Boron acceptor concentration in diamond from excitonic recombination intensities

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Excitonic recombinations are investigated by cathodoluminescence in a series of homoepitaxial diamond layers doped with boron in the range (2×10^{16})–(5×10^{18}) at cm^{-3}. As opposed to earlier observations made on polycrystalline boron-doped diamond, we show that the ratio between the neutral-boron bound exciton and the free-exciton recombination intensities is proportional to the boron content up to 6×10^{17} cm^{-3} and starts to saturate above this value. The probability of an exciton in diamond being trapped by only one boron impurity is calculated and appears to be in good agreement with the observed saturation, suggesting the formation of excitons bound to near-neighbor boron pairs at high boron concentrations.

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Diamond is a wide-band-gap semiconductor combining ultimate electronic properties (highest hole mobility, saturation velocity, and breakdown voltage) and exceptional physicochemical properties.[1] For instance, it shows an exceptional biocompatibility, one of the largest window potentials for electrochemistry in a water solution, a legendary hardness, a thermal conductivity above that of copper, an unbeaten transparency from ultraviolet to infrared light, chemical and radiation inertness, etc. This has motivated a large panel of potential applications for this material.[1] On the other hand, its synthesis is not straightforward, though it has been rapidly developing since the success of vapor phase epitaxy, assisted by hot filament or microwave plasma, in the 1980s. Today, its *p*-type doping is relatively well-controlled via the addition of boron impurities in the gas phase during growth. Boron introduces an acceptor level at ∼0.37 eV above the valence band of diamond.[2]

The luminescence properties of synthetic boron-doped diamond were first investigated in 1993 by Kawarada *et al.*[3] with polycrystalline layers grown on silicon substrates. The authors show that the intensity ratio *r* between neutral-boron bound excitons and free-exciton recombinations observed in cathodoluminescence (CL) increases with the boron acceptor concentration [B]—estimated from electrical transport measurement—and this occurs with a sublinear dependence $r \sim [B]^{0.76}$. For larger boron concentrations, the authors show a saturation of *r* above 6×10^{18} cm^{-3}. Up to now, these results have served as calibration guides in many studies in which a nondestructive and contactless quantification of the boron acceptor concentration is required. However, as yet they seem not to have been updated with the progress achieved in diamond synthesis during the past two decades.

In this work, we study the exciton recombination properties in a series of 17 boron-doped homoepitaxial layers with concentrations ranging from 2×10^{16} to 5×10^{18} cm^{-3} as measured by secondary-ion mass spectrometry (SIMS). From these monocrystalline samples, it is shown that the ratio *r* is *proportional* to the boron acceptor concentration up to 6×10^{17} cm^{-3} and *saturates* above this value. This provides a more accurate quantification of the boron acceptor concentration by CL. The origin of the saturation effect is discussed with the exciton Bohr radius and nearest-neighbor statistic arguments.

The diamond samples analyzed in this work were elaborated in two different laboratories. Twelve samples were grown at the LIMHP. They consist of boron-doped homoepitaxial layers grown on (100)-oriented Ib 3×3 mm^2 diamond substrates purchased from Sumitomo Electric. Before growth, the substrates were chemically cleaned to remove metallic and organic contaminants, and they were submitted to an H$_2$/O$_2$ plasma pretreatment, the benefits of which have been demonstrated in the case of undoped thick-film growth.[4] The microwave power density was fixed at 100 W cm^{-3}, the substrate temperature at 850–950 °C, and the methane concentration at 7%, corresponding to growth conditions optimized according to the procedure developed for intrinsic diamond.[5] The deposition time is adjusted to obtain typically 10–20-μm-thick films. For boron doping, B$_2$H$_6$ precursor is added in the gas phase, with a ratio ([B]/[C])$_{gas}$ that varied in the range 0.5–200 ppm. Five other samples were grown at CEA-LIST; detailed information on the growth procedure and their electrical properties is given in Ref. 6.

