Diffusion of hydrogen in undoped, p-type and n-type doped diamonds

C. Saguy[a,*], C. Cytermann[a], B. Fizgeer[a], V. Richter[a], Y. Avigal[a], N. Moriya[a], R. Kalish[a],
B. Mathieu[b], A. Deneuville[b]

[a]Physics Department and Solid State Institute, Technion City, Haifa 32000, Israel
[b]CNRS, LEPES, B.P. 166, Grenoble 38042, France

Abstract

Hydrogen is a key impurity in diamond since it is unintentionally incorporated in all chemical vapor deposition (CVD) grown diamond layers. Its presence in the material can grossly affect its electrical and optical properties. Theoretically, hydrogen has been predicted to be present in diamond in one of the three charge states, H^+, H^0 and H^-. Moreover it may form complexes with impurities, native defects or with other hydrogen atoms. This paper is comprised of two parts: (a) a review of previous results of studies investigating different aspects of the diffusion of hydrogen (deuterium) in various kinds of diamonds. The diamonds studied are: undoped type IIa diamonds, undoped CVD diamond layers containing growth defects only, p-type B-doped homoepitaxially CVD grown diamond layers or B ion implanted type IIa diamonds and n-type P doped homoepitaxially CVD grown diamond or N-doped type Ib natural diamonds. Hydrogen is introduced in diamond by exposing the diamond surface to hydrogen plasma or by using hydrogen ion implantation. The following issues are discussed: (1) the influence of the interaction between H and the dopants and defects on the hydrogen diffusion. (2) The kinetic of (B, H), (P, H) and (N, H) pair formation and dissociation. (3) The modification of the optical and electrical properties as a result of hydrogen incorporation and annealing. It is found that, under certain conditions, H diffuses into the B containing layer and it passivates B acceptors. In contrast, no H diffusion could be observed in n-type diamonds, up to 1000 °C. (b) Recent results of our group regarding other aspects related to the diffusion of H in diamond are presented. These include results on: (i) the influence of ion implantation related defects on the diffusion of deuterium. For this study type IIa samples implanted with B or non-dopant ions are used. (ii) The determination of the charge state of H or H/defects complex as a function of diamond type. For that, annealing under bias is applied to deuterated diamond layers. We show that the presence of implantation defects retards the deuterium diffusion in a B-implantation doped diamond, demonstrating that D strongly interacts with defects, thus inhibiting diffusion. The new-formed complexes deteriorate the electrical properties of the diamonds and are very stable up to high temperatures. We confirm that, as expected, in highly B-doped CVD diamond layers, H diffuses as a positive ion. In lightly B-doped homoepitaxial layers, however, D is incorporated in complexes which seem to be negatively charged.
© 2003 Elsevier Science B.V. All rights reserved.

1. Introduction

The study of hydrogen diffusion in diamond is most important, since chemical vapor deposition (CVD) developed into the main technique to obtain undoped, p- and n-type doped diamond layers and hydrogen is the carrier gas in the growth process; it is thus unintentionally incorporated into all CVD grown diamond layers. In polycrystalline diamond layers, the concentration of H may be as high as 1×10^{21} cm^{-3} [1] while in

good quality homoepitaxially grown layers, the H concentration is not well determined [2] since it is generally below the H (D) SIMS detection limit (1×10^{19} cm^{-3}). H, being a light atom, may interact with defects and dopants that may influence its motion in the crystal. Furthermore, hydrogen is likely to be captured by electrically active centers such as dopants or native defects, thus affecting the electrical properties of the layer. Hydrogen termination is responsible for surface p-type high conductivity and for the negative electron affinity of some diamond surfaces [3,4]. The present work deals with topics related to the H diffusion into diamond bulk only. The influence of H on the diamond surface properties is not discussed here.

*Corresponding author. Tel.: +972-4-829-3908; fax: +972-4-823-5107.
E-mail address: sscecile@tx.technion.ac.il (C. Saguy).

The diffusion of hydrogen was extensively studied in other semiconductors, since the presence of hydrogen in the materials was observed to induce changes in their electrical and optical properties [5]. More recently, diffusion of H in p-type doped diamond layers has been investigated. One of the most striking result of these studies is that, while in a low compensated, highly B-doped p-type diamond layer, H was found to passivate B acceptors [2], no interaction between H and B seems to occur in a p-type, B-doped layer containing defects [6,7]. This point emphasizes the need for understanding the interaction of H with defects and their influence on the diffusion of H in various diamond types.

The present paper is divided into two parts: the first part is a review of the theoretical and experimental data available on the diffusion of H in diamond and on its interaction with impurities in the material. The second part presents our recent contributions to two major issues: (1) the influence of defects on the diffusion of H in type IIa implantation-damaged diamond and (2) preliminary results on the study of the charge state of H during post-diffusion annealing in various types of diamonds. For this study we anneal the diamonds under an electrical field. We show that the diffusion of H, in a B-doped implanted diamond containing residual implantation related defects, is retarded as compared to H diffusion in a B-doped homoepitaxial layer. We also demonstrate that the diffusion of H, in a type IIa undoped diamond containing implantation defects, is enhanced by the presence of these defects. We confirm that, in a highly B-doped, low compensated p-type homoepitaxial diamond layer, H diffuses as an H^+ ion, whereas, in a low B-doped p-type layer, negatively charged hydrogen containing complexes seem to be the diffusing species.

