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Hydrogen-boron interactions in *p*-type diamond

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We report on experimental evidence of hydrogen-boron interactions in boron-doped diamond from hydrogen diffusion investigations. Original deuterium diffusion studies in homoepitaxial B-doped diamond films reveal that hydrogen diffusion is limited by the B concentration with a low effective diffusion activation energy. These results are consistent with hydrogen ionization and diffusion of fairly mobile H^+ that form pairs with B^-. Infrared spectroscopy experiments show that boron acceptor electronic transitions are removed under hydrogenation. [S0163-1829(98)06235-3]

The complex behavior of hydrogen in conventional semiconductors is now widely recognized.[1] In particular, hydrogen removes from the band gap the deep levels associated with dangling or reconstructed bonds and it interacts with the dopant atoms. This often results in the neutralization of the dopant atoms by hydrogen through the formation of hydrogen-dopant complexes, which prevents the doping control of semiconductors.

Theoretical studies have pointed out a particular behavior of hydrogen in diamond compared to silicon: (i) H^+would exhibit a low migration energy E_m of 0.1 eV in diamond[2] (instead of 0.4–0.5 eV in silicon);[3–5] (ii) conversely, H^0 and H^- would have very high migration energies in diamond (1.9 eV and 2.5 eV, respectively), compared to the values in silicon (less than 1 eV for H^0 and 0.7 eV for H^-);[4,6,7] (iii) B-H complexes would have a low binding energy E_b (0.3 eV) in diamond[2] (instead of 0.6–0.8 eV in silicon).[4,5] Until now, there has been no experimental study of hydrogen diffusion in *p*-type diamond. However, it has been recognized that the exposure, at 300 K, of undoped or *p*-type doped diamond to a hydrogen plasma induces a superficial (20 nm) highly *p*-type conductive layer,[8,9] making quite difficult the investigation of hydrogen-acceptor interactions through the electrical studies. The physicochemical nature, as well as the electronic properties of this superficial layer remain somewhat controversial.[9]

The understanding of the behavior of hydrogen in diamond is even more important because the deposition of both polycrystalline and monocrystalline diamond (instead of graphite) films has to be done within a very active hydrogen plasma.[10] As a result, the electrical properties of diamond films depend on the detail of the cooling process. This is usually ascribed to hydrogen incorporation.[8,9,11] Consequently, the understanding of this incorporation is obviously crucial for a proper control of the conductivity of boron-doped diamond films.

The presence of up to several atomic percent of hydrogen at the grain boundaries of polycrystalline diamond films[10] precludes the study of hydrogen interactions in undoped as well as boron-doped material, and well-documented monocrystalline samples should be used. To our knowledge, there is only one reported experimental value for the effective diffusion coefficient of 2.4×10^{-13} cm^2 s^{-1} at 860 °C with no report on the activation energy.[12] Additionally, the measurements have been done on an ill-defined sample obtained after diffusion of several very different chemical species: starting with IIa diamond crystal (the purest natural crystals with nitrogen content $<10^{18}$ cm^{-3}), there is a first step of N, Li, and O diffusion at 860 °C, before codiffusion of B and H.

In this work, we present results on hydrogen diffusion in boron-doped diamond. We show that, in *p*-type diamond, hydrogen is a fairly mobile impurity migrating with a low effective diffusion activation energy and that the hydrogen diffusing species are trapped on boron acceptors.

We have used homoepitaxial films of diamond in order to control the boron incorporation level and to avoid parasitic trapping of hydrogen at grain boundaries. Several films with various boron contents from 2×10^{18} to 3×10^{20} cm^{-3} and a low compensation ratio[13] from electrical measurements have been deuterated or hydrogenated at various temperatures from 235 to 490 °C. From their secondary-ion-mass spectroscopy (SIMS) deuterium profiles, we have studied the hydrogen diffusion process. From infrared transmission experiments, we have investigated the influence of hydrogenation on the boron acceptor electronic transitions.

