Electron-beam-induced dissociation of (B,D) complexes in diamond mediated by multiple vibrational excitations

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In this work, we investigate the dissociation kinetics of boron-deuterium (B,D) pairs under an electron beam (e-beam) in diamond. This technique is of high interest as it would enable the fabrication of electrically isolating/conductive pathways in diamond using e-beam direct writing. Cathodoluminescence is used to follow the concentration of boron acceptors, via the bound and free-exciton recombinations. We observe that (i) the dissociation rate critically depends on the e-beam excitation current (ii) the dissociation of (B,D) pairs is more efficient at 10 K than at 100 K. This demonstrates that a multiple vibrational excitation is involved in the dissociation of (B,D) complexes in diamond under e-beam. In the theoretical framework of a vibrational dissociation mechanism of hydrogen-related complexes, an analysis of the experimental data indicates that the injection of minority carriers lowers the energy of the dissociation barrier from 2.5 to 0.7 eV.

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I. INTRODUCTION

Hydrogen as well as its isotope, deuterium, are known to passivate impurities and defects in many semiconductors because of the formation of complexes. This passivation process is routinely used in device technologies for microelectronic and optoelectronic applications. In metal-oxide-semiconductor (MOS) structures, the hydrogenation of the oxide-semiconductor interface passivates its dangling bonds in order to decrease the interface density of states.[1] More generally, the stability of hydrogen-related complexes under different stresses is of basic interest for further applications.

Several kinds of excitations could induce the dissociation of hydrogen-related complexes. The most common is induced by their thermal excitation through heating of the crystal lattice. The injection of hot electrons also induces an efficient dissociation process. It is, for example, responsible for breakdown to occur in SiO_2 thin films[2] as well as one of the main causes of the SiO_2/Si interface degradation[1] in MOS transistors.

Studies of H desorption from a silicon surface under the tip-emitted current of a scanning tunneling microscope (STM) have provided a powerful description of the molecular bond breaking: the desorption yield is strongly dependent on the electron energy.[3] For electron energies above 6 eV, the H desorption from Si surfaces is due to the electronic excitation of the Si-H bond.[4,5] At lower energies, Shen *et al.*[3,6] showed that hydrogen desorption is also possible from the vibrational excitation of the bond by tunneling electrons. A comparison between hydrogen and deuterium desorptions showed very strong isotope effect, the dissociation yield being much lower for Si-D bonds than for Si-H bonds.[7] Finally, for this vibrational dissociation, Foley *et al.*[8] showed a strong and counter intuitive increase in the desorption yield when the temperature decreases.

The presence of hydrogen inside the crystalline structure of semiconductors is also of high practical interest as it can passivate donors or acceptors, bringing ultimately the semiconductor back to its intrinsic conduction regime. The passivation by hydrogen of Si donors in GaAs (Ref. 9) or Mg acceptors in GaN (Ref. 10) are well-known examples. In the GaAs case, an electronic excitation is responsible for the dissociation of the (Si,H) or (Si,D) complexes under electron beam (e-beam) at room temperature.[11–14] With the development of microwave plasma-assisted vapor-phase epitaxy for the growth of thin diamond layers, semiconducting diamond properties began to be exploited. The diffusion of deuterium in boron-doped diamond is known to induce the passivation of boron acceptors by the formation of (B,D) complexes.[15,16] Recently, it has been shown that electron-beam irradiation at low temperature (100 K) is an efficient way to dissociate such (B,D) pairs.[17] In these conditions, the dissociation yield, defined as the average number of dissociated complexes per incident electron, is strongly dependent on the irradiation beam current. This observation discards the *electronic excitation* of the (B,D) complex by hot electrons from being the mechanism responsible of the dissociation, because in this case the amount of dissociated complexes depends only upon the received dose independently of the electron-beam current.[3,12] The same authors also studied the isotope effects of (B,H) and (B,D) complex dissociation.[18] They observed comparable dissociation kinetics for (B,H) and (B,D) complexes at 102 K.

In the present study, a mechanism involving a *cumulative vibrational* excitation of complexes via interactions with incident electrons is proposed to explain the dissociation of (B,D) complexes by e-beam in diamond. We first describe the theoretical basis of this mechanism. Then, experimental results concerning the influence of the current on the dissociation kinetics is presented and analyzed. In the framework of the truncated harmonic oscillator (THO) model, they indicate that the dissociation barrier of the complexes is significantly lowered under e-beam excitation when compared to pure thermal dissociation. Then, we present experimental results on the temperature dependence of the dissociation rate under e-beam excitation. We show that the dissociation

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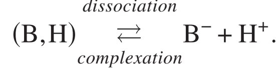
of (B,D) complexes becomes more efficient as the temperature decreases. Together with the current dependence previously described, these are strong signatures of the vibrational character of the dissociation process.