2. Part I: review

2.1. Theoretical predictions

The diffusion of H in diamond is mainly controlled by (i) H solubility in diamond, which in fact is related to H formation energy in diamond, (ii) H migration energy in diamond and (iii) the height of the surface barrier for H to enter into the crystal, prior to bulk diffusion.

Theoretical calculations have shown that hydrogen may exist in diamond in one of the three charge states, positive, neutral or negative (H^+, H^0 or H^-) and, hence, its formation and migration energies may vary as a function its charge state [8–10].

2.1.1. Hydrogen in a pure intrinsic, highly insulating, diamond

H is expected to diffuse as an interstitial atom, i.e. as a neutral H atom. Most calculations agree that the lowest energy site for neutral H is the bond centered (BC) site [8–10], although some other sites were also suggested [11,12]. H^0 in diamond has a relatively high formation energy of 2.6–5.2 eV and a low solubility. Its migration energy was calculated to be 1.6–1.9 eV [9]. Isolated hydrogen was predicted to interact with other hydrogen forming dimers like two isolated H^0_{BC} dimers, H^*_2 defects or H_2 molecules [9,10]. The defect H_2^* was found to have a lower energy than the molecule or two isolated H^0_{BC} dimmers. The binding and migration energies of the H^*_2 defect were calculated to be 2.5 and 3.5 eV, respectively, indicating that this complex is stable and immobile up to high temperatures. The H^*_2 defects were also theoretically found to be bound to dislocation cores with binding energies of 4 eV [9].

2.1.2. Hydrogen in defects or dopants containing diamond

In diamond layers that contain native defects or impurities, only a very small fraction of H diffuses as an interstitial due to the presence of many traps. In this case, hydrogen diffusion is controlled by trapping by defects like dangling bonds, grain boundaries or vacancies, or by shallow acceptors or donors, and other impurities. The presence of H may also deactivate (passivate) electrically activate dopants and defects or activate non-active dopants or defects.

In p-type diamond, H was calculated to be a deep donor with a level located 2.2 eV [11] or 3 eV [9] below the conduction band. The lowest energy configuration of H^+ was theoretically found to be in a puckered bond-center site with a C–H–C bond angle of 100° [9]. Its formation energy in a heavily B-doped diamond is approximately 0.3–0.4 eV. H^+ was predicted to be a fast diffuser with migration energy of 0.1–0.2 eV [9,10]. H interacts with B and forms (B, H) pairs. Their dissociation energy was calculated to be 1.8–2 eV.

In n-type diamond, H is predicted to form an acceptor level located 2.3 eV below the conduction band [9]. The lowest energy site for H^- was calculated to be also the BC site [9]. The formation energy of H^-, in a strongly P-doped diamond, was estimated to be approximately 1 eV. With a calculated high migration energy (2.5 eV), H^- is predicted to be a slow diffuser. H was predicted to pair with P and N with dissociation energies of 1 and 3.5 eV for the (P, H) and (N, H) pairs, respectively [9].

The surface barrier H to be overcome to penetrate into the bulk obviously depends on the surface structural and electronic properties. Specific treatments of the diamond surface may change this barrier.

2.2. Experimental data

Muonium, being a light pseudo-isotope of H, has been used to experimentally depict the structural and

electronic state of H in diamond [13]. From muon spin rotation (μSR) experiments, it was deduced that the stable site for neutral muonium is the BC site suggesting that it will be also the stable site for neutral H in diamond. Moreover, it was shown that, in high resistivity diamond, neutral muonium residing in the BC site is non ionized up to 800 °C, suggesting that the donor level associated with H in BC site is a deep level, thus preventing the formation of H^+ at this temperature [14].

One way to study the diffusion of H and its influence on the activation of defects and dopants in diamond is to deliberately introduce H into the matrix by exposing the diamond surface to a hydrogen plasma [2] or by using H ion implantation [6] and to measure the changes induced by the presence of H by using various characterization methods: it should be noted that as different methods for the introduction of H like microwave, RF, DC or ECR [15] may be used to create the plasma, different distributions of H concentration may be obtained. Hence, care should be taken in the comparison of deuteration experiments performed in different laboratories using different modes of deuteration. RF plasma was shown to create surface roughness and surface damage which acts as trapping centers for the diffusing H, thus yielding a strong D accumulation in the subsurface layer. In contrast, almost no D accumulation is observed in a sample deuterated in a microwave plasma, indicating that less defects are created by this method [7].