Monocrystalline boron-doped diamond epitaxial layers were grown on (100) type Ib synthetic diamond substrates by Microwave Plasma assisted Chemical Vapor Deposition (MPCVD) at $T=820$ °C with 4% of methane in hydrogen and at a total pressure of 30 torr. The boron doping was achieved by adding diborane into the gas phase with $[B]/[C]$ ratios in the gas phase of 25, 200, and 800 ppm. The deposition process is stopped, first by cutting off the methane and diborane flows, then by switching off the plasma 10 min later, and finally by cooling the sample down to room temperature under a hydrogen gas flow. The epitaxial layers are treated at 80 °C during 30 min in boiling H_2SO_4 saturated by CrO_3, which is known to remove the effect of hydrogen from the near surface region of the film.[9,11] Under such preparation conditions, these boron-doped epitaxial diamond films exhibit a low compensation ratio (10%) from

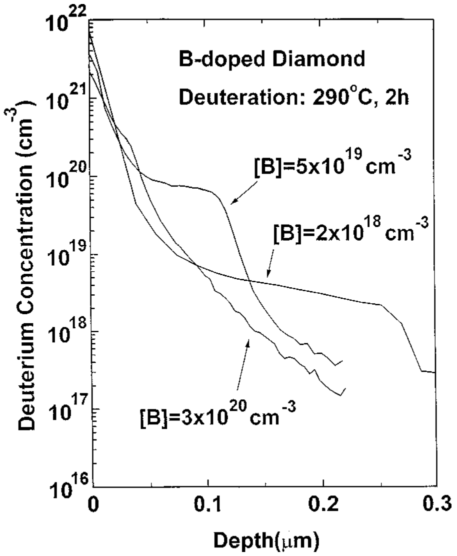

FIG. 1. Evolution of the deuterium profile in homoepitaxial boron-doped diamond as a function of the boron concentration.

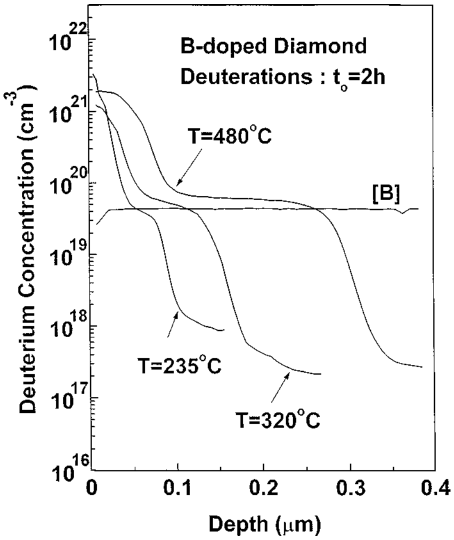

FIG. 2. Evolution of the deuterium diffusion profile in homoepitaxial boron-doped diamond as a function of the diffusion temperature. The uniform boron concentration is also shown.

conductivity measurements up to 1000 K and the infrared absorption bands characteristic of the electronic transitions from the ground to the excited states of almost unionized boron acceptors at 300 K.[13] Then, they are exposed for 2 h to a radiofrequency deuterium or hydrogen plasma at the above-mentioned temperatures. The depth diffusion profiles of deuterium and the absolute boron concentration in these epilayers were measured using a CAMECA IMS 4f SIMS. Quantifications of deuterium and boron were carried out by using a homoepitaxial undoped MPCVD diamond standard where the two elements were coimplanted. For $[B]/[C]$ ratio in the gas phase of 25, 200, and 800 ppm, the boron concentrations found in the diamond epilayers are, respectively, 2×10^{18}, 5×10^{19}, and 3×10^{20} cm^{-3}. The infrared absorption experiments on the as-grown and the hydrogenated boron-doped diamond films were measured at 10 K with a BOMEM DA 8 Fourier transform interferometer. The resolution of 0.5 cm^{-1} was well below the half-widths of the absorption bands.

Figure 1 shows the deuterium diffusion profiles in different boron-doped diamond epilayers exposed together to a deuterium rf plasma ($T=290$ °C, $t_0=2$ h). The diffusion profile is composed of a surface deuterium accumulation region followed by a plateau where the deuterium concentration is very close to the boron concentration and finally a sharp decrease of the deuterium concentration. The plateau extent increases as the boron concentration decreases. The dependences of the plateau deuterium solubility and of the plateau extent L_D on the boron concentration are strong evidences for boron limited diffusion of hydrogen[5] and for (B,H) pair formation in diamond.

