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To cite this version:

Julien Barjon, A. Mehdaoui, François Jomard, Jacques Chevallier, Christine Mer-Calfati, et al.. Stability of B-H and B-D complexes in diamond under electron beam excitation. Applied Physics Letters, 2008, 93, pp.062108. 10.1063/1.2965115 . hal-00853438

HAL Id: hal-00853438

https://hal.science/hal-00853438v1

Submitted on 27 Apr 2022

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Stability of B-H and B-D complexes in diamond under electron beam excitation

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The substitution of hydrogen by deuterium is generally known to increase the stability of the defect passivation in semiconductors, occasionally giving rise to giant isotope effects. In this work, the stability under an electron beam irradiation of boron-hydrogen and boron-deuterium pairs in diamond are compared. The dissociation kinetics was followed *in situ* by cathodoluminescence spectroscopy. Surprinsingly, B-H complexes are more stable than B-D complexes under electron beam at low temperature (~ 100K), with a dissociation rate about twice smaller. These experimental results are coherent with a dissociation mechanism involving a cumulative vibrational excitation of the complexes.

In many semiconductors, hydrogen is known to passivate impurities, defects and dangling bonds via the formation of hydrogen-related complexes. The effective use of hydrogen-based passivation processes for operating optoelectronic devices depends on the stability of the complexes under different stresses. The lattice thermal excitation is the most common dissociation process. Injection of hot electrons also induces an efficient dissociation of hydrogen-related complexes, being for instance responsible for the SiO_2 thin film breakdown[1] and one of the main cause of the SiO_2/Si interface degradation[2] in metal-oxide-semiconductor (MOS) transistors. These effects have been well-described with distinct mechanisms proposed earlier[3-5] to account for the hydrogen desorption from a silicon surface under the tip-emitted current of a scanning tunneling microscope. They involve either an electronic or a vibrational excitation of the Si-H bond by the tunneling electrons. When replacing hydrogen by deuterium, its isotope, Si-D bonds are dramatically more stable under hot electron injection. It gives strong isotope effects when electronic excitation dominates and the so-called giant isotope effects in the case of a vibrational excitation[4, 5].

The presence of hydrogen in bulk semiconductors is also an interesting case where hydrogen can form complexes with doping impurities. Hydrogen interactions result in the passivation of donors or acceptors, bringing the semiconductor back to its intrinsic conduction regime. The case of the Mg acceptor in GaN is famous, if we consider that without an e-beam irradiation[6, 7] or a high temperature annealing[8] it remains passivated by the hydrogen introduced in GaN from the decomposition of precursor

gases. Band-gap engineering by hydrogenation of GaAsN structures is an other promising field recently proposed to build semiconductor nanostructures by e-beam writing[9].

Si-H(D) complexes in GaAs have been shown to be dissociable under e-beam or above band gap illumination, with strong isotope effects providing several evidences that the H(D) release under e-beam is induced by an electronic excitation[10-13]. On the other hand, B-D pairs in diamond do not follow this scheme. In our previous paper[14], we have shown that the dissociation efficiency of B-D complexes is strongly dependent on the excitation current, discarding the electronic excitation mechanism. We proposed that deuterated boron-doped diamond is a candidate for which the vibrational dissociation mechanism could apply. More recently, Goss et al have theoretically studied the influence of a carrier minority injection on the stability of the B-H complexes in diamond[15]. They concluded that the electronic excitation and the negative charging of B-H complexes significantly lower the dissociation barrier.

In this work, we investigate the effect of replacing deuterium by hydrogen on the boron acceptor reactivation by electron beam exposure in order to get further insight on the involved dissociation mechanisms. To this end, two identical boron-doped diamond layers were grown and passivated, one by a deuterium diffusion (deuteration), the other by a hydrogen diffusion (hydrogenation). The electron irradiation was performed in a scanning electron microscope (SEM) close to the liquid nitrogen temperature (~100 K) and the dissociation of complexes was followed by an *in situ* cathodoluminescence (CL)

analysis at a sufficiently low current so that complexes are not dissociated during the CL acquisition[14].

The two boron-doped layers were grown by microwave plasma assisted chemical vapour deposition (MPCVD) on the (100) face of 3x3 mm^2 synthetic diamond substrates (Sumitomo), using H_2-CH_4 mixtures. The incorporation of boron in the diamond films is due to the residual boron in the reactor chamber. The substrate surface was prepared by a hydrogen plasma during 1 hour before diamond deposition. The following process parameters were used for deposition : 0.3 % of CH_4/H_2 ratio, 100 mbar total gas pressure, 600 W input microwave power, and 920°C substrate temperature. The boron-doped samples were then exposed to a microwave plasma of hydrogen or deuterium at 550°C during 20 minutes at a pressure of 10 torr for each sample.

Secondary-ion mass spectrometry (SIMS) concentration profiles were taken with Cs^+ primary ions accelerated at 10 keV in a Cameca IMS 4f equipment. Absolute boron and deuterium concentrations were calculated by using implanted standards. The deuterated sample (BM100706) has a thickness of 0.9 µm, a boron concentration of 2.6×10^{17} cm^{-3} well homogeneous in depth. The deuterium concentration matches the boron concentration in the whole depth of the layer, as classically observed when the layer is fully passivated. In the hydrogenated sample (BM070706), the thickness is 1.2 µm, the boron concentration 3.0×10^{17} cm^{-3} well homogeneous in depth while the hydrogen concentration could not be measured being below the H detection limit (~ 10^{19} cm^{-3}). As deuteration and hydrogenation were performed following rigorously the same

experimental procedure, it is assumed that the D and H in-depth diffusion are comparable.

Electron irradiation and cathodoluminescence (CL) spectroscopy were performed at 102 K under the 10 keV electron beam produced in a JEOL840 SEM. At 10 keV, the stopping depth of electrons in diamond is about 0,8 µm so that the incident e-beam energy is fully deposited into the layer. The epitaxial layers were coated with a semi-transparent gold layer (~ 50 Å) in order to evacuate electric charges. For photon detection, a high sensitivity UV set-up from Horiba Jobin Yvon SAS was used to analyze the CL emission. The light was collected by a parabolic mirror and injected with metal optics into a monochromator equipped with a UV enhanced-silicon CCD camera and a 1800 grooves/mm diffraction grating. The spectral resolution was 0.14 nm.

Figure 1 shows the cathodoluminescence spectra of the 2 samples before and after the passivation process. In the as-grown state, the spectra of both samples are dominated by the neutral-boron bound exciton (BE) recombination with a maximum at 5.21 eV when assisted with a transverse optical (TO) phonon, well recognizable with its 11 meV splitting. The maximum of the free exciton (FE) recombination, also assisted by a TO phonon, is observed at 5.27 eV with its characteristic asymmetrical lineshape. After passivation, the BE recombinations are dramatically quenched and as a consequence, the excitonic spectra are dominated by the FE recombinations. These results attest that after hydrogenation or deuteration, boron atoms do not act any more as acceptors, giving an

indirect evidence of the electrical passivation of the layer, induced by the trapping of hydrogen (deuterium) on boron atoms.

The concentration of B-D (respectively B-H) complexes can be evaluated considering that $[BD]=[B_T]-[N_A]$, where $[B_T]$ is the total boron concentration and $[N_A]$ is the acceptor concentration. If we assume that all boron atoms act as acceptors in the as-grown samples, $[N_A]_{as\ grown} = [B_T]$ measured by SIMS. The ratio r, measured in CL, between BE and FE recombination intensities is proportional to N_A[16, 17]. As a result, the concentration of B-D pairs remaining after a dissociation during a time t may be evaluated combining CL and SIMS with the expression:

$$[BD] = [B_T]\left(1 - \frac{r(t)}{r_{asgrown}}\right) \quad (1)$$

The case t =0 corresponds to the as-passivated diamond layer, and from expression (1) the passivation rate can be evaluated. It gives 94% of the boron atoms are passivated after hydrogenation and 92% after deuteration. The CL spectra of Fig.1 first confirm that the passivation is almost total in both cases and is almost as efficient with deuterium as with hydrogen.