The main characterization methods used for the study of diffusion of H in diamond are: (i) SIMS measurements, to study the H profile in the layer. (Deuterium is usually introduced instead of hydrogen because of the higher sensitivity of the SIMS to D than to H: the detection limit for deuterium being approximately 5×10^{16} cm^{-3}.) (ii) Optical measurements, like IR spectroscopy, to detect hydrogen-related complexes [16,17], (iii) nuclear method combined with channeling to determine the location of D or H in the crystal and to get hydrogen concentration profiles in the near surface region [18,19], (iv) micro-scanning heavy ion elastic recoil detection analysis (ERDA) to measure the H concentration profile in the near-surface region (the H detection limit of this technique is approximately 1×10^{19} cm^{-3}) [20], (v) electrical measurements to study the activation or deactivation of specific dopants and defects caused by pairing with H [21,23]. Finally, effusion experiments carried out on hydrogenated (deuterated) diamond layers which give information on the dissociation kinetics of specific H (D)-related complexes [24]. Many experiments were already carried out on H in or on diamond. The main results obtained from these studies are summarized below.

2.2.1. Deuteration of p-type doped diamonds

The first deuteration experiments performed on highly B-doped homoepitaxially grown diamond layers were carried out by Chevallier [2]. They indicated that, for deuteration performed at temperatures lower than 550 °C, the SIMS D profile overlaps with B profile suggesting that trapping on B acceptors controls D diffusion in p-type diamond. Further experiments which include characterization of neutral B related signal in IR experiments [7], persistent decrease in capacitance after deuteration [21], increase of the hole mobility combined with a decrease of carrier concentration observed by Hall effect measurements [23] all clearly show that H passivates B by forming neutral (B, H) pairs. The onset temperature for pair dissociation was found to be approximately 550 °C with a dissociation energy of 2 eV deduced experimentally, very close from the theoretically predicted value of 1.8 eV [2]. At temperatures higher than 600 °C, the B–H interaction decreases and the D concentration profile is found to be below that of B and it follows an erfc function at 700 °C [7]. However, it was also shown that in a B-doped layer containing defects from the CVD growth or due to ion implantation, the deuterium interact predominantly with the defects and no more with B [6,7]. Effusion experiments have revealed that in B-doped homoepitaxial layers deuterated by RF plasma, the temperatures of D (H) loss from the surface and subsurface region are 840 and 720 °C, respectively. For B-doped layers deuterated by microwave plasma, out-diffusion starts at 750 °C and is maximum at 880 °C. It is limited by the diamond surface barrier [25].

2.2.2. Deuteration of undoped diamonds

In a previous publication, we have shown that a microwave plasma deuteration of type IIa diamond performed at 550 °C for 7 h resulted in a thin D accumulation layer near the surface, yet without any in-depth diffusion [23]. This result was suggested to be due to the low solubility of H in a pure diamond, probably lower than the D SIMS detection limit. The diffusion profile of H in the near surface region of type IIa diamond was also studied by Machi et al. [20] by ERDA. Their results also did not reveal any hydrogen that has in-diffused into single crystal type IIa diamond exposed to microwave H plasma at 800 °C for 40 min.

In contrast, Laikhtman et al. have shown (by SIMS) that D did diffuse into a single crystal diamond, following deuteration in a microwave plasma (at 800 °C for 40 min) at high concentrations, penetrating as deep 0.5 μm [26]. The difference between these results and those of Refs. [20,22] may be explained by some difference in the type IIa diamonds used or in differences related to the deuteration process.

2.2.3. Deuteration of n-type diamonds

The D SIMS depth profiles measured following microwave deuteration of N containing type Ib natural diamonds and P-doped homoepitaxially grown diamond layers at temperatures varying between 550 and 1000 °C [27] did not reveal any significant D diffusion neither in ⟨1 1 1⟩ P-doped diamond layer nor in ⟨1 0 0⟩ N-doped type Ib diamond. These results were later confirmed by our group [28]. The following may explain the non-diffusion of D in n-type diamond: (i) the high migration energy of H in n-type diamond, (ii) the formation of N–H and P–H complexes, which inhibit in-diffusion, (iii) the surface barrier for diffusion and finally (iv) the possible low solubility of H in n-type diamond.

2.2.4. Deuteration of defect containing diamonds

Type IIa diamonds pre-damaged by shallow implantations of inert ions were deuterated at 800 °C for 40 min in a microwave plasma. ERDA [20] measurements did not reveal any H diffusion after deuteration, perhaps because large concentrations of vacancies were introduced into the diamond by the implantation process.

In Ref. [23], we have shown that deuteration performed at 550 °C in a C- or B-doped ion implanted diamond did yield to deuterium penetration into depths which increased with increasing deuteration time. Below, we propose an explanation to the differences between the results of Ref. [20] and our results.

It is clear, from this literature review, that much work has been devoted to the study of diffusion of H into p-type diamonds and to understanding the interaction between H and B. Clear results, much resembling those obtained for the diffusion of H in p-type doped Si, were obtained for this case. As regard to the diffusion of H in undoped diamond and in defect containing diamonds, controversial results were published and some comprehensive study of the subject is required. Diffusion of H in n-type diamond was found to be non-existent up to 1000 °C, in contrast to the clear diffusion of H into n-type Si.

3. Part II: recent results

In the following, we present our experimental results on:

1. the influence of ion implantation related defects on the diffusion of hydrogen in B-doped diamond layers, and
2. the charge state of hydrogen, in defects containing B-doped diamond layers.

For the first set of experiments, boron-implantation doped diamonds containing different degree of damage were used and the penetration of D into them was studied, while, for the second set, B-doped homoepi-taxial diamond layers were used and the diffusion of D under bias was measured.

4. Experimental

The samples used in this work were ⟨1 0 0⟩ undoped type IIa natural diamonds from Drukker (0.25-mm thick) and B-doped CVD homoepitaxially grown layers on ⟨1 0 0⟩ oriented type Ib substrates. p-type B-doped layers were also obtained by implanting in type IIa substrates B ions at various energies and doses to get a box profile (extending from the surface up to a depth of 0.3–0.55 μm) with a rather constant B concentration. The cold implantation rapid annealing (CIRA) method followed by a high temperature annealing (1400 °C) was employed [30,31]. Three different type IIa diamonds were implanted to various doses to obtain samples containing various densities of defects. The diamonds were deuterated at 550 °C in microwave plasma for 4 h. D diffusion was studied as a function of B concentration. Since the defect concentration increases with increasing B implantation doses, this is equivalent to study the D diffusion as a function of defect concentration. Another diamond was deuterated at the same temperature for various durations to deduce D diffusion coefficient and to compare it with D diffusion coefficient in a homoepitaxially B-doped diamond layer. A type IIa diamond was also implanted with C, a non-dopant ion, to differentiate the effects of B to that of defects on the D diffusion.

Deuterium (for hydrogen) was incorporated into the diamonds by exposing the samples to D microwave plasma at 550 °C for various durations. Post-deuteration annealings were performed in vacuum at temperature varying between 550 and 1400 °C for duration ranging between 1 and 22 h. For annealing under bias, an external field was applied to half of the sample by biasing two graphite electrodes pressed against the two half faces of the sample [29]. This procedure allowed us to differentiate the diffusion effect due to thermal heating alone from that due to diffusion caused by the combined effect of the electric field and the temperature. The voltage that was applied varied between 50 and 250 V depending on the sample's electrical conductivity. Since the voltage is applied across the whole sample, type Ib substrate + B-doped epi-layer, a significant part of the applied voltage will drop across the substrate. It is therefore difficult to precisely calculate the electrical field across the B-doped epi-layer.

Following deuteration and post-deuteration diffusion experiments, all samples were thoroughly cleaned for a few hours in boiling acids and in organic solvents to remove any deuterium adsorbed on the surface, hence ensuring that no surface conductivity that can affect the electrical measurements or any residual impurities that can be driven into the sample during the SIMS profiling
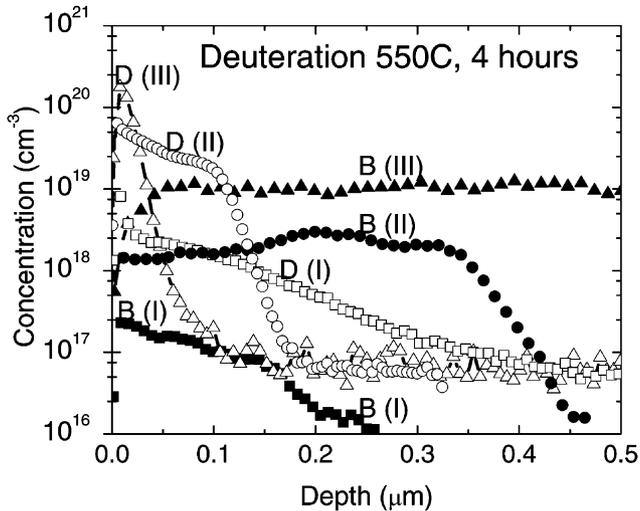
Fig. 1. B and D SIMS depth profiles in implantation doped samples measured after deuteration at 550 °C for 4 h for three type IIa diamonds. B and D profiles measured on diamond I, II and II are represented in solid and open squares (diamond I), solid and open circles (diamond II) and solid and open triangles (diamond III).

remained on the surface. SIMS and electrical measurements were performed before diffusion, after diffusion and cleaning processes and following each annealing step. The depth profiles of boron, deuterium and carbon were measured in a Cameca ims-4f SIMS apparatus using a Cs^+ primary ion beam and monitoring the $^2D^-$, ^{11}B and $^{12}C^-$ ions. Resistivity and Hall effect measurements in the Van der Pauw configuration were performed as a function of temperature from 77 to 900 K to deduce the electrical characteristics of the diamond layer.

5. Results and discussion

5.1. Retardation of the D diffusion in type IIa diamonds implanted with B

In this experiment, three type IIa diamonds were implanted, using the CIRA procedure, to obtain an homogenous B-doped layer extending from the surface to a few hundreds of nanometer with a concentration of approximately 1×10^{17} for the first stone (diamond I), 2×10^{18} for the second one (diamond II) and 1×10^{19} cm^{-3} for the third diamond (diamond III). The diamonds were then annealed at 1400 °C for 10 min and etched in boiling acids to remove any surface graphitic layer. A fourth type IIa diamond (diamond IV) was implanted and annealed under the same conditions as those used for the three first diamonds, however, with C implants instead of B. This diamond serves as a control to distinguish the effects of the B acceptors from those of the defects on the D diffusion. The as-prepared diamonds were deuterated at 550 °C for a duration

ranging between 2 and 22 h and etched again in boiling acids to remove deuterium related surface effects. D SIMS depth profiles were measured in the three stones following each deuteration or annealing stages. For diamond II, electrical properties were also measured as function of deuteration time and annealing temperatures.

Fig. 1 shows the D and B SIMS depth-profiles for diamonds I, II and III deuterated at 550 °C for 4 h. It is obvious from this figure that, in the same conditions of deuteration used for the three diamonds, the D penetration depth *increases* with *decreasing* B concentration. In samples I and II, where the deuterium penetration depth is measurable, the deuterium concentration level is about one order of magnitude higher than the B concentration.

Fig. 2 shows the D and B SIMS depth profiles measured in diamond II subjected to various deuteration times (2, 6 and 22 h). As seen in the figure, the D penetration depth increases with increasing deuteration time while the D concentration remains constant at a concentration level about one order of magnitude higher than that of B.

Moreover, we showed in a previous publication [6] that the D depth profile measured in a type IIa C implanted and annealed diamond (diamond IV) was similar to that obtained in diamond (II), both diamonds being deuterated for 2 h. Figs. 3 and 4 show the electrical properties of diamond II after each deuteration or annealing stages. The variation of the carrier concentration as a function of $1/T$, exhibited in Fig. 3, remains almost unchanged when increasing the deuteration duration and after the various annealing stages at 600, 900 and 1400 °C and exhibits the expected 0.37 eV activation energy. In contrast, the mobility decreases continu-
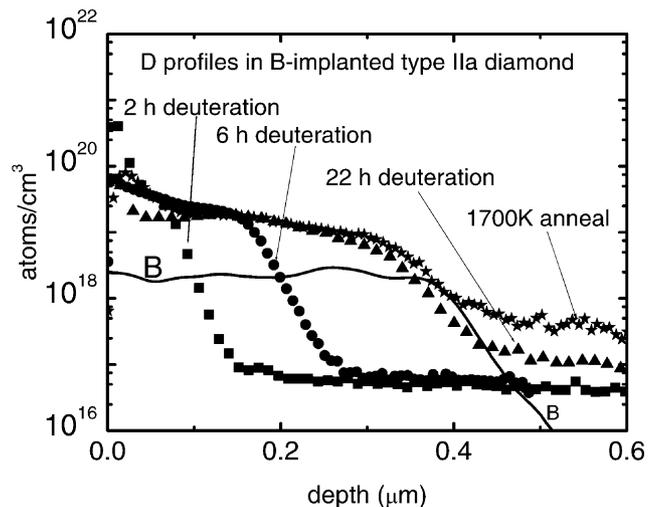
Fig. 2. D SIMS depth profiles measured in implantation doped samples after deuteration at 550 °C for 2 h (■), 6 h (●) and 22 h (▲) and following 1400 °C annealing (*). The B profile is in full line.
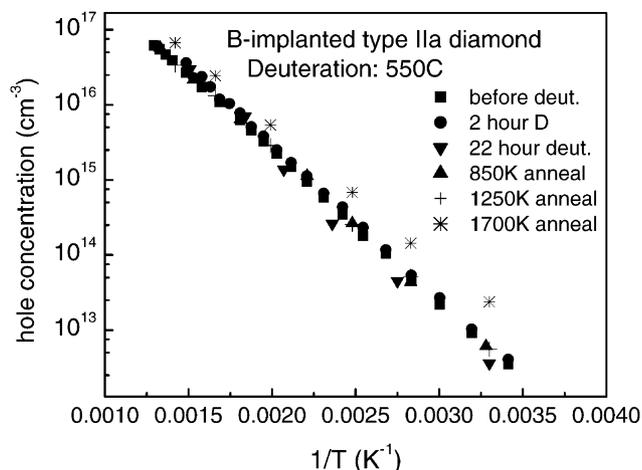
Fig. 3. Carrier concentration as a function of inverse temperature for diamond II before deuteration (■), after deuteration at 550 °C for 2 h (●), and 22 h (▼) and following subsequent annealing at 850 K (▲), 1250 K (+) and 1700 K (*).

ously with increasing the deuteration time (Fig. 4). After 600 and 800 °C annealing, the mobility begins to increase but again decreases after a high temperature anneal of 1400 °C.

The present results are drastically different to those obtained on a deuterated B-doped homoepitaxially grown diamond layer: the SIMS profiles of B and D are identical, the carrier concentration decreases and the mobility increases upon deuteration, demonstrating that D has passivated B acceptors [6]. In the present case, of a B implantation doped layer, the following points are observed:

- The D concentration level is one order of magnitude higher than the B concentration.
- Similar SIMS results are found in C- and B-implanted diamonds exposed to D plasma in the same conditions.
- The carrier concentration does not change by the deuteration while the mobility does decrease strongly.

An effective diffusion coefficient can be deduced by using the D SIMS depth profiles measured on diamond II for deuteration performed at 2, 6 and 22 (Fig. 2). A diffusion coefficient of 5×10^{-15} cm^2 s^{-1}, is deduced for hydrogen (deuterium) in a B containing (2×10^{18} cm^{-3}) implanted diamond concentration of. In contrast, the H diffusion coefficient in a B-doped homoepitaxial diamond layer deuterated at 550 °C was found to be 5×10^{-13} cm^2 s^{-1} for a B concentration of 5×10^{19} cm^{-3}, indicating that it might be even higher for a B concentration of 2×10^{18} cm^{-3} [25].

Our results suggest that the D profile follows the profile of unannealed residual implantation defects and that the D diffusion is limited by trapping on the residual implantation defects. This diffusion process is retarded

as compared to diffusion which is limited by trapping on B. It is not clear to us if single or multi-trapping are involved in the process. Following B ion implantation the concentration of defects, as determined by TRIM computer code [32], is about two orders of magnitude higher than that of B. However, it appears from the above measurements, that the annealing stages performed following the implantation are not sufficient to completely remove the implantation damage and that a concentration of defects which is at most one order of magnitude higher than the B concentration remains, even after the high temperature annealing stage at 1400 °C. Our results seem also to explain the results of Machi et al. [20]. In this work, high doses of Ne were implanted in an attempt to enhance the H diffusion in type IIa diamond. The concentration of implantation defects introduced into the diamond layer in that experiment is very high ($>10^{19}$ cm^{-3}). Thus, the lack of H diffusion in this work must be related to all H atoms being captured by the ion implantation defects already in the first subsurface layers.

The observed decrease of the mobility when increasing the deuteration time may indicate that the cross section for D capture by the already existing defects increases with increasing deuteration times, as more and more D are introduced into the B-doped layer. Since the carrier concentration remains almost unchanged, it can be concluded that these defect centers do not compensate the B-related electrical activity, yet they do affect the carrier mobility. When annealing the B-doped diamond layer to higher temperatures, some defect/D complexes may agglomerate to form larger clusters, thus reducing the probability of carrier scattering hence slightly increasing the mobility. It seems that the high temperature annealing at 1400 °C dissociates these clusters,
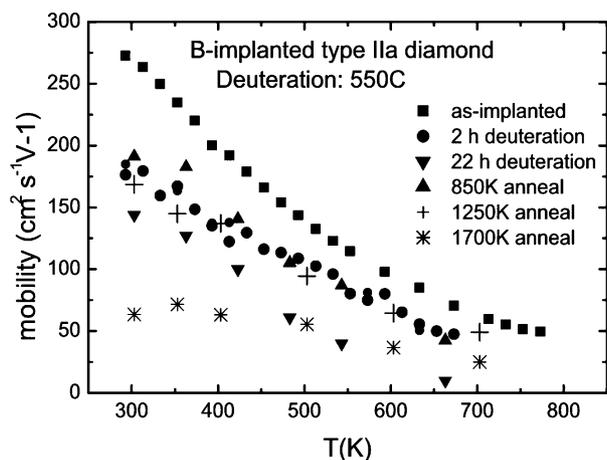
Fig. 4. Mobility as a function of temperature for diamond II before deuteration (■), after deuteration at 550 °C for 2 h (●), and 22 h (▼) and following subsequent annealing at 850 K (▲), 1250 K (+) and 1700 K (*).
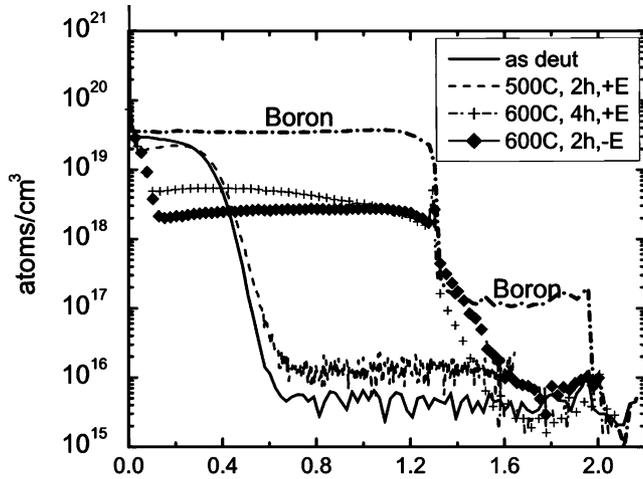
Fig. 5. B (dashed dotted line) and D SIMS depth profiles measured in a highly B-doped homoepitaxial diamond CVD layer after deuteration at 550 °C for 4 h (full line), following annealing under a positive bias at 500 °C (dashed line) and 600 °C (+), and upon annealing at 600 °C for 2 h with a negative bias (♦).

leading again to a high concentration of the complexes defects/D which strongly limit the hole mobility.

5.2. Hydrogen diffusion under the influence of an electrical field

Below we present preliminary results of experiments searching for 'forced diffusion', due to an external electric field, of H in B-doped diamond [33].

Diamond 1 was a 1.3-μm thick highly B-doped, low compensated homoepitaxial diamond layer grown on a low B-doped buffer layer deposited on a ⟨1 0 0⟩ Ib substrate at the LEPES of Grenoble, deuterated at 550 °C for 2 h. It was first annealed at 500 °C for 4 h under an electrical field so as to push positive species to the depth (positive bias). It was then annealed at 600 °C for 4 h under an electrical field applied in a direction where positive charges are drifted to the depth (positive bias). It was finally annealed at 600 °C for 2 h with electrical field applied in the opposite direction (negative bias). The voltage applied across the sample was between 100 and 250 V. The SIMS D depth profiles were measured following each annealing stages.

Diamond 2 was a 0.3-μm thick low B-doped, low compensated homoepitaxial diamond layer grown on an undoped buffer layer deposited on a ⟨1 0 0⟩ type Ib diamond at the AIST of Tsukuba, deuterated at 550 °C for 4 h. The electrical field was applied in such a way that positive charged species should drift to the depth of layer while negatively charged species will diffuse out (positive bias). A voltage between 50 and 100 V was applied to half of the sample.

Fig. 5 shows that the D SIMS depth profile measured in diamond 1 after 500 °C anneal has barely changed.
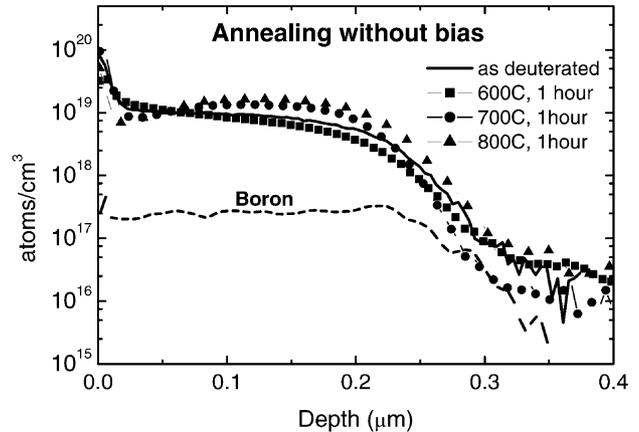
Fig. 6. B (dashed line) and D SIMS depth profiles measured in a lightly B-doped homoepitaxial diamond CVD layer after deuteration at 550 °C for 4 h (full line), following annealing at 600 °C (■), 700 °C (●), and 800 °C (▲) for 1 h without bias.

This result is expected since the onset temperature for the (B, H) pair dissociation is approximately 550 °C. After anneal at 600 °C for 4 h under positive bias, Fig. 5 shows that the D has diffused to fill the complete B-doped layer and accumulated at the interface with the buffer layer. The D penetration depth is therefore at least 1.3 μm which is much deeper than that obtained after diffusion in the same conditions without bias [34], hence confirming that H^+ has been liberated from the (B, H) pairs and that the electrical field has caused H to migrate in the H^+ ionic state [22]. After a new annealing at 600 °C for 2 h with negative bias, the D SIMS profile moves towards the surface, suggesting the effect of the electrical field on the positively charged H ion.

Figs. 6 and 7 show the D SIMS depth profile for diamond 2 following annealing at 600, 700 and 800 °C
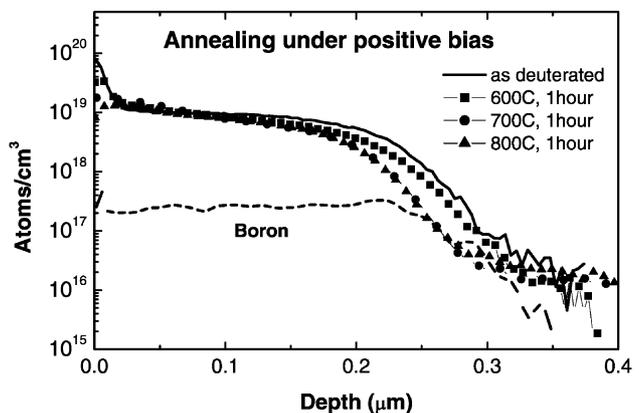
Fig. 7. B (dashed line) and D SIMS depth profiles measured in a lightly B-doped homoepitaxial diamond CVD layer after deuteration at 550 °C for 4 h (full line), following annealing at 600 °C (■), 700 °C (●), and 800 °C (▲) for 1 h with a positive bias.

for 1 h without and with positive bias, respectively. It is obvious from Figs. 6 and 7 that the D concentration level, directly measured after deuteration, is much higher than that of the B, demonstrating that, in this specific sample which had a low boron concentration the D solubility is not controlled by trapping on B acceptors. By comparing the SIMS raw data (not shown here), it appears that the D signal measured on the diamond part annealed under bias is higher by a factor of approximately 5 than the D signal measured after annealing without bias. Although, as we later see, we relate the higher intensity of the D signal measured for annealing under bias to some SIMS artifact induced by some physical effect occurring during the annealing under bias, the D profiles measured with bias were numerically normalized to the area under the profile 'as-deuterated' in order to compare the D profiles. These 'normalized' results are shown in Figs. 6 and 7.

For T above 600 °C, the general shape of the D profiles measured in the annealed part differs from that measured in the part annealed under bias. The D profiles measured in the part annealed without bias exhibit a depletion-like region located in the near-surface layer at approximately 0.03 μm followed by a D accumulation region roughly extending from 0.1 to 0.25 μm. This effect becomes more pronounced with increasing temperature. The D profiles measured in the part annealed with bias do not show any of the above features. In contrast, they are flat and tend to show a slight D out-diffusion with increasing annealing temperature; in both parts, no D diffusion into the undoped diamond layer grown under the B-doped layer is observed. Electrical measurements were performed on this sample and their results can be summarized as follows.

(1) Before deuteration, the sample is p-type with a low B-doping level (the hole concentration is 5×10^{13} cm^{-3} at room temperature and saturates at 500 °C at a concentration equal to 2×10^{17} cm^{-3}) and a mobility of 450 cm^2 V^{-1} s^{-1}, at room temperature.

(2) After deuteration, the sample shows very high resistivity and no Hall effect measurements are possible.

(3) After annealing at 800 °C, the electrical behavior is different in the two parts of the sample. In the part annealed under bias, the resistivity has increased by two orders of magnitude compared with the resistivity in the as-grown layer and shows the same activation energy as in the as-grown layer, however, with saturation at a higher temperature. The mobility has strongly decreased while the carrier concentration remains almost unchanged as compared to that of the as-grown layer. In contrast, in the part annealed without field, the resistivity values have increased by four orders of magnitude and resistivity vs. temperature data show new activation energy of 0.65 eV for temperatures above 200 °C. No Hall effect measurements were possible is this part.

Since the SIMS D concentration is much larger than that of B, it is suggested that only a small part of D interacts with B acceptors. This is confirmed by the electrical measurements which shows that the carrier concentration is recovered after 600 °C. In contrast, the D incorporated in excess in the B-doped layer may form complexes with other D atoms or with some native defects. Increasing the annealing temperature to 800 °C yields an accumulation of D complexes which seemed to be partly locked-into the B-doped layer since out-diffusion starts at 750 °C. This result may be correlated with the new activation energy observed in the electrical measurements, which is probably connected to some new electrically active defect complexes. The effect of the electrical field is probably to break these complexes and enhance their motion out of the layer. Since the D profiles measured after annealing under bias are some-what shifted towards the surface, it seems that the D containing complexes are negatively charged species. At this stage, the D configuration most probably changes, inducing a change in the D ionization energy for the SIMS measurements [35]. We suggest that this change may explain the high D signal measured after annealing under bias.

6. Conclusions

We have shown that in B-doped diamond layers containing implantation defects, H mainly interacts with the defects to form complexes which are stable up to high temperatures. The interaction between the hydrogen and some native defects and not that of hydrogen with boron seems to limit the H diffusion.

By performing diffusion experiment under bias, we confirm that, in highly B-doped homoepitaxial diamond layer, H diffuses as a positive ion. In contrast, in a low B-doped CVD layer, hydrogen seems to form stable complexes which diffuse as negatively charged species.

References

[1] R.D. Maclear, J.D. Butler, S.H. Connel, et al., Diamond Relat. Mater. 8 (1999) 1615.

[2] J. Chevallier, B. Theys, A. Lusson, C. Grattepain, A. Deneuville, E. Gheeraert, Phys. Rev. B 58 (1998) 7966.

[3] J.B. Cui, J. Ristein, L. Ley, Phys. Rev. Lett. 81 (1998) 429.

[4] K. Hayashi, S. Yamanaka, H. Watanabe, T. Sekiguchi, H. Okushi, K. Kajimura, J. Appl. Phys. 81 (1997) 744.

[5] S.J. Pearton, J.W. Corbett, M. Stravola, Hydrogen in Crystalline Semiconductors. Spring Series in Materials Science 16, Springer, Berlin, 1992.

[6] C. Uzan-Saguy, A. Reznik, C. Cytermann, et al., Diamond Relat. Mater. 10 (2001) 453.

[7] J. Chevallier, A. Lusson, D. Ballutaud, et al., Diamond Relat. Mater. 10 (2001) 399.

[8] S.A. Kajihara, A. Antonelli, J. Bernholc, R. Car, Phys. Rev. Lett. 66 (1991) 2010.

[9] J.P. Goss, R. Jones, M.I. Heggie, C.P. Ewels, P.R. Bridon, S. Oberg, Phys. Rev. B 65 (2002) 115207.

[10] S.P. Mehandru, A.B. Anderson, J. Mater. Res. 9 (1994) 383.

[11] D. Saada, J. Adler, R. Kalish, Phys. Rev. B 61 (2000) 10711.

[12] A. Shimizu, H. Tachikawa, M. Inagaki, Solid State Ionics 127 (2000) 157.

[13] T.L. Estle, S. Estreicher, D.S. Marynick, Phys. Rev. Lett. 58 (1987) 1547.

[14] E. Holzschuh, W. