



Hydrogen passivation of boron acceptors in as-grown boron-doped CVD diamond epilayers

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ABSTRACT

A homoepitaxial boron-doped diamond single layer is investigated by means of Fourier transformed infrared spectroscopy (FTIR) and cathodoluminescence (CL). Both techniques are shown to be complementary. μ -FTIR mapping allows to determine the location of active boron while CL allows discernability between passivation and compensation. Hydrogen incorporation during chemical vapour deposition (CVD) growth is revealed to passivate boron acceptors. The obtained results highlight that plasma etching can induce a dissociation of B–H centres.

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1. Introduction

Since the attribution of p-type doping to boron acceptors, strong variations in the diamond properties depending on the growth conditions (blue colour for gemological application, carrier densities, defect densities, superconducting critical temperature T_c , etc.) have been repeatedly reported in the scientific and technical literature over the last twenty years. However, the way in which boron is incorporated within the diamond lattice is still an open question. Indeed, the formation of hydrogen–acceptor complexes with point defects, boron pairs and clusters or interstitial sites can lead to electrically inactive boron incorporation and to an impurity-induced damage to the crystalline quality which may, for instance, explain the brown colour of metallic CVD epilayers. Such kind of defects should reduce the mobility of the carriers without improving their density. The way in which the hydrogen passivates the boron acceptor is also an open question. Recently, Barjon et al. [1] reported the difference in the reactivation of boron after deuterium and hydrogen related passivation. They found that B–H complexes are twice more stable than B–D ones. This behaviour seems to be the inverse to conclusions of other authors as, for example, Goss and Briddon [2], who argue for a higher stability of B–D complexes. Thus, both the location of hydrogen and the B–H complexes binding energy are still under discussion. The presence of hydrogen in some cases even changes the doping character, from p- to n-type, of boron-doped diamond as reported by Teukam et al. [3]. This illustrates the importance of controlling

hydrogen incorporation during and after CVD growth. Recently, Muret et al. [4] reported a highly resistive behaviour located in the last micron of boron-doped CVD grown layers that contrasts with the behaviour of the buried material. Indeed, after plasma etching of 1 μ m diamond, their epilayer becomes conductive. They attribute this character to a boron passivation by hydrogen or a compensation by donor defects located just in the surface of the epilayers.

In this contribution, we study further this behaviour by means of spectroscopic techniques in order to understand the reasons for such a superficial effect. FTIR (Fourier Transform infrared spectroscopy in reflection mode) allowed the detection of the activated N_A – N_D density, while cathodoluminescence (CL) informs on the activated acceptor density N_A through the relative intensity of free and bound exciton recombinations.

2. Experimental

The sample here studied is a boron-doped CVD homoepitaxial diamond. Previous results of conductivity and photoinduced current transient spectroscopy (PICTS) of the presently studied sample have been reported by Muret et al. [4]. The boron-doped film has been deposited on an E6 CVD (100) substrate (optical grade quality, 3 mm \times 3 mm \times 0.5 mm), at a pressure of 50 Torr and a temperature of 910 °C in a NIRIM type reactor with a [B]/[C] ratio of 50 ppm, and a [CH₄]/[H₂] ratio of 1%. The homoepitaxial layer obtained is 700 nm thick, with an increasing B-content from $1.5 \times 10^{18} \text{ cm}^{-3}$ at the substrate–epilayer interface to $2 \times 10^{18} \text{ cm}^{-3}$ at the surface. The substrate boron concentration is below the SIMS detection limit ($5 \times 10^{15} \text{ cm}^{-3}$).

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To study the buried part of the epilayer, a 500 nm deep ECR (microwave electron cyclotron resonance plasma of oxygen) etching has been performed on half of the sample surface. A detailed description of the ECR equipment has been already given elsewhere [5,6]. The layer was etched at room temperature for 8 min under a RF self-bias voltage of 27.5 V, a microwave power of 1600 W, and an oxygen pressure of 2.35 mTorr.

Room temperature FTIR spectra were collected with a FTIR Nicolet Impact 410 equipment attached to a FTIR microscope IR Plan Advantage using both transmission and reflection modes with a resolution of 4 cm^{-1} . All the spectra were converted into absorbance spectra for calculations. The absolute active boron concentration values were deduced from the absorbance spectra using the calibration of Collins and Williams [7] from the absorption at the 2800 cm^{-1} absorption line. An identical CVD substrate was used as a reference, to remove the intrinsic diamond related peaks and thus to illustrate the boron-related behaviour.

The CL analyses have been performed at 100 K and a 5 K with a Quanta 200 SEM coupled with a collecting mirror and an ANDOR spectrometer system (EM-CCD 1600×400 pixels and a 160 mm focal length spectrometer). At 235 nm, the spectral resolution is better than $2 \times 10^{-3}\text{ eV}$ for the chosen experimental conditions. The CL spectra were carried out at an acceleration voltage of 20 kV and 5 kV to show effects occurring near the sample surface. All the spectra presented here have been normalized in counts to the FE_{TO} maxima (free exciton with transverse optical phonon replica) peak.

3. Results and discussion

In the following the as-grown region is labelled “region A” and the etched one “region B” as shown in the inset of Fig. 1. First, FTIR absorption spectra were recorded to obtain the absolute active boron concentration. Second, reflectance spectra allowed a much higher spatial resolution but gave only a relative variation of the boron-related peak. Then, absolute mapping of active boron concentration became possible. Finally, cathodoluminescence measurements were carried out to confirm the FTIR conclusions.

Fig. 1 spectra present absorbance measurements on both regions. Intrinsic diamond shows usually absorption bands in the two and three-phonon range, between 1500 and 4000 cm^{-1} . Those peaks overlap the present boron-related signals attributed to hole transition between dopant levels of the hydrogen-like system. For this reason the intrinsic absorption was subtracted from each spectrum using an identical CVD substrate as reference. The two absorption bands at 2450 and 2800 cm^{-1} , respectively attributed to the ground state to first excited state electronic transition and to the ground state to second excited state electronic transition of neutral boron acceptor [8], are detected only in the region B. These two bands are not detected in region A. Quantifying the total neutral boron present in the substrate + epilayer (region B) system crossed by the optical beam during the transmittance experiment using the integral of the 2800 cm^{-1} absorption peak, and reducing it to the 200 nm thick epilayer, a concentration of neutral boron acceptors of around $1 \times 10^{18}\text{ cm}^{-3}$ is deduced. This value is close to that obtained in SIMS experiments: $2 \times 10^{18}\text{ cm}^{-3}$. This is reasonable taking into account that the epilayer thickness of region B after plasma etching is not precisely known. In region A, in spite of an identical boron concentration, there is a total disappearance of both the 2450 and 2800 cm^{-1} absorption bands (see Fig. 1).

Such results seem to corroborate the Muret et al. [4] results. They found that region A was not conductive while region B behaved as a doped layer. However, they concluded that the surface was probably passivated by hydrogen or compensated by a donor-type defect. The FTIR measurements are performed across the whole sample thickness, thus the conductive/non-conductive transition should not occur depending on the depth in the epilayer. In region A the whole layer

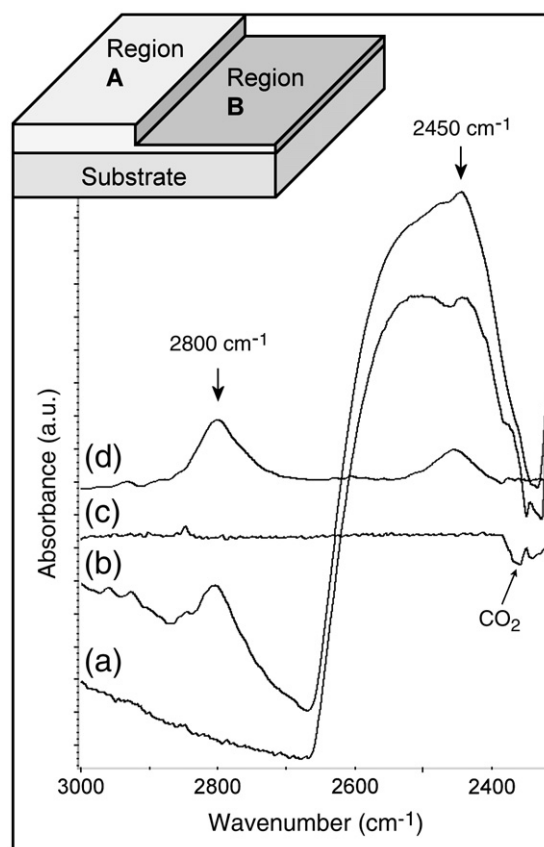


Fig. 1. Absorbance FTIR spectra acquired in (a) as-grown region A and (b) etched region B. The spectra (c) and (d) correspond to the same spectra after subtraction of the substrate contribution. Peaks at 2800 cm^{-1} and 2450 cm^{-1} correspond to boron-related hole transitions. Spectrum (c), corresponding to region A, did not reveal the presence of boron while the (d), corresponding to region B, shows both boron-related transitions.

is not conductive as no active boron is present, while in the region B a large fraction of the boron atoms seem to be electrically active. This seems to indicate that the insulating character of region A is probably due to a hydrogen passivation, as plasma etching cannot remove structural defects without removing the crystal itself.

To investigate this point in more details, FTIR mappings in reflectance mode were carried out. In Fig. 2a an optical microscopy (OM) observation is shown, where the square indicates the reflectance FTIR mapping zone of Fig. 2b. The spectra linescan position of Fig. 2c is also indicated. The FTIR mapping and spectra are recorded in the reflecting mode giving then relative boron variation information. To obtain the absolute values of active boron incorporation, transmittance measurements on both regions A and B of Fig. 1 were used to “calibrate” the reflectance spectra. In Fig. 2b, the map is obtained using the ratio between the corrected heights at 2800 cm^{-1} and at 1980 cm^{-1} (corresponding to the intrinsic two-phonon absorption LO + TA(X)). Both mapping and linescan show the sharp transition between active and non-active boron region. The only difference is the plasma etching operation.

As the absorption coefficient of the 2800 cm^{-1} absorption peak gives the $N_A - N_D$ concentration [9], this change in the intensity can be due to hydrogen passivation or dopant compensation across the whole thickness. To determine which a mechanism occurs, cathodoluminescence (CL) experiments were carried out. Indeed, the ratio between intensity peaks attributed to free exciton (FE) and bound exciton (BE) recombinations, with the transverse optic (TO) replica, depends directly on the active dopant concentration and can be used to quantify independently donor and acceptor concentrations. Donors induce a BE_{TO} recombination at 5.175 eV [10] while boron acceptors

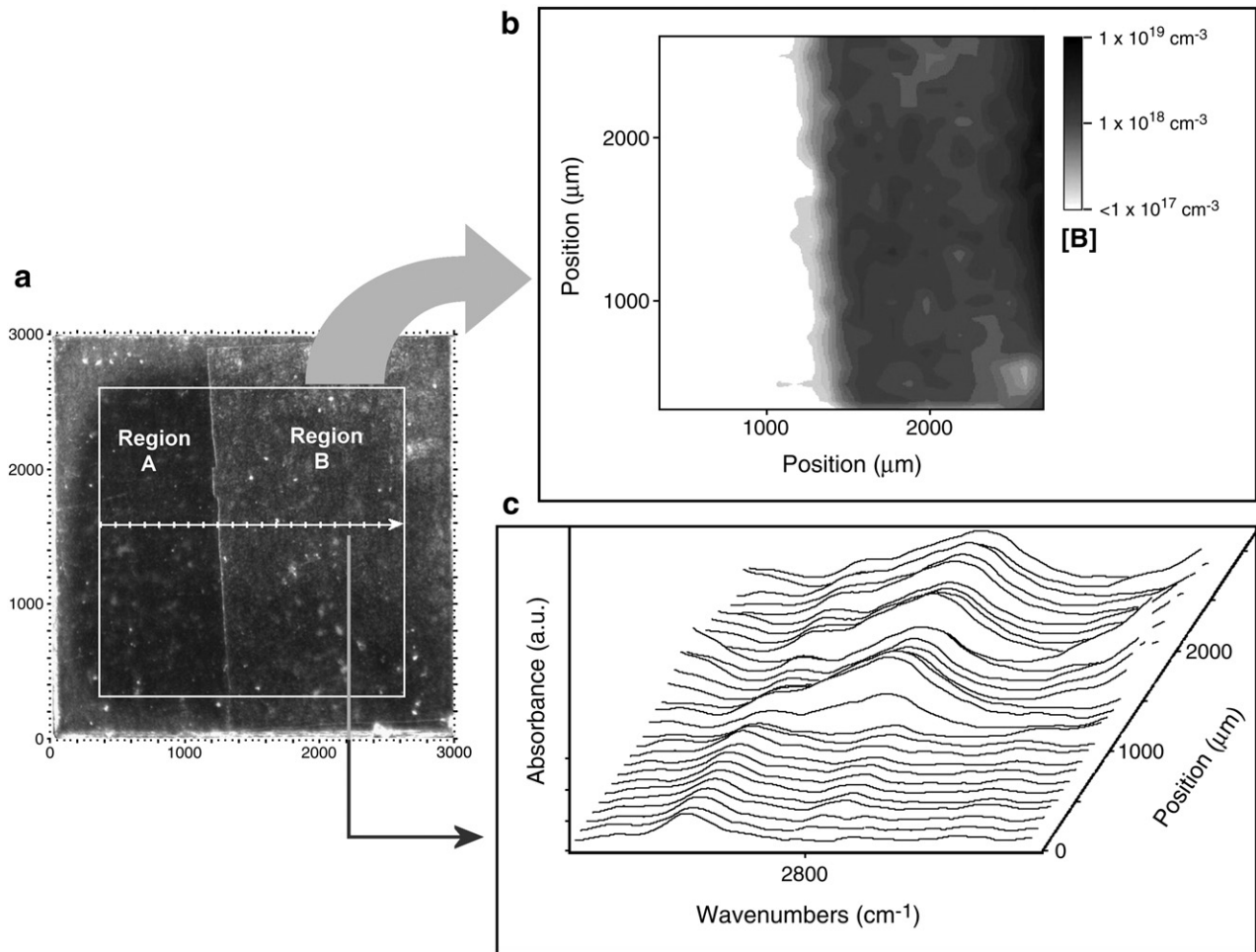


Fig. 2. (a) Optical microscopy image of the studied sample indicating the region of the FTIR mapping in (b) and the spectra linescan location in (c). The FTIR spectra are recorded in reflectance mode and then converted in absorbance spectra. The 2800 cm^{-1} peak related to the presence of neutral boron dopant is used to build the map in (b). A clear transition in the boron activity is revealed between regions A and B.

give a BE_{TO}^B recombination at 5.209 eV [11] and both peaks can be observed on the same spectrum [10]. Thus, in the case of a compensation of boron by donors, we expect to observe the two peaks but, if a full passivation of boron occurs, the boron-related BE_{TO}^B excitonic peak is expected to vanish as the excitons cannot anymore be bound to acceptors. Fig. 3 shows the CL spectrum at 5 K of the 0.2 μm thick etched epilayer (region B). The spectrum has been taken at 5 keV to ensure an e–h pair generation mostly in the epilayer. Due to the contribution of the BE_{TA}^B component in the recombination at 5.27 eV, the $I(BE_{TO}^B)/I(FE_{TO})$ ratio is higher than 12.5. The BE_{TO}^B peak lays at 5.220 eV. The ratio corresponds to the boron concentration saturation value above $7 \times 10^{17}\text{ cm}^{-3}$. The BE_{TO} peak stands just before the decreasing of the peak energy value occurring above $2 \times 10^{18}\text{ cm}^{-3}$ [12–14]. These results are consistent with that obtained from the FTIR and the SIMS experiments.

Fig. 4a shows the comparison between the two CL spectra at 100 K obtained on regions A and B for incident electrons of 20 keV. A clear absence of the boron acceptor related BE_{TO}^B peak is shown in region A, while this peak is present in region B, as already seen in Fig. 3, confirming that active boron is present there. This undoubtedly indicates that boron is passivated in region A and that no significant compensation occurs. The ratio $I(BE_{TO}^B)/I(FE_{TO})$ in region B gives a boron concentration of about $1 \times 10^{17}\text{ cm}^{-3}$ lower than that deduced in Fig. 1. This is a consequence of the high electron beam energy used (20 keV) generating e–h pairs in both the substrate and the epilayer. Even though the penetration depth, R , reaches 3 μm , it is important to note that the e–h pair generation is maximum at about the first third

of R [15,16]. Some of the pairs are generated and recombine in the substrate providing an extra contribution to the FE_{TO} peak and consequently an underestimation of the $I(BE_{TO}^B)/I(FE_{TO})$ ratio. This

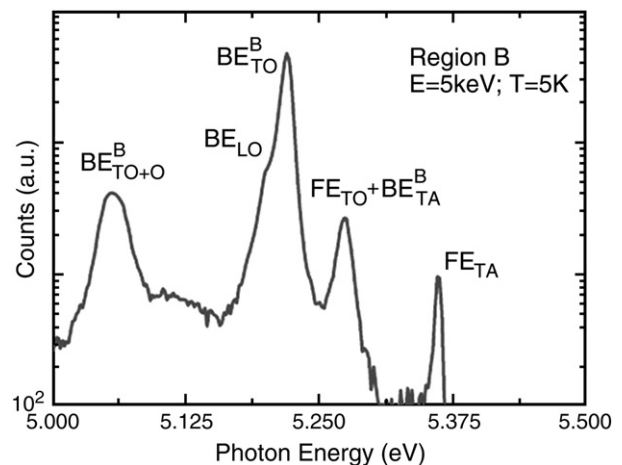


Fig. 3. CL spectrum recorded at $T=5\text{ K}$ and a beam energy of 5 keV on the plasma etched region B. Assuming a E_g of 5.49 eV, an exciton binding of 0.085 eV, an acceptor binding of 0.055 eV and a phonon energy of $\hbar\omega_{TA}=0.087\text{ eV}$ and $\hbar\omega_{TO}=0.141\text{ eV}$ for acoustic and optical transverse phonons, the BE_{TA} and FE_{TO} transitions stand at 5.263 eV and 5.268 eV respectively.

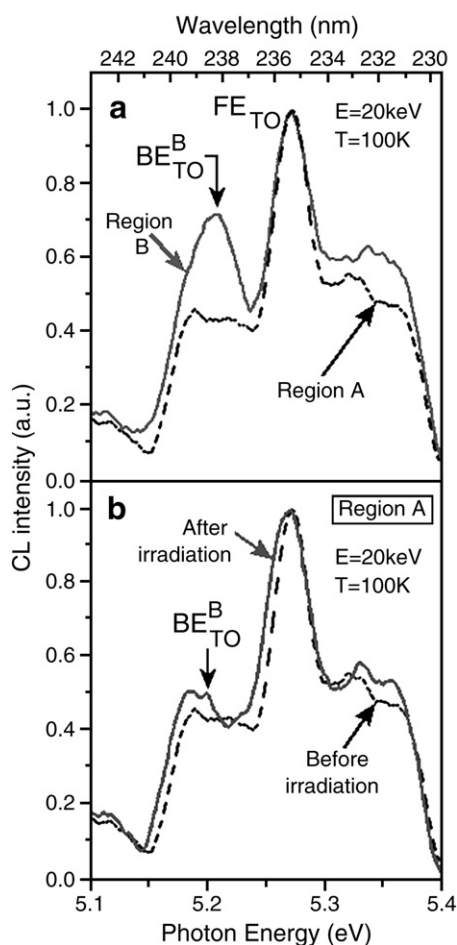


Fig. 4. CL spectra recorded at a temperature of 100 K and a beam energy of 20 keV and normalized in counts to the FE_{TO} maxima peak intensity. (a) Spectra recorded on regions A and B showing a clear difference in the BE_{TO}^B intensity. The relative importance of the BE_{TO}^B peak in region B is shown to decrease with respect to that of Fig. 3 recorded at 5 keV. This mainly results from the higher beam energy that induces a smaller proportion of e–h generation into the boron-doped epilayer. The absence of BE_{TO}^B in region A is due to a hydrogen passivation of boron acceptors. (b) Spectra recorded before and after electron irradiation of region A. A slight reactivation of passivated boron is observed (see arrow).

explains why the boron concentration deduced from CL with 20 keV incident electrons in region B is significantly underestimated.

On the other hand, boron acceptors can be reactivated by electron irradiation as recently reported [1]. When irradiating with electrons the passivated region A, using the experimental conditions ($T=100\text{ K}$, $t=15\text{ min.}$, beam conditions: 10 keV, 57 nA, on square surface of $25\ \mu\text{m}^2$) reported by Barjon et al. [1], some reactivation is observed (see arrow in Fig. 4b). The relatively reduced BE_{TO}^B peak intensity after irradiation suggests a lower reactivation than that reported by Barjon et al. We tentatively attribute it to a different hydrogen incorporation mechanism than that occurring during diffusion. Indeed, in this case,

the incorporation takes place during CVD growth. The hydrogen location and, thus, its binding energy might be higher, making the B–H complex more stable. The exact mechanism of B–H complex dissociation of the underlying diamond epilayer during ECR O_2 plasma etching remains to be determined.

4. Conclusions

FTIR and CL experiments were carried out on a boron-doped homoepitaxial layer. Previously published results point out to hydrogen passivation or defect related compensation taking place near the surface. The present investigation highlights the mechanisms here involved: hydrogen passivation during growth is responsible for the insulating character of the 700 nm thick epilayer doped with $2 \times 10^{18}\ \text{cm}^{-3}$ boron. The plasma etching applied on part of the sample surface seems to induce a dissociation of the B–H complexes which would explain the conductive character of the plasma etched region. The B–H complexes seem to be more stable in this growth-related mechanism than upon the usual plasma hydrogen diffusion. Finally, the FTIR mapping method is revealed to be a very powerful technique to determine absolute densities of active dopants in diamond.

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