II. THEORY

The (B,H) complex concentration in the material depends upon the equilibrium between dissociation and formation of these complexes.



$$(\mathrm{B,H}) \underset{complexation}{\overset{dissociation}{\rightleftarrows}} \mathrm{B}^- + \mathrm{H}^+.$$

This evolution of the complex concentration as a function of time is given by the relation

$$\frac{\partial[\mathrm{BH}]}{\partial t} = \sigma([\mathrm{B}_{tot}] - [\mathrm{BH}])[\mathrm{H}^+] - \nu[\mathrm{BH}]. \quad (1)$$

In Eq. (1), [BH] is the concentration of (B,H) complexes and $\sigma([\mathrm{B}_{tot}]-[\mathrm{BH}])[\mathrm{H}^+]$ is the complexation (or retrapping) term with σ the capture coefficient,

$$\sigma = 4\pi R_c D_i. \quad (2a)$$

R_c is the capture radius of ionized boron B^- with

$$R_c = \frac{e^2}{4\pi\varepsilon\varepsilon_0 K_B T}, \quad (2b)$$

where ε is the dielectric constant of diamond, ε_0 is the vacuum permittivity, and K_B is the Boltzmann constant.

D_i is the intrinsic diffusion coefficient of D^+, i.e., in the absence of impurities (such as B^-). It can be written as

$$D_i = D_0 \exp\left(-\frac{E_m}{K_B T}\right). \quad (3)$$

E_m is the migration energy of H^+ (or D^+). According to Goss *et al.*,[19] this energy is 0.2 eV. In Eq. (1), ν[BH] is the dissociation term where ν is the dissociation frequency. Dissociation may be due to thermal heating and/or to e-beam exposure. Next, we will treat each phenomenon separately.

A. Thermal dissociation of (B,H) complexes

The thermal dissociation of (B,H) and (B,D) complexes has been studied theoretically and experimentally thanks to diffusion experiments.[19] In a regime where the deuterium diffusion is controlled by the trapping-detrapping mechanism, the effective diffusion coefficient is independent of the intrinsic diffusion coefficient. It is given by the expression:

$$D_{eff} = \frac{\nu}{4\pi R_c[\mathrm{B}]}, \quad (4)$$

where ν is the dissociation frequency of the complexes and [B] the active boron concentration. The dissociation frequency can be written as

$$\nu = \nu_0 \exp\left(-\frac{E_\mathrm{d}}{K_B T}\right), \quad (5)$$

where ν_0 is the attempt frequency and E_d the thermal dissociation energy of the (B,D) complexes. The authors reported

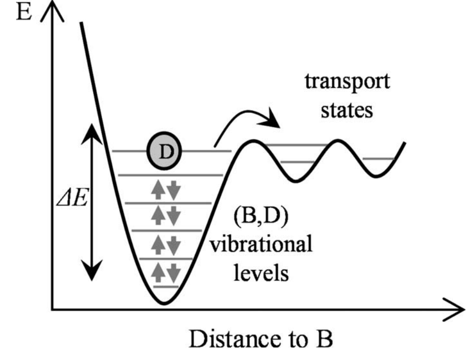


FIG. 1. Schematic potential energy curve as a function of the separation between B and D showing the vibrational levels.

a value of 2.5 ± 0.2 eV for E_d and 2×10^{14} s^{-1} for ν_0 by fitting the experimental values of D_{eff} as a function of T, in good agreement with *ab initio* calculations.[19]

B. Multivibrational excitation of (B,H) complexes

The vibrational excitation mechanism of hydrogen-related local vibrational modes has been extensively described by the THO model.[20,21] It is based on the fact that the transitions between the vibrational levels (Fig. 1) are induced by inelastic tunneling of electrons and energy exchange with surrounding atoms of the crystal. This model was successfully introduced to account for hydrogen desorption from silicon surfaces under a STM. In this paragraph, we will see how it could apply to hydrogen-impurity complexes in a bulk semiconductor.

In the case of an electron-beam exposure, the desorption rate depends on the equilibrium between the up-pumping rate of the complex in the vibrational levels of the local vibrational mode (LVM) and the down-pumping rate for the relaxation of the molecule.[20] The up-pumping rate can be written as a function of two terms taking into account the inelastic interaction of electrons and the energy exchange (gain) with the substrate. Then the up-pumping rate is given by

$$\Gamma_{up} = \sigma_{in}\left(\frac{j}{q}\right) + \Gamma_{vib} \exp\left(-\frac{\hbar\omega_{vib}}{K_B T_s}\right), \quad (6)$$

where σ_{in} is the inelastic cross-section of a complex with an incident electron, j is the current density, q is the elementary charge, Γ_{vib} and ω_{vib} are the decay rate and the frequency of the LVM, respectively, and T_s is the substrate temperature.

The down-pumping rate is written the same way

$$\Gamma_{down} = \sigma_{in}\left(\frac{j}{q}\right) + \Gamma_{vib}. \quad (7)$$

The dissociation rate is given by the general expression for the vibrational dissociation mechanism[21]

$$\nu = \nu_0 \left(\frac{\Gamma_{up}}{\Gamma_{down}} \right)^n, \tag{8}$$

where n is the quantum number of the first unbound vibrational state in the potential energy well (0 for the fundamental).

In the case of our experiments, the temperature is below 105 K. Consequently the second term of expression (6) can be neglected when compared to the first one. Moreover, we assume that $\sigma_{in}(\frac{j}{q}) \ll \Gamma_{vib}$ which simplifies also expression (7). These assumptions will be justified in Sec. IV C. Under these approximations, expression (8) can be simply written as

$$\nu = \nu_0 \left[\frac{\sigma_{in} j/q}{\Gamma_{vib}} \right]^{\Delta E/\hbar\omega_{vib}}. \tag{9}$$

This expression highlights that the vibrational dissociation process results from a balance between up-pumping by the current density j and relaxation of the LVMs as expressed by their decay rate Γ_{vib}. In this expression, $\sigma_{in} j/q$ is the number of electrons per second that transfer a quantum vibrational energy to one (B,H) complex. We use $\frac{\Delta E}{\hbar\omega_{vib}}$ as an approximation for n, ΔE being the energy barrier to overcome for dissociation under e-beam.

It should be underlined that the THO model only provides a rough description of the vibrational bond breaking: (i) it is well known that real bonds are anharmonic, which causes the level spacing to decrease with increasing quantum number. This will affect n, the quantum number associated with the last bound vibrational state and hence the desorption rate predicted in the model; (ii) the assumption involving a single LVM mode may not be justified, since several modes (e.g., stretching and/or bending modes) may play a role in the dissociation process; (iii) tunneling between the upper vibrational states and the transport states is not taken into account. Despite these assumptions, the THO model provides a framework for discussing bond dissociation via the vibrational excitation mechanism.

III. EXPERIMENTAL PROCEDURES

This study is conducted on homoepitaxial boron-doped diamond grown by the microwave assisted chemical vapor deposition from a mixture of methane (CH_4), hydrogen (H_2), and diborane (B_2H_6) on a (100)-oriented high-pressure high-temperature Ib synthetic substrate of 3×3 mm^2.

Exposure to pure deuterium under microwave plasma was achieved at 550 °C for 12 h to passivate the boron-doped layer via deuterium diffusion through its whole thickness. Deuterium is preferentially used for basic studies since its detection limit by secondary-ion mass spectrometry (SIMS) ($\sim 1 \times 10^{16}$ cm^{-3}) is much lower than that of hydrogen ($\sim 1 \times 10^{19}$ cm^{-3}). SIMS was performed using a Cameca IMS 4f equipment to measure the depth distribution of boron and deuterium atoms into the diamond volume with Cs^+ primary ions accelerated at 10 keV. The concentrations of boron and deuterium were quantified by comparison with implanted standards. The boron concentration is 3×10^{18} cm^{-3} and the thickness of the epilayer is 1.85 μm.

