the nitrogen-vacancy defect. Additionally, we assume that NV_2 dissociates into a NV and a V at an annealing temperature below the annealing temperature at which the NV defect is lost.

The model consists of a set of simultaneous equations describing defect migration and complex formation (aggregation). For simplicity, we start with isolated vacancies (V) and single-substitutional nitrogen (N_s) defects, and do not consider different charge states of any species. Vacancies and N_s are assumed not to interact with interstitials or interstitial complexes, but diffuse at sufficiently high annealing temperatures. The vacancies aggregate to form multivacancy complexes (V_2 , V_3 , and V_4) or can aggregate with N_s to form nitrogen-vacancy (NV) and nitrogen-divacancy (NV_2) defects and all multivacancy complexes are assumed to be immobile. Two temperature regimes are considered: T_1 and T_2 , where $T_2 > T_1$. At annealing temperature T_1 it is assumed that V_2 , V_3 , V_4 , NV and NV_2 are stable and do not dissociate. At annealing temperature T_2 it is assumed that V_2 , V_3 , and NV_2 dissociate (e.g., $V_2 \rightarrow V + V$, $V_3 \rightarrow V_2 + V$, and $NV_2 \rightarrow NV + V$) but NV and V_4 are both stable. The boundary conditions are assumed to be infinite sinks for vacancies and the finite difference method is used to calculate concentrations of all defects during annealing. The full set of rate equations used to implement the model can be found in the supporting information, but the simultaneous partial differential equations are as follows:

$$\begin{aligned} \frac{\partial[V]}{\partial t} = & D_V \frac{\partial^2[V]}{\partial x^2} - k_2[V]^2 - k_3[V][V_2] - k_4[V][V_3] \\ & + 2l_2[V_2] + l_3[V_3] - k_{NV}[V][N_s] \\ & - k_{NV2}[V][NV] + l_{NV2}[NV_2], \end{aligned} \quad (2)$$

$$\frac{\partial[V_2]}{\partial t} = +\frac{k_2}{2}[V]^2 - k_3[V][V_2] - l_2[V_2] + l_3[V_3], \quad (3)$$

$$\frac{\partial[V_3]}{\partial t} = +k_2[V]^2 - k_4[V][V_3] - l_3[V_3], \quad (4)$$

$$\frac{\partial[V_4]}{\partial t} = +k_4[V][V_3], \quad (5)$$

$$\frac{\partial[N_s]}{\partial t} = -k_{NV}[V][N_s], \quad (6)$$

$$\frac{\partial[NV]}{\partial t} = +k_{NV}[V][N_s] - k_{NV2}[V][NV] + l_{NV2}[NV_2], \quad (7)$$

$$\frac{\partial[NV_2]}{\partial t} = +k_{NV2}[V][NV] - l_{NV2}[NV_2], \quad (8)$$

where $[S]$ is used to denote the concentration of species S , and t and x are time and distance respectively. D_V is the diffusion coefficient of vacancies and k_s and l_s are the rate constants

associated with the various aggregation and dissociation processes involved. The vacancy diffusion coefficient and all the rate constants are assumed to have an Arrhenius temperature dependence, with an activation energy appropriate for the specific reaction/process.

B. Simulation results

To demonstrate the output of this model at a temperature $T_1 = 1000^\circ\text{C}$ we choose $k_2 = k_3 = k_4 = 2 \times 10^{-5} \text{ s}^{-1}/\text{ppb}$, $k_{NV} = k_{NV_2} = 2 \times 10^{-4} \text{ s}^{-1}/\text{ppb}$, $l_2 = l_3 = 2 \times 10^{-6} \text{ s}^{-1}$, $l_{NV_2} = 3 \times 10^{-6} \text{ s}^{-1}$, and $D_V = 1.5 \times 10^{-6} \text{ } \mu\text{m}^2\text{s}^{-1}$ [19]. The parameter k_2 for second-order loss of vacancies (forming divacancies) at $T_1 = 1000^\circ\text{C}$ was chosen, such that with a starting vacancy concentration of 1000 ppb after a 1 h anneal the concentration would have reduced by approximately 100 times (due to the formation of small vacancy clusters). This is consistent with results in the literature [28] and the those presented here. The parameters for trivacancy k_3 and quad-vacancy k_4 clusters were set equal to k_2 . Adding a first-order annealing term for vacancies would of course reduce the vacancy concentration at the expense of the formation of vacancy clusters. The rate constants for NV and NV_2 production were set 10 times larger than k_2 , because nitrogen is known to be an effective trap for the vacancy [28]. The defect dissociation rates, for V_2 , V_3 , and NV_2 , were chosen to be smaller than the formation rates so that these defect concentrations increased on annealing at 1000°C . The NV defect was presumed not to dissociate or migrate over significant distances at temperatures below 1200°C . This assumption is consistent with many reported annealing studies.