Figure 2 presents the temperature dependence of the deuterium diffusion profiles for the boron concentration of 5×10^{19} cm^{-3}. The hydrogen plateau concentration remains very close to the boron concentration for diffusion temperatures as high as 480 °C. The effective diffusion coefficient L_D^2/t_0 increases from 8×10^{-15} cm^2/s at 235 °C to 1×10^{-13} cm^2/s at 480 °C. Plotting L_D^2/t_0 as a function of the reciprocal diffusion temperature yields an activation energy of 0.35 eV for the deuterium diffusion.

Qualitatively, the above results are similar to those for deuterium diffusion in boron-doped silicon.[5,14] In silicon, the features of (B,H) pair formation during hydrogen diffusion disappear for diffusion temperatures above 250 °C as a result of the thermal dissociation of (B,H) pairs.[15] However, in diamond, we observe that the trapping of hydrogen on boron acceptors remain at diffusion temperatures as high as 480 °C, which means that (B,H) pairs are more stable in diamond than in silicon. Assuming that the (B,H) pairs dissociate into B^- and H^+as in silicon, this result seems to contradict the calculations giving a lower dissociation energy of these pairs in diamond $[E_b+E_m(H^+)=0.4$ eV$]$ compared with silicon (1.0–1.3 eV).[4,5]

Until now, only one hydrogen diffusion coefficient of 2.4×10^{-13} cm^2/s at 860 °C has been reported by Popovici *et al.*[12] It was calculated from a nearly erfc type hydrogen diffusion profile in the 10^{19} cm^{-3} range, in initially type lla natural diamond containing nearly erfc-type distribution in the 10^{20} cm^{-3} range of N, B, and O, and in the 10^{17} cm^{-3}range of Li. The existence of vacancies, vacancy complexes, microvoids and dislocations in lla natural diamond crystals was invoked to justify the close values (2.4 to 4.4×10^{-13} cm^2/s) of the reported diffusion coefficients of H, N, and O in this sample.

In Figs. 1 and 2 we observe, near the surface, more usual deuterium diffusion profiles with low diffusion coefficients and high-surface concentrations. These profiles are of the same type than those existing after film deposition[9] or room-temperature plasma deuteration (hydrogenation) of CrO_3/H_2SO_4 treated samples.[8] While this accumulation layer induces a strong superficial *p*-type conductivity,[8,9] the knowledge of the physicochemical characteristics of this layer remains very poor. For a concentration of 5×10^{19} cm^{-3} boron acceptors, its depth increases from about 50 to 100 nm as the diffusion temperature increases from 235 °C to 480 °C (Fig. 2). Because the hydrogen concentration in this superficial layer is higher than that of boron, diffusion of single hydrogen cannot take place as H^+ and

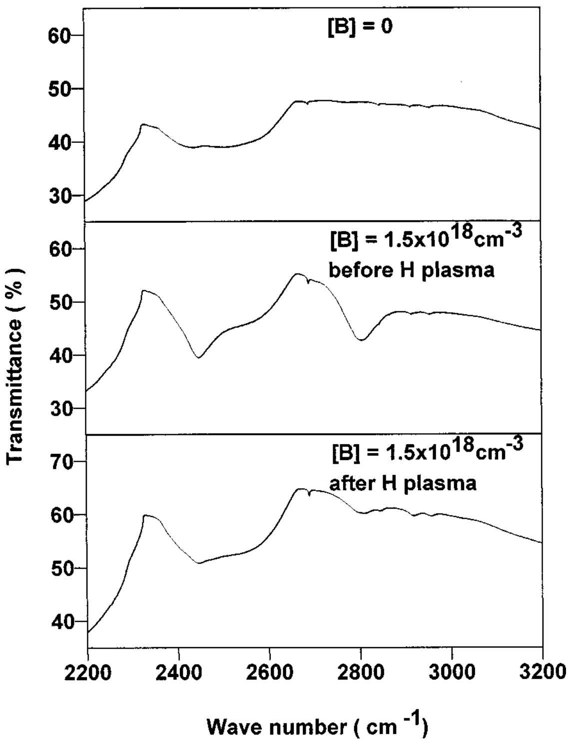

FIG. 3. Infrared transmission spectrum of a boron-doped diamond film before and after hydrogen plasma ($t = 14$ h, $T = 490$ °C). The spectrum of an undoped diamond film is shown for comparison.

theoretical works[2,3] predict much higher migration energy (1.9 and 2.5 eV, respectively, for H^0 and H^-) leading anyway to much lower diffusion coefficients for hydrogen as found here. It would be interesting to know whether this layer contains point defects with hydrogen atoms or extended defects like platelets as found at these very high hydrogen concentrations in silicon.[16] A theoretical work predicts a higher stability for H_2^* complexes (with one hydrogen at the bond center site and the other one at the antibonding site of a C-C bond[17–19]) than for H_2 molecules in tetrahedral sites.[3] On the contrary, in silicon, H_2 molecules are slightly more stable than H_2^* complexes, but both species have been detected.[3,20,21]

In order to study the modification brought by hydrogen on the electronic properties of boron dopants in diamond, we have investigated the evolution under hydrogenation of the infrared absorption spectrum related to the electronic transitions from the ground to the excited states of boron acceptors. Figure 3 presents the infrared transmission spectrum of a diamond film doped with boron at a concentration of 1.5×10^{18} cm^{-3} before and after hydrogen plasma exposure. For comparison, it also shows the spectrum of an undoped diamond film. Before hydrogen plasma, we clearly observe two absorption peaks at 2450 and 2820 cm^{-1}, respectively, attributed to the ground state→first excited state electronic transitions and to the ground state→second excited state transitions. After hydrogen diffusion for 14 h at 490 °C, these absorption peaks almost vanish, which means that the concentration of neutral boron acceptors has decreased under hydrogenation. The remaining absorption after hydrogen diffusion is likely due to The residual neutral boron acceptors in the hydrogenated region and/or an insufficient hydrogen diffusion depth.

In terms of (B,H) pair formation mechanism, we expect some difference between silicon and diamond since, in silicon, all boron acceptors are ionized while, in diamond, most of the boron acceptors are neutral because of their high ionization energy (0.38 eV). For example, in diamond containing 10^{18} cm^{-3} boron acceptors and having a compensation ratio of 10%, 84% of boron acceptors are neutral at a temperature of 320 °C. This difference will have some consequences on the (B,H) pair formation mechanism. Because there is experimental evidence that $H^+$is a diffusing species in p-type silicon,[22] the (B,H) pair formation is considered as the result of a compensation of free holes followed by the coulombic attraction between H^+ and B^-.A theoretical work has predicted that hydrogen introduces a midgap $H^{+/0}$ donor level in the band gap of diamond,[2] therefore above the fundamental level of boron. As a result, neutral hydrogen atoms entering in boron-doped diamond will provide their electron (i) to compensate the small concentration of free holes coming from the ionization of boron acceptors knowing that only a small fraction of the boron concentration is ionized in diamond, and (ii) to ionize all the remaining neutral boron acceptors. This second effect is specific to the high ionization energy of boron acceptors in diamond. Then, in the plateau region where the hydrogen concentration is equal to the boron concentration, diamond behaves as a compensated semiconductor similar to silicon with all boron acceptors ionized in B^- and all hydrogen atoms ionized as H^+. The resulting formation of (B,H) neutral pairs should be at the origin of a neutralization of boron acceptors by hydrogen in diamond as in silicon.

In conclusion, we have provided direct evidence of deuterium diffusion limited by boron concentration in p-type diamond as a result of a trapping of deuterium by boron acceptors. The effective diffusion coefficient of deuterium varies from 8×10^{-15} cm^2/s at 235 °C to 1×10^{-13} cm^2/s at 480 °C for a boron concentration of 5×10^{19} cm^{-3}. Due to a midgap donor behavior of hydrogen in diamond (theoretical work), boron acceptors become negatively charged under hydrogen incorporation. Hydrogen diffuses as H^+ and form pairs with charged boron acceptors. Additionally, there is a superficial deuterium accumulation layer with the usual diffusion profile and temperature behavior at least up to 480 °C, but whose physicochemical nature (hydrogen in platelets or hydrogen containing point defects) remains unknown. The (B,H) pair formation should give rise to a neutralization of boron acceptors by hydrogen in diamond. We hope that the above results will open the way to the study of the various hydrogen related complexes in this semiconductor.

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