After deuteration, SIMS shows that the deuterium concentration follows the boron concentration ([B]≈[D]) in the whole depth profile, as expected for a diffusion limited by a trapping-detrapping mechanism.[22]

Electron-beam irradiation and cathodoluminescence measurements at 100 K were performed at GEMaC. The experimental conditions are detailed in Refs. 17 and 18. Low-temperature electron-beam irradiation and cathodoluminescence (CL) measurements were performed at Institut Néel in Grenoble using a Quanta 200 SEM equipped with a GATAN variable temperature cryostage (4–300 K) and a parabolic collector mirror coupled to a CCD detector through a HR460 Jobin Yvon spectrometer. Irradiation and spectra were recorded under excitation using a 10 kV electron beam giving a penetration depth of about 0.8 μm in diamond. The study of the complex dissociation by electron exposure is generally carried out in two steps: the dissociation step under exposure to the electron beam (writing step) at high current followed by the recording of the CL spectrum (reading step) at low current to avoid dissociation while acquiring the CL spectrum. However, another measurement protocol has also been used in this study, named the "reading *during* writing" protocol. In this case, the CL spectrum is recorded while dissociation is carried out. This procedure is used to reduce the influence of the retrapping phenomenon presented later.

At a given temperature, the intensity ratio of bound-exciton (BE) and free-exciton (FE) recombinations is proportional to the dopant concentration over several decades.[23] Consequently, cathodoluminescence spectroscopy is a tool enabling *in situ* quantification of the boron concentration resulting from the complex dissociation under e-beam.[24] In order to evaluate the concentration of dissociated (B,D) complexes at different temperatures, we have studied the evolution of the CL spectra of a reference sample as a function of temperature from 5 to 300 K. The aim of these experiments was to evaluate precisely the proportionality factor $K(T)$ in the expression giving the acceptor concentration as a function of the excitonic intensity ratio

$$N_a = K(T) \times \frac{I_{BE}}{I_{FE}}, \tag{10}$$

where I_{BE} and I_{FE} are the amplitudes of the peaks corresponding to the recombination of BE and FE, respectively. The values of the proportionality factor used in this work are $K(10) = 3.5 \times 10^{16}$ cm^{-3} and $K(100) = 1.3 \times 10^{17}$ cm^{-3}.

The acceptor concentration, N_a, is measured by CL using this quantification procedure. As (i) the initial complex concentration $[BD]_0$ equals the boron concentration measured by SIMS, $[B]_{SIMS}$, and (ii) N_a equals the concentration of dissociated complexes, i.e., $[BD]_0 - [BD]$, we obtain: $Na/[B]_{SIMS} = 1 - [BD]/[BD]_0$. Moreover, the solution of Eq. (1) is given, in the absence of retrapping [$\sigma \approx 0$ in expression (1)], by

$$\frac{[BD]}{[BD]_0} = \exp(-\nu t). \tag{11}$$

The dissociation rate is deduced from the plot of the dissociated complex concentration normalized to $[B]_{SIMS}$ as a function of time.

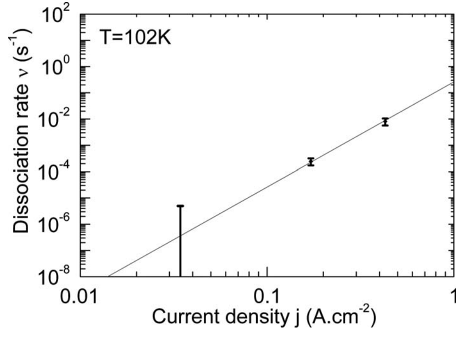


FIG. 2. Dissociation rate as a function of the electron-beam current density at 102 K (data from Ref. 17).

IV. RESULTS AND DISCUSSION

A. Retrapping of deuterium atoms by boron

In a previous publication,[17] we showed that (B,D) complexes are dissociated under e-beam irradiation. More recently, we also established the existence of a retrapping effect of deuterium atoms by boron once electron-beam irradiation is stopped.[25] For a given concentration of complexes, the concentration of retrapped deuterium atoms was found to decrease as the temperature increases. Whereas this effect cannot be neglected at low temperatures, the retrapping of deuterium becomes negligible at 90 K and above.[27] This is coherent with the observations made by Barjon *et al.*[17] where a single exponential was used to fit the time decay of (B,D) complex concentration during e-beam irradiation, as expected if $\sigma=0$ in Eq. (1). The retrapping of H^+ by B^- has also been investigated (not shown here) and a remarkable isotope effect is observed in the sense that, as opposite as for D, H retrapping is still efficient above 120 K. This means that a comparison between the (B,D) and (B,H) dissociations at 100 K as it was proposed in Ref. 18 is not relevant to estimate ν since σ is not negligible for H. Such a detailed study of isotope effects will be proposed as a future complementary study.

B. Dissociation kinetics of (B,D) complexes at 102 K as a function of the current

Figure 2 plots the values of the dissociation frequency extracted from dissociation experiments obtained in a previous paper.[17] Dissociation was performed using the "reading after writing" protocol on a 2.6×2.2 μm^2 area and at a temperature of 102 K. For the lowest current value, the (B,D) dissociation was not observable after 45 min, thus enabling to estimate the upper limit of the dissociation rate in this case.

Figure 2 shows that the dissociation rate varies over more than three decades when the current increases only by a factor 12. Using relation in Eq. (9) to account for these results, we see that the slope of the curve $\nu(I)$ plotted in log-log scale gives the number n of vibrational states in the THO model. We find $n=4\approx\frac{\Delta E}{\hbar\omega_{vib}}$ which gives an estimate the energy ΔE of the dissociation barrier. It would be equal to 1 eV if the dissociation occurs via stretching modes or to 0.7 eV via bending modes [vibrational frequencies of bending and stretching modes calculated by Goss *et al.* are given in Table I (Ref. 19)]. We see that the dissociation energy involved in the vibrational excitation dissociation is significantly lower than the value of 2.5 eV corresponding to the thermal dissociation energy. This is probably due to the injection of minority carriers that lowers the dissociation barrier of (B,D) complexes as proposed recently by Goss and Briddon[26] and as observed experimentally for (B,H) complexes in silicon.[27] The minority carriers (electrons in our case) are created by the band to band transitions induced by the primary e-beam. In the electron-hole bath created by exposure to the e-beam, the B-D complexes can be negatively charged. These B-D$^-$ complexes are less stable than the neutral B-D complexes according to *ab initio* calculations.[26] The values of 0.5–0.7 eV calculated by Goss *et al.* for the dissociation barrier of charged $(B,D)^-$ are in good agreement with the one deduced from the fitting of our experimental data in the case of the bending mode. The analysis of our experimental data confirms the lowering of the dissociation barrier in the case of charged complexes in diamond. Additional experiments could be done in the future to confirm the role of the minority carriers in the lowering of the dissociation barrier. For example, electrical biasing of the sample during the electron-beam irradiation should prevent the formation of $(B\text{-}D)^-$ complexes. In this case, the energy of the dissociation barrier should be 2.5 eV as in the case of the thermal dissociation.

TABLE I. Vibrational frequency of the stretching and bending modes of (B,H) and (B,D) complexes calculated by *ab initio* methods (Ref. 19).

Local vibrational mode	(B,H)	(B,D)
Stretching (cm^{-1})	2657	1965
Bending (cm^{-1})	1501	1366

C. LVM in diamond

The lifetime of a LVM depends on the number of phonons that take part in its decay process; the lower the number of phonons involved the shorter the lifetime. Sun *et al.*[28] have established a universal frequency gap law that gives the lifetime τ_0 at low temperature as a function of the decay order of the relaxation (i.e., the number of phonons involved) for H and D bending modes in various semiconductors. This law is

$$\tau_0=\frac{1}{\Gamma_0}=\alpha\exp(\beta N), \qquad (12)$$

where α and β are fitting parameters with a value of 0.15 ps and 2.01, respectively, N is the decay order and Γ_0 is the decay rate at 0 K corresponding to τ_0.

Goss *et al.*[19] have calculated the vibrational frequency of the stretching and bending modes of (B,H) and (B,D) complexes in diamond using *ab initio* methods. They are listed in Table I. On the basis of these *ab initio* calculations, the stretching and bending modes of (B,D) and (B,H) complexes should decay by a two-order process ($N=2$) as the phonon modes in diamond are below or equal to 1332 cm^{-1}. At 5 K,

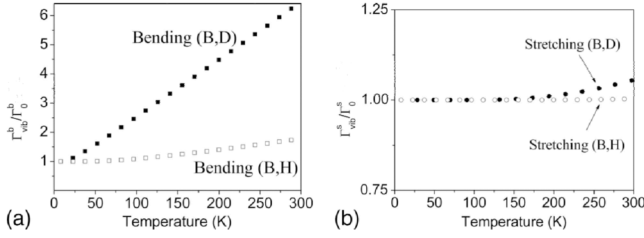


FIG. 3. Evolution of the decay rate as a function of temperature for (B,H) (open dots) and (B,D) (full dots) complexes considering (a) their bending and (b) stretching vibrational modes.