For an initial vacancy concentration distribution decaying exponentially into the sample $[V] = V_0 \exp(-x/x_0)$, where $V_0 = 1000 \text{ ppb}$ and $x_0 = 12 \text{ } \mu\text{m}$, and a uniform doping with single substitutional nitrogen $[N_s] = 5 \text{ ppb}$, we find after a 1 h anneal there is a small peak in the concentration of vacancies approximately $40 \text{ } \mu\text{m}$ into the diamond, displayed in Fig. 2(d). The position and intensity of the vacancy peak can be changed by adjusting the rate constants, but we have resisted the temptation to fit the experimental data as there are too many variable parameters and too little data to constrain the fit. Further experimental studies with different starting concentrations of both V and N_s , and a range of annealing times and temperatures are required to constrain the fitting parameters. However, what we find is that the peak in the concentration of V cannot be produced by simple second order kinetics for the loss of vacancies ($V + V \rightarrow V_2$). It is the production of multiple vacancy complexes, Fig. 2(d) (e.g., traps for vacancies) that results in a peak in vacancy concentration significantly far into the diamond.

The resulting profiles of $[N_s]$, $[NV]$, and $[NV_2]$ after the simulated anneal are shown in Fig. 5(a). For the starting V concentration we can see that at depths $< 58 \text{ } \mu\text{m}$ $[V] > [N_s]$ and at depths $> 58 \text{ } \mu\text{m}$ $[N_s] > [V]$, as indicated by the dotted line in Fig. 1(c). Indeed at the surface $[V] = 200 \times [N_s]$ ($[V] \gg [N_s]$) and at a depth of $100 \text{ } \mu\text{m}$ $[N_s] \approx 20 \times [V]$ ($[N_s] > [V]$). Setting k_{NV} , $k_{NV_2} > k_2$, k_3 , k_4 ensures that although even though $[V] \gg [N_s]$ in the first $\approx 40 \text{ } \mu\text{m}$ the vacancies are efficiently trapped by the nitrogen, and nearly

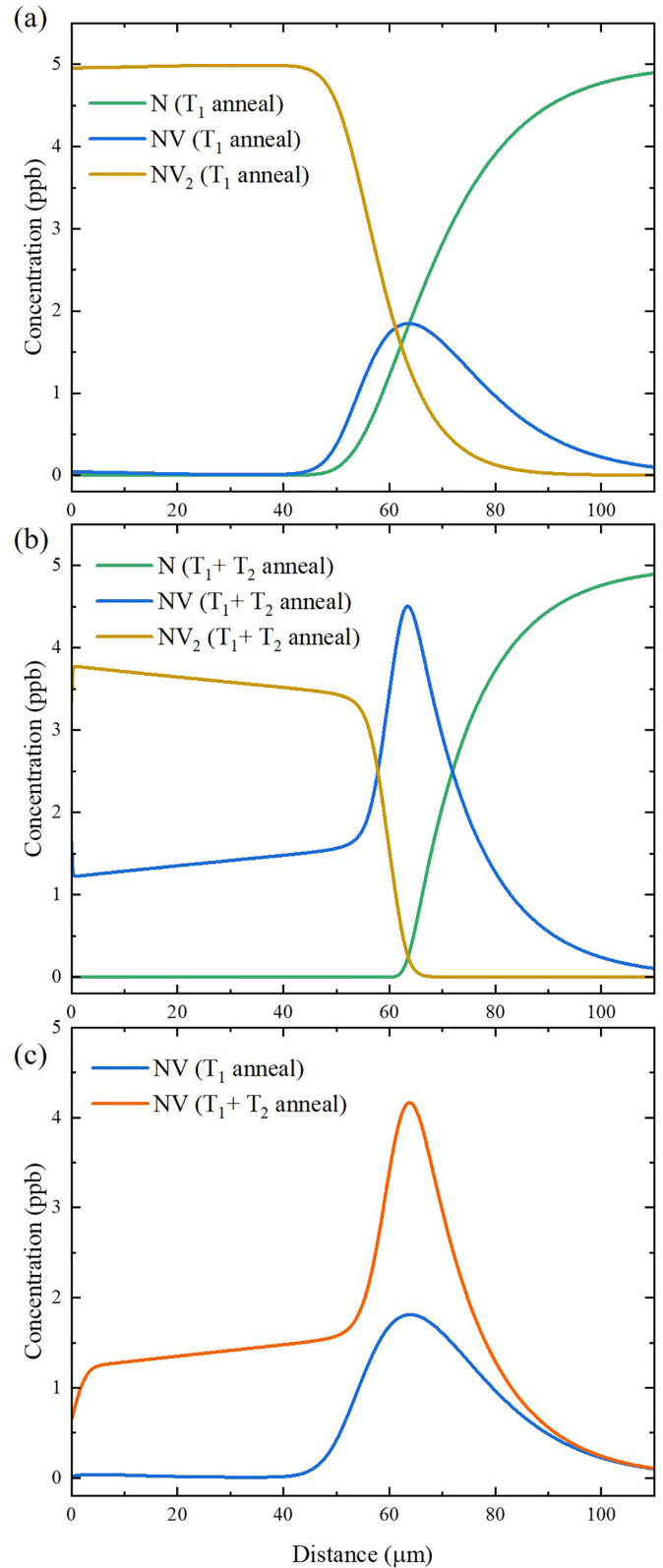


FIG. 5. (a) Simulation of the N, NV, and NV_2 concentrations after 1 h annealing at $T_1 = 1000^\circ\text{C}$. (b) Simulation of the N, NV, and NV_2 concentrations after 1 h annealing at $T_1 = 1000^\circ\text{C}$ followed by 1 h annealing at $T_2 = 1200^\circ\text{C}$. (c) NV concentrations from (a) and (b) convolved with a Gaussian to approximate the spectrometer response function.

all the N_s is converted to NV_2 . At greater depths, there are insufficient vacancies to achieve this conversion and measurable concentrations of NV are produced. Moving even further into the diamond the concentration of NV reaches a maximum at $\approx 64 \mu\text{m}$ into the diamond and then decreases, as there are now insufficient vacancies to produce significant concentrations of NV. Deep in the diamond all the nitrogen remains as N_s . Again the size and position of the peak in NV concentration can be altered by changing the rate constants, but for the same reasons as discussed above no fit to the experimental data has been attempted. Nevertheless, this simple approach explains the experimentally observed NV PL profile (Fig. 3).

To simulate a second anneal at $T_2 = 1200^\circ\text{C}$ the rate and diffusion constants must be recalculated to account for the increase in temperature. For the purpose of simulation we have assumed an activation energy for the formation of V_2 , V_3 , V_4 , NV, and NV_2 of 2.2 eV [28], an activation energy for vacancy diffusion of 2.0 eV, a V_2 and V_3 dissociation energy of 3.5 eV [54], and a NV_2 dissociation energy of 3.8 eV. Thus on increasing the temperature from 1000 to 1200°C the rate constants become $k_2 = k_3 = k_4 = 1.4 \times 10^{-3} \text{ s}^{-1}/\text{ppb}$, $k_{NV} = k_{NV_2} = 1.4 \times 10^{-2} \text{ s}^{-1}/\text{ppb}$, $l_2 = l_3 = 1.7 \times 10^{-3} \text{ s}^{-1}$, $l_{NV_2} = 4.6 \times 10^{-3} \text{ s}^{-1}$ and $D_V = 7.2 \times 10^{-5} \mu\text{m}^2\text{s}^{-1}$. If the 1 h anneal at $T_1 = 1000^\circ\text{C}$ is followed by a further 1 h at $T_2 = 1200^\circ\text{C}$, then the simulation shows that the 97% of vacancies are now in the form of V_4 clusters, with only a very few V, V_2 , and V_3 remaining. If V_3 is responsible for the 733 nm emission (Fig. 4) then the loss is overestimated in this simulation. Figure 5(b) shows the predicted concentration of N_s , NV, and NV_2 after this second anneal. In the shallow regions, the dissociation of NV_2 results in an increase in the concentration of NV, especially in the first 40 μm of the diamond [Fig. 5(b)] and this seen in the experimental PL intensity data [Figs. 3(a) and 3(c)]. In the deeper regions where initially $[N_s] > [V]$ all the nitrogen is not consumed after the 1000°C anneal.

C. Charge transfer

NV centers give insight into the surrounding donor concentrations by their charge state. If there are nearby donors it is energetically favorable for NV centers to be negatively charged; as stated $NV^0 \rightarrow NV^-$ can also be achieved via photoionization. The differences in the NV^0 and NV^- depth profiles with different excitation in Fig. 3 are a result of such charge transfer.

In the experimental data, the emission from NV^0 dominates over that from NV^- in the first 40 μm [Figs. 3(a) and 3(c)] which is consistent with the simulated higher concentration of competing NV_2 traps. Overall the relative emission from NV^- to that from NV^0 has increased on annealing at 1200°C suggesting the number of competing electron traps has been reduced. Photoionization of NV^- with 488 nm excitation is again apparent [Figs. 3(a) and 3(c)]. Figure 5(c) shows the simulated total NV concentration after the first anneal at T_1 , and after both anneals at T_1 and T_2 . The concentration profiles have been convolved with a Gaussian (FWHM 5 μm) to approximate the spectrometer spatial response function. No quantitative agreement between Fig. 5(c) and Fig. 3 is claimed, but qualitatively the simulation is predicting the

observed behavior. There is no merit to simply varying the rate constants to improve this agreement, without more data to constrain these parameters.

It can be seen the optimal V^0 concentration for NV^- creation efficiency in the sample is the concentration present at a depth of $60 \pm 5 \mu\text{m}$, i.e., $5 \pm 3 \text{ ppb } V^0$.

VI. CONCLUSIONS AND FUTURE WORK

The radiation damage depth profile for low energy 200 keV electrons in electronic grade diamond has been measured and the creation efficiency of the vacancy production has been quantified. The depth profile was found to follow an exponential decay, with a decay constant of $12 \pm 1 \mu\text{m}$. This is not what has been predicted by theory [24,25] and more theoretical input is required to reconcile this. A dose of $10^{19} \text{ e}^-/\text{cm}^2$ resulted in a peak vacancy concentration of $(1.1 \pm 0.2) \times 10^{17} \text{ V}/\text{cm}^3$ at the surface.

Assuming vacancies anneal to form vacancy clusters results in a change in the vacancy distribution consisting of a small surviving peak in the concentration of V^0 below the surface. The position and size of the peak depend on the rate constants used in the model. In this work no attempt has been made to fit the experimental measurements, as more data are required.

The simulation supports assignments of the 733 nm ZPL PL feature to a vacancy cluster, as the concentration depth profile follows that of a vacancy cluster (see supporting information) and we speculate that this might be V_3 .

Our simple model predicts the observed NV distributions, but relies on the formation of NV_2 . At higher temperatures NV_2 dissociates, additionally changing the NV distribution. NV_2 plays an important role in determining the charge state of the NV defect by acting as an electron trap.

Near the surface ($< 20 \mu\text{m}$) there are many more vacancies than substitutional nitrogen; experimental data suggests 200 to 1. In this regime, we do not successfully form a high concentration of NV centers and instead form NV_2 . This could explain the relatively poor yield of NV defects by ion implantation; it is well known that correct surface termination is necessary for maximising yield however implantation also results in a regime where $[V] \gg [N_s]$. For example, implantation of diamond with 2×10^9 30 keV nitrogen ions/ cm^2 results in approximately 5 ppb ($9 \times 10^{14} \text{ cm}^{-3}$) of nitrogen atoms (calculated using SRIM) at a depth of 40 nm, whereas the concentration of vacancies produced at this depth is approximately 400 ppb. Thus $[V] \gg [N_s]$ and our analysis suggests that the production efficiency of NV on annealing would be significantly reduced by the formation of NV_2 . Santonocito *et al.* [52] also cite the production of NV_2 during ion implantation and annealing. Further study and detection of NV_2 (in either the neutral or negative charge state) must be a priority in order to understand how NV production may be optimised.

In electronic grade diamond with a concentration of 5 ppb N_s the optimal V^0 concentration for NV^- creation is $5 \pm 3 \text{ ppb}$. To optimize NV concentration close to the surface after an electron irradiation dose of $10^{19} \text{ e}^-/\text{cm}^2$ removal of the top 30-50 μm would be recommended in such samples.

Further work to study both the electron dose and energy dependence of the depth profiles for vacancy creation and NV production would be beneficial, and variation of the nitrogen concentration in the sample is required.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [30]; embargo periods may apply.

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