SIMS using Cameca IMS 4f equipment was performed on the samples to measure the depth distribution of boron atoms into the diamond films with Cs+ primary ions accelerated at 10 keV. The boron concentrations were quantified using implanted standards. For each sample, an accurate value of the boron concentration ($\pm 10\%$ in the best conditions) was obtained by an average on the probed depth. The optical properties of the samples were investigated by CL spectroscopy using a Horiba Jobin Yvon SA system installed on a JEOL840 scanning electron microscope (SEM). The
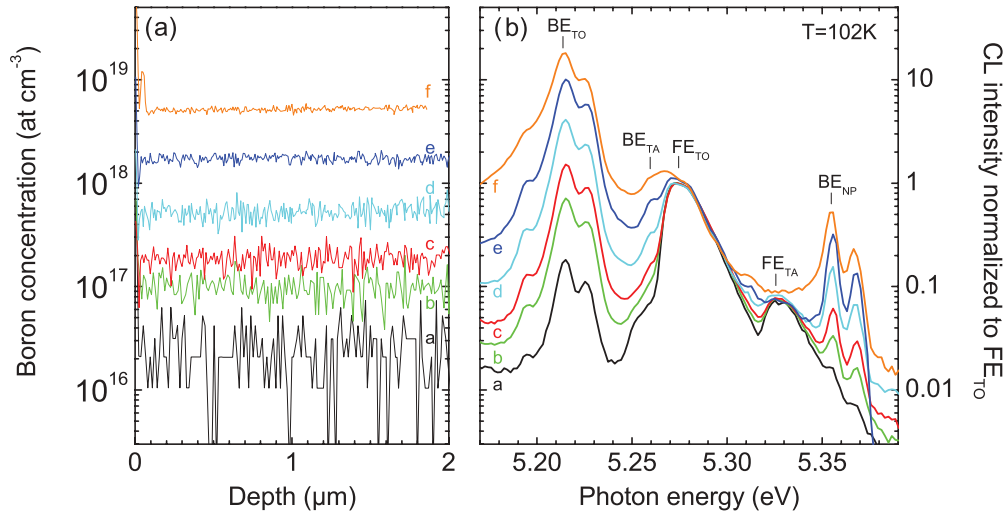
FIG. 1. (Color online) (a) SIMS profiles of the boron concentration in homoepitaxial diamond layers labeled a, b, c, d, e, and f with increasing boron content; (b) near band-edge CL spectra of the corresponding samples after normalization to the FE maximum recombination intensity (FE$_{TO}$). When compared to the FE, the boron-bound exciton recombination intensities (BE$_{TO}$, BE$_{TA}$, and BE$_{NP}$) increase with the boron content in diamond.

boron-doped diamond layers were excited with a 10-keV focused e-beam (stopping depth of $\sim$0.8 μm) and a typical beam current of 5–10 nA. To evacuate the electrical charges, the epitaxial layers were coated with a semitransparent gold layer ($\sim$5 nm). Samples were cooled down to 102 ($\pm$2) K thanks to a liquid nitrogen cold finger. The CL emission was collected by a parabolic mirror and injected with metal optics into a monochromator of 0.55-m focal length, equipped with a uv enhanced-silicon charge-coupled-device (CCD) camera and a 600 grooves/mm diffraction grating. The spectral resolution was equal to 0.26 nm in the spectra, reported here as recorded, and the calibration was performed using an Hg lamp.

Figure 1(a) presents 2-μm-depth SIMS profiles of boron in different epilayers. The boron concentration is remarkably constant in depth as a result of the well-controlled vapor pressure of the boron precursor during growth. Facing the SIMS profiles, Fig. 1(b) shows the CL spectra at a temperature of 102 K of the corresponding samples in the near-band-gap region. The free-exciton (FE) recombinations are assisted by the emission of phonons to cross the indirect band gap of diamond. Their maxima are located at 5.272 eV for FE^{TO} recombination assisted by a transverse optical (TO) phonon and 5.324 eV for FE^{TA} recombination assisted by a transverse acoustic (TA) phonon. At 102 K, the line shape of FE recombinations is asymmetric due to the thermal distribution of exciton kinetic energy. In boron-doped diamond, free excitons can complex with neutral acceptors with a binding energy of $E_{loc} = 51$ meV to give neutral-boron bound exciton (BE) recombinations with maxima at 5.214, 5259, and 5.354 eV for the TO, TA, and no-phonon (NP) lines, respectively. The line shape of the neutral-boron BE is also easily identifiable thanks to its 11-meV fine-structure doublet thermally activated at 102 K. A more detailed description of excitonic transitions in boron-doped diamond can be found in Refs. 7 and 8.

CL spectra of Fig. 1(b) were normalized to the FE^{TO} maximum recombination intensity. At high boron doping,

this normalization is not straightforward since the BE^{TA} recombination clearly overlaps with FE^{TO}, and no accurate value of the recombination intensity ratio $r = $ BE^{TO}/FE^{TO} can reasonably be extracted for boron concentrations above 6×10^{18} cm^{-3}. In this work, note that we define r as the ratio between the maximum intensity (height) of the luminescence peaks BE^{TO} to FE^{TO} and not as their integrated intensity; this is done to simplify its use in a calibration curve. Comparing Figs. 1(a) and 1(b), a clear correlation between the boron concentration and the ratio r appears. This ratio r is plotted in Fig. 2 as a function of the boron concentration measured by
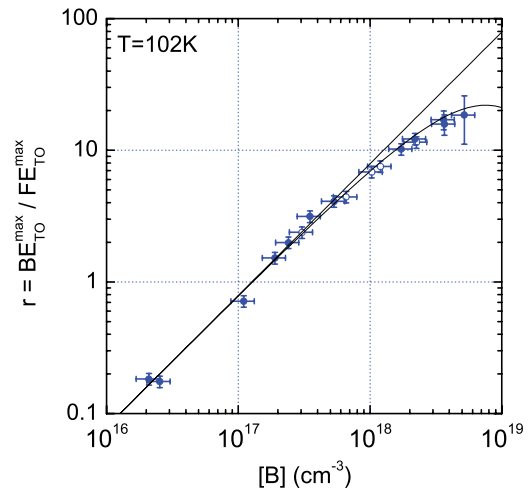

FIG. 2. (Color online) Intensity ratio r between the CL recombinations of the neutral-boron bound exciton BE$_{TO}$ and the free exciton FE$_{TO}$ as a function of the boron concentration measured by SIMS. The continuous curves $r = 7.9 \times 10^{-18}$ [B] and $r = 7.9 \times 10^{-18}$ [B] exp(-1.32×10^{-19} [B]) are also plotted. The experimental dependence of the excitonic intensity ratio with respect to the boron concentration is almost linear up to $\sim$6 $\times 10^{17}$ cm^{-3} and begins to saturate above this value.

SIMS. The relationship is linear with a 7.9×10^{-18} cm³ sensitivity factor for boron concentrations below 6×10^{17} cm⁻³ and saturates above this value.

Here, we discuss the use of Fig. 2 as a calibration curve for the accurate determination of the boron acceptor concentration in diamond, N_A, by CL. Such an optical method for the measurement of the dopant concentration, gathering a contact-free, nondestructive, and extremely low detection limit, is very attractive when compared to the relatively heavier electrical or physicochemical characterization techniques. However, luminescence techniques are often considered to be poorly reliable due to the many and uncontrolled radiative and nonradiative recombination paths that could affect the reproducibility of measurements from a specimen, and from one experiment to another. The first attempts at dopant quantification with photoluminescence were reported more than 30 years ago with silicon,[9] but it is only recently that the whole experimental procedure was thoroughly detailed to provide the required reproducibility.[10] For the photoluminescence of silicon, the use of a very-low-excitation power is necessary to avoid the formation of undesirable recombination channels (e.g., bound multiple-exciton complexes, electron-hole liquid, etc.) that could compete with impurity bound-exciton recombinations. Under these conditions, the ratio r finally reflects the quasiequilibrium between the BE and FE populations. Furthermore, the authors of Ref. 10 show that electron-hole injection under laser excitation (even very weak) provides efficient dopant neutralization. As a result, the electrical compensation does not apply and both donor and acceptor concentrations can be measured independently from the ratios of each impurity-bound to free-exciton recombination intensity (bound excitons generally recombine at different energies according to the impurity).

This situation seems to also apply in diamond, and with less restrictive excitation conditions, as already shown in a previous paper in the case of n-type phosphorus-doped diamond containing compensating boron acceptors.[11] We have demonstrated that neutral-phosphorus donor and neutral-boron acceptor BE recombinations can be observed simultaneously by CL. In addition, we have shown that their associated ratio r is not dependent on the excitation beam current in a wide intensity range (0.1–100 nA). As a result, the use of calibration curves such as that reported in Fig. 2 in the case of the CL of diamond seems very reasonable for a direct measurement of the dopant concentrations.

Let us emphasize here that, since an exciton basically binds to a neutral boron atom, the ratio r is sensitive to the acceptor concentration, N_A. Since $[B]_{SIMS} = N_A$, an assumption that is widely accepted for boron-doped diamond in this range of doping level, the relationship $r = 7.9 \times 10^{-18} \, N_A$ provides an accurate determination of N_A (cm⁻³) from a CL spectrum when $N_A < 6 \times 10^{17}$ cm⁻³. Above this value, it is better to directly refer to the calibration curve reported in Fig. 2 or to use the relationship given later.

To close this discussion with metrology arguments, we have seen that the maximum acceptor concentration that is measurable with this optical method is 6×10^{18} cm⁻³ at a temperature of 102 K. On the low concentration side, the limiting factor is the signal-to-noise ratio of the apparatus,

and one can achieve an $\sim 10^{14}$ cm⁻³ detection limit from a CL spectrum taken at 102 K, which is typically two orders of magnitude below the SIMS detection limit for boron ($\sim 10^{16}$ cm⁻³). A calibration curve at lower temperatures further improves this detection limit ($\sim 10^{13}$ cm⁻³), since the detrapping of free excitons from the boron dopants is quenched at lowest temperatures. The same samples were also measured at 10 K with the same method (not shown here). At 10 K, the calibration relationship becomes $r = 2.0 \times 10^{-17}$ Na.

In silicon, the application of this luminescence method is limited to ultrapure ingots, because of the much higher sensitivity factor: 10^{-12}–10^{-13} cm³ in silicon at 4.2 K (Ref. 10) compared to 1.0×10^{-17} cm³ in phosphorus-doped diamond[11] and 7.9×10^{-18} cm³ in boron-doped diamond at 102 K (this work). The basic origin of such a large difference in the sensitivity factors may be found by analyzing equation rates, where the decay times of bound excitons appear to play a major role. BE decays are usually controlled by Auger processes, and are predicted to be three orders of magnitude shorter in diamond than in silicon.[12] Additional time-resolved CL experiments should be performed to elucidate this point.

In this last part, we discuss the origin of the saturation of r above 6×10^{17} B cm⁻³. Looking at the phosphorus donor calibration curve at the same temperature,[11] we also notice a saturation effect in the same range of concentrations. This suggests that the saturation effect comes from a basic diamond property. Free excitons in diamond are very stable, with a binding energy of 80 ± 5 meV.[7] Thus, the associated optical effective mass in the Wannier model is $m_{\mathrm{eff}} = 0.191 m_0$, leading to a Bohr radius of $a^*_B = 15.8$ Å. Excitons in diamond are then much more compact than in silicon (42 Å). Statistically, the FE wave function overlaps *in average* with two boron atoms, as soon as $(3/4\pi [B])^{1/3}$, the average distance between two isolated boron atoms, equals $2a^*_B$. In diamond this scenario is reached at a boron concentration $[B]_s = 7.6 \times 10^{18}$ cm⁻³, which corresponds remarkably well with the saturation region observed in Fig. 2. This would suggest that when a free exciton probes two boron traps, it binds only to one of them (one boron atom is lost for the quantification), or it binds to the pair of boron atoms (in this case, two boron atoms are lost for the quantification). At $[B]_s$, the factor observed in Fig. 2 between the linear extrapolation from low doping levels and the measured excitonic ratios is larger than 2, which suggests the higher likelihood of the second interpretation. An exciton bound to a pair of dopants would exhibit a higher localization energy than one bound to a single dopant. If its oscillator strength is sufficient, it will recombine radiatively at a lower energy, as already observed for phosphorus pairs in diamond[13] and in many other semiconductors.

Pushing the argument further with a statistical approach, the probability p for a boron atom to have no other boron atom in its vicinity below a distance R is given by $p(R,[B]) = \exp(-4\pi R^3 [B]/3)$.[14] As a consequence, the probability to have only one boron atom in the exciton wave function is given by $\exp\{-4\pi (2a^*_B)^3 [B]/3\}$. The fraction of isolated boron atoms trapping an exciton is then $[B]\exp\{-4\pi (2a^*_B)^3 [B]/3\}$. This means that $[B]$ must be replaced by this expression in the relationship $r = 7.9 \times 10^{-18}$ $[B]$. Numerically it gives

$r = 7.9 \times 10^{-18}$ [B] $\exp(-1.32 \times 10^{-19}$ [B]) as plotted in Fig. 2. In this figure, we can see that this simple statistical model gives a fair description of the experimental dependence of $r = f([B])$, suggesting that the ratio r gives a measurement of the boron acceptors that are *separated* by a distance above the spatial extension of the excitonic wave function. It may be noted that such a saturation effect has never been observed in materials other than diamond. In silicon, the saturation value [B]$_s$ is expected at a value of 4×10^{17} cm^{-3}, which is well above the upper limit of the measurement range ($\sim 10^{15}$ cm^{-3}), due to the higher sensitivity factor already discussed.

The excitonic recombinations in a series of monocrystalline diamond layers homogeneously doped with boron have been studied by CL at low temperatures. As opposed to earlier studies on boron-doped diamond, the ratio between the neutral-boron BE and the FE recombination intensities is found to be proportional to the boron content up to 6×10^{17} cm^{-3} and starts to saturate above this value. The probability of an exciton being trapped by only one boron impurity is in good agreement with the saturation observed experimentally, suggesting the formation of excitons bound to several near-neighbor boron atoms at high boron concentrations. These results make it possible to accurately measure boron acceptor concentrations in insulator and conductive diamond (from 10^{13} to 10^{18} cm^{-3}) by a nondestructive and contactless CL analysis.

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