the lifetime of (B,D) and (B,H) bending modes should be around 8 ps according to Eq. (12). However, the LVM lifetime depends on temperature. Referring to Persson,[29] the decay rate can be written as

$$\Gamma_{vib} = \Gamma_0\left(1 + \frac{1}{\exp\left(\frac{\hbar\omega_1}{K_BT}\right) - 1} + \frac{1}{\exp\left(\frac{\hbar\omega_2}{K_BT}\right) - 1}\right). \quad (13)$$

For the bending modes, $\Gamma_0^b = 1.25\times10^{11}$ s^{-1} and ω_1, ω_2 are the frequencies of the two acceptor modes. In the case of the bending mode of (B,D), if we consider the Raman mode of diamond (1332 cm^{-1}) as one of the acceptor modes, the second one has a frequency of 34 cm^{-1}.[30] Figure 3(a) shows the temperature dependence of the relative decay rate, $\Gamma_{vib}^b/\Gamma_0^b$, calculated for the bending modes of (B,H) and (B,D) complexes in diamond.

For the bending mode of (B,D) complexes, the decay rate increases by a factor of 6 when the temperature increases from 5 to 300 K. For the (B,H) complexes, the decay rate of bending modes increases by a factor of 1.5. Such a decrease in the decay rate at low temperature should induce a dramatic increase in the dissociation rate due to the nonlinear character of the excitation process [exponent 4 in expression (9)].

In the case of the stretching modes, the situation is not that simple since the accepting modes can be bending modes and/or bulk phonons.[30] For this reason, it is difficult to evaluate the decay rate Γ_0^s at 0 K. Nevertheless, Fig. 3(b) shows the temperature dependence of the relative decay rate $\Gamma_{vib}^s/\Gamma_0^s$ of the stretching modes of (B,H) and (B,D) complexes in the case where one of the acceptor modes is the bending mode. It should be noted that the same evolution is obtained in the case where the acceptor modes are bulk phonons modes (not shown here). For (B,D) and (B,H) complexes, no significant evolution of the decay rate is observed in the range of 0–300 K.

Introducing the above calculated value of $\Gamma_{vib}=3.2\times10^{11}$ s^{-1} at 100 K for the bending LVM relaxation rate and $\nu_0=200$ THz for the attempt frequency[22] in Eq. (9), we could extract from the fit of Fig. 2 an inelastic cross-section σ_{in} of 9.7×10^{-12} cm^2. From this we can check the approximations made in Sec. II B. At 100 K, for the bending modes of (B,D) complexes, Γ_{vib} equals 3.2×10^{11} s^{-1} and $\exp(-\frac{\hbar\omega_{vib}}{K_BT_s})\approx6\times10^{-10}$.

The second term in expression (6) is then $\approx$190. For a current density of 0.17 A cm^{-2} (10 nA), the first term is $\approx1\times10^7$. Consequently, the second term in expression (6) is negligible when compared with the first one. Moreover, in the case of our experiments, the value of the ratio $\frac{\sigma_{in}.j/q}{\Gamma_{vib}}\approx3\times10^{-5}\lll1$ is coherent with the simplification of expression (9).

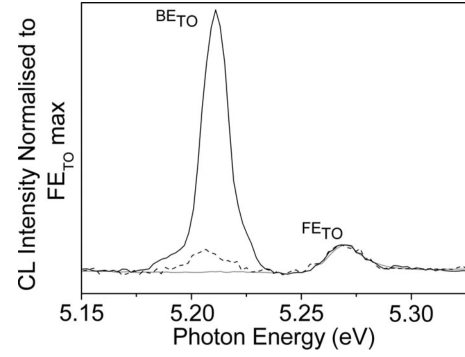


FIG. 4. CL spectra of a passivated sample (gray line), after exposure to a 10 nA ($j=0.04$ A cm^{-2}) e-beam during 2 min at 90 K (dashed line) and during 2 min at 10 K (black line).

D. Dissociation kinetics as a function of temperature

All the dissociation experiments as a function of temperature consisted in irradiating a surface of 5×5 μm^2 of the sample with a high current intensity (20 nA) during a given time (the dissociation time). Then the CL spectrum is recorded under the same high current excitation for 10 s to evaluate the concentration of the dissociated complexes ("reading during writing" protocol).