The experimental protocol used for dissociation is described in the following paragraph. Each electron irradiation was performed on a new blank area (non cumulative) for a single duration t, with a 60 nA electron beam scanning an area of 5.7 x 4.5 μm^2. The current was measured with a Faraday cup. Under these conditions, the focused beam diameter was ~ 1 µm. The CL emission was collected in a second step with a lower excitation current (2 nA) - at which we checked that the dissociation is negligible- and

from a smaller window of 2.8 x2.2 μm^2 taken at the center of the dissociation area – in order to avoid non linear effects that could be induced by different residence times of the beam at the window edges.

The consequences of a 4 minutes irradiation are illustrated on figure 1. One can observe that the boron bound exciton strongly recovers after the e-beam exposure, indicating that the boron atoms are back as active acceptors. In fact, the real electrical activity of such a layer depends on the fate of the released hydrogen (deuterium). Indeed if hydrogen is set free as an interstitial, its charge state in the resulting p-type material should be positive[18], thus compensating boron acceptors. However we do not believe that it is the case, due to infrared absorption experiments at low temperature (8K) that have shown that, after e-beam irradiation, the absorption due to neutral boron atoms recovers[19]. Another possibility is that hydrogen could be released as hydrogen dimers, for instance H_2*, consisting of a pair of interstitial hydrogen atoms in bond center and in the symmetrical antibond center position. Such a scenario has also been suggested by the recent calculations of Goss et al[15].

Figure 2 presents a plot of the B-D and B-H concentrations respectively calculated for each sample with relation (1) after different irradiation durations. It is remarkable that the decrease of the complex concentration is well fitted by a single exponential decay, which suggests a first order kinetics $d[BD]/dt=-A[BD]$ where A is the dissociation rate. For long times, it also noticeable that almost all boron atoms have been reactivated. The first order kinetics means that the deuterium and the hydrogen are not

recaptured by boron during the dissociation of the complexes. We also report here that, though performed at low temperature, the reactivation of boron acceptors by e-beam irradiation remains stable at room temperature: after several days spent at room temperature, the CL spectra of the irradiated areas remain unchanged.

The dissociation rate for deuterium and hydrogen extracted from the fits are respectively A_D=0.36 min^{-1} et A_H=0.17 min^{-1}, meaning that B-H complexes are about twice more stable than B-D complexes under e-beam exposure.

This unexpected result is contradictory with a dissociation mechanism induced by an electronic excitation of the complex. In an electronic excitation, the quenching of the antibonding state gives rise to an isotope effect where the D-related complexes are significantly more stable than the H-related complexes. In this case, assuming the same lifetime of the excited state for the H- and D-related complexes, the isotope effect is due to the larger mass of D and consequently to its higher inertia along the potential energy curve of the antibonding state. Our observation of B-H complexes slightly more stable than B-D complexes confirms that the dissociation excitation process is not an electronic excitation from the bonding state to the antibonding state.

The question now is: does a weak reverse isotope effect coherent with the multiple vibrational mechanism of H-related modes ? This mechanism is usually described by the truncated harmonic oscillator model[5]. In this model, transitions between the vibrational levels of the local vibrational mode (LVM) are induced by inelastic

tunneling electrons (up) and by energy exchange with the semiconductor (down). From their investigations on hydrogen desorption under STM-tip emitted electrons, Foley et al concluded that the lifetime τ_H (τ_D) of the H (D) vibrational mode is the main factor that controls the dissociation rate of Si-H and Si-D bonds in this mechanism[5]. Biswas et al provided an approximate value of the ratio of the H and D emission rates[20]:

$$A_D/A_H \approx \tau_D/\tau_H \quad (2)$$

where τ is the lifetime of the H (D) local vibrational mode (LVM).

The lifetime of the H (D) vibrational mode depends on the number of phonons involved in the relaxation process of the LVM. The lower the number of phonons, the shorter the lifetime.

In the case of hydrogen bending modes, Sun et al[21] have shown that the vibrational lifetime of these modes varies exponentially with the frequency separation between the LVM and the receiving modes. This frequency-gap law is given by $\tau = \alpha e^{\beta N}$ where α= 0.15 ps and β=2.01. N represents the decay order of the relaxation process i.e. the number of phonons necessary for this relaxation. For these bending modes, the receiving modes are basically the bulk modes[21].

On (100) silicon surfaces, the vibrational lifetimes of the Si-H and Si-D stretching modes are respectively 10 ns and 0.25 ns[22]. On the other hand, Lüpke et al found that the lifetime of the Si-H stretching modes of several H-related defects in bulk silicon varies over a range of two decades[23]. For most of these defects, the vibrational lifetime of the

Si-D stretching mode is longer than the lifetime of the Si-H stretching mode. This is opposite to the situation found for Si-H bonds at the surface of silicon. First-principle calculations[24] have shown that pseudolocal modes and H-bending modes play a critical role in the decay process of the H-stretching modes of these defects.

Unfortunately, in the case of diamond, there is a lack of experimental data concerning the LVM of hydrogen and deuterium complexes with boron, probably because of their too low optical activity to be observed in infrared absorption. Nevertheless the LVM have been calculated with ab-initio methods giving 1501 cm^{-1} (1366 cm^{-1}) for the B-H (B-D) bending modes and 2657 cm^{-1} (1965 cm^{-1}) for the B-H (B-D) stretching modes[25]. Since the maximum phonon frequency of diamond is 1332 cm^{-1}, it is expected that the relaxation process of both the stretching and the bending modes will occur with two phonons for both the B-H and the B-D complexes. According to the frequency-gap law, the lifetimes of the B-H and B-D bending modes should be comparable. A similar conclusion can be drawn for the stretching modes of these complexes. As a consequence of expression (2), the dissociation rates of B-H and B-D complexes in diamond are expected to be of the same order of magnitude in a multiple vibrational mechanism, in good agreement with our experimental data.

Following the conclusions of Goss et al[15], we have to consider the consequences of the lowering of the dissociation barrier induced by an electron capture on the B-H complexes. The dissociation barrier remains too high (0.5-0.7 eV) to account for the experimental data with a classical thermal escape at 100K, but a tunnel effect could also

occur. Assuming that H (D) has to cross a 0.3 eV barrier as proposed by Goss et al and taking a 1 Å thick rectangular barrier, B-D complexes would be much more stable than B-H complexes (the ratio of the tunnel barrier transparencies for D and H gives $5x10^{-5}$). The assumption of a tunneling effect in the dissociation mechanism is in contradiction with our results.

However, we do not rule out the possibility that minority carriers play an important role in the dissociation mechanism of the B-H complexes in diamond. In the case of GaAs containing Si-H complexes, a 1 mW/cm^2 ultraviolet illumination is able to induce an efficient Si-H dissociation by the electronic mechanism. On the contrary, no dissociation is observable at this illumination power for a red illumination, just above GaAs band-gap[10]. The effect of enhanced complex dissociation by a minority carrier injection induced by above near band gap illumination is observed for higher illumination powers (~ 20 mW/cm^2 in Ref. 26). In the case of diamond, both the multiple vibrational excitation and the enhanced dissociation by minority carriers may occur simultaneously but their respective contribution probably depends on the injected current value. A detailed investigation of the temperature dependence of the B-H and B-D stability under electron injection should bring a more clear view on which mechanism is dominant for a given current value.

Acknowledgments: The authors acknowledge the support of the French Agence Nationale de la Recherche (ANR), under grant DOPEN (ANR-06-BLAN-0339) “n-type

diamond by (boron,deuterium) doping". The authors are grateful to J.P. Goss for constructive discussions and to P. Giroux for technical support and development in deuteration and hydrogenation processes.

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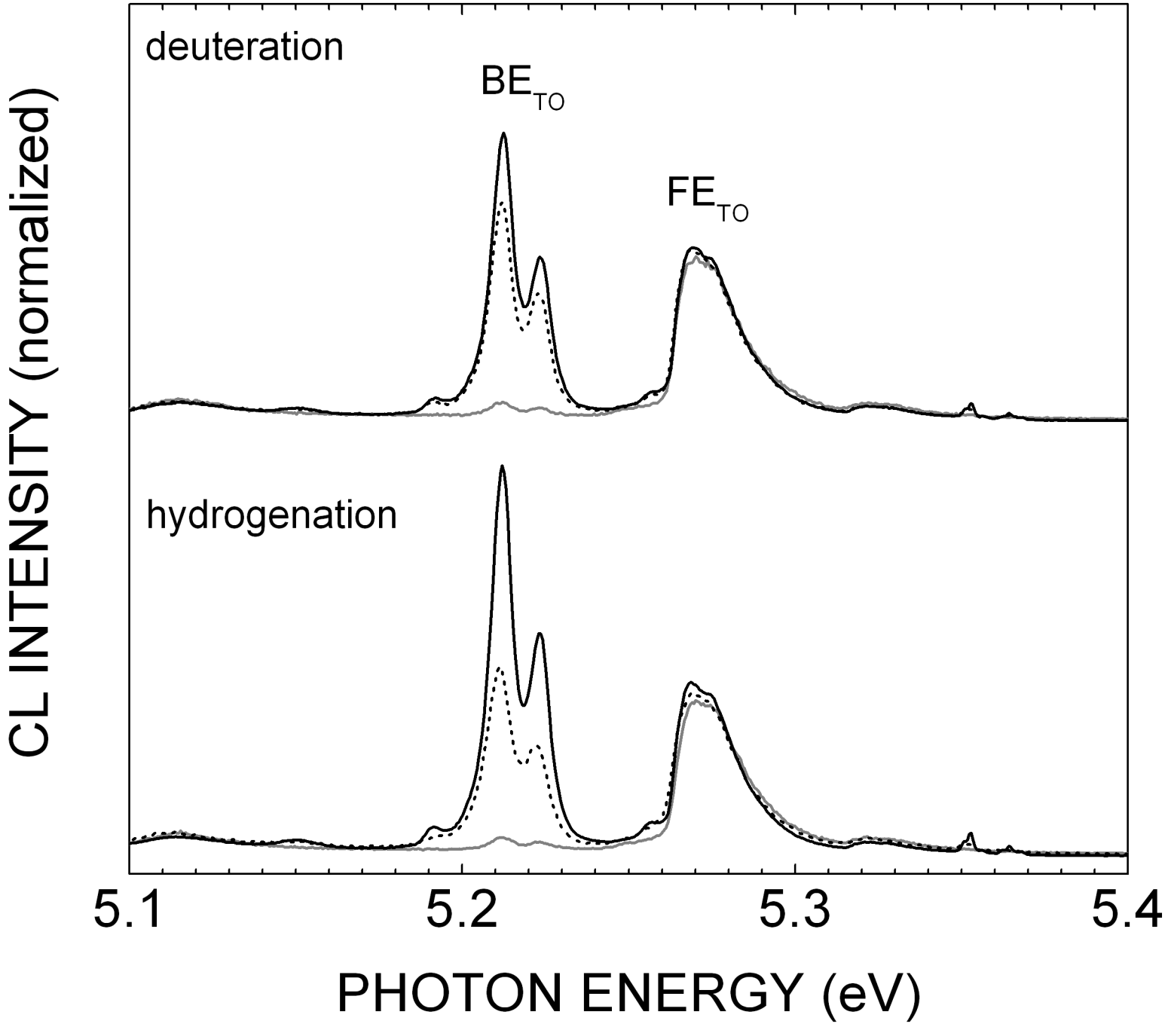
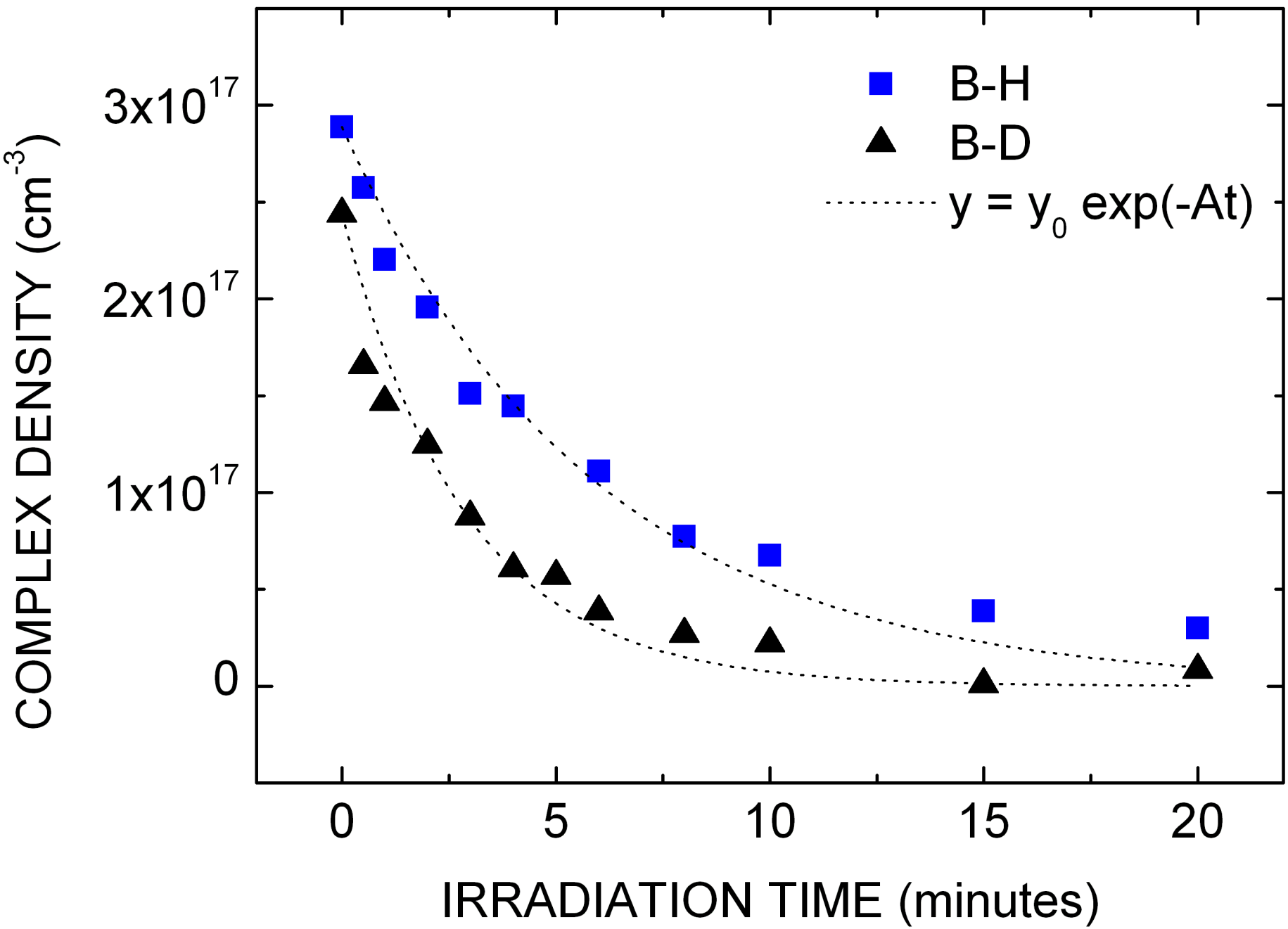
Figure captions:

Fig.1: CL spectra at 102 K of the boron-doped diamond epilayers before (black) and after (grey) passivation by deuteration or hydrogenation. The dashed spectrum was taken after an e-beam irradiation of 4 minutes (details given in the text). All spectra are normalized to the maximum of the free exciton recombination.

Fig. 2: evolution of the B-H and B-D pair concentrations in diamond as a function of the irradiation time. A first order kinetic was used to fit the experimental results with a dissociation rate A.


deuteration
BE$_{TO}$
FE$_{TO}$
hydrogenation
CL INTENSITY (normalized)
5.1
5.2
5.3
5.4
PHOTON ENERGY (eV)


B-H
B-D
y = y0 exp(-At)
3x10^17
2x10^17
1x10^17
0
COMPLEX DENSITY (cm^-3)
0
5
10
15
20
IRRADIATION TIME (minutes)