Figure 4 shows the CL spectrum of the deuterated sample recorded at 10 K and at low current (0.5 nA) for which dissociation is not significant. This spectrum shows the free-exciton recombination peak assisted by a TO phonon (FE$_{TO}$) at 5.27 eV. The boron bound-exciton recombination peak assisted by a TO phonon (BE$_{TO}$) at around 5.21 eV is not detected confirming that almost all boron acceptors are passivated. After exposure of the sample to a 10 nA e-beam during 2 min the spectra exhibit the BE$_{TO}$ peak. This implies that some of the boron acceptors were reactivated under the e-beam exposure. The BE$_{TO}$ peak intensity is drastically enhanced at the lowest temperature indicating that the low temperatures accelerate the dissociation kinetics.

The dependency of the dissociation kinetics on temperature is plotted in Fig. 5. In this figure, the reactivated acceptor concentrations deduced from the CL quantification are normalized to the boron concentration of the sample and plotted for different dissociation times. At 90 K, the fraction of the reactivated boron concentration has a much slower dependence with the dissociation time than at 10 K. Fitting the data as explained in Sec. III, we obtain a dissociation rate ν of about 1×10^{-5} s^{-1} at 90 K for a current density of 0.08 A cm^{-2} (further experimental work is needed to elucidate faster dissociation rate near $t=0$). This value is consistent with the data of Fig. 2.

At 10 K, we also observe an increase in the reactivated boron concentration with the electron dose but with a much steeper slope. We use the same fitting procedure than previ-

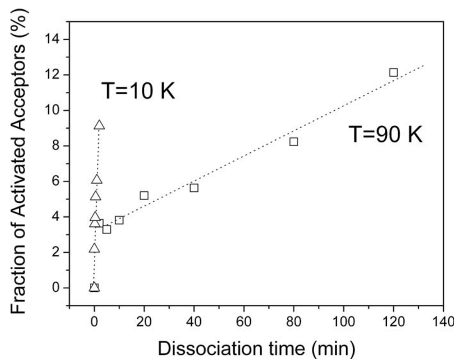


FIG. 5. Evolution of the fraction of activated acceptors by the e-beam irradiation as a function of the dissociation time at 10 K (triangle) and 90 K (squares) for an electron-beam current of 20 nA ($j=0.08$ A cm^{-2}) at 10 keV.

ously. We deduce that the dissociation frequency at 10 K is 5×10^{-4} s^{-1}. However at 10 K, the retrapping phenomenon is not negligible ($\sigma\neq0$).[25] Consequently, the dissociation rate is underestimated. This shows that the dissociation frequency at 10 K is at least 50 times faster at 10 K than at 90 K.

This strong temperature dependence provides an additional evidence that the mechanism of multiple vibrational excitation is involved in the dissociation of (B,D) complexes under e-beam excitation. To the best of our knowledge, such an increase in dissociation rate with decreasing temperatures has never been seen in mechanisms other than vibrational. Finally, considering the negligible effect of temperature on the decay rate of (B,D) stretching modes (Fig. 3), the vibrational mode involved in the dissociation is likely to be the bending mode of (B,D) complexes. In this scenario, the dissociation energy under e-beam of (B,D) complexes would be 0.7 eV in close agreement with the most recent theoretical predictions.[26]

V. CONCLUSION

We have investigated the dissociation rate of (B,D) complexes in diamond as a function of the electron-beam current and the temperature. At first, we showed that the variation in the dissociation rate is a power law function of the e-beam current giving a first signature of a vibrational mechanism. Further, the dissociation rate increases by more than a factor of 50 fold as the temperature decreases from 90 to 10 K. The counter intuitive instability of the (B,D) complexes at low temperature has been interpreted according to the THO model considering the increase in the bending mode decay rate with temperature. This gives an additional signature of the vibrational origin of dissociation under e-beam. From the experimental data, the energy barrier ΔE to overcome for (B,D) dissociation under e-beam excitation is estimated to be 0.7 eV. This value is smaller than the thermal dissociation energy ($Ed=2.5$ eV). The injection of minority carrier is probably responsible for this lowering of the energy barrier, in good agreement with recent *ab initio* calculations. As a perspective to this work, the isotopic effects on the dissociation kinetics should be studied by investigating the effect of e-beam exposure on (B,H) complexes in diamond. Finally, these findings are of high interest to develop a technique of electrically insulating/conductive pathway fabrication in diamond using direct e-beam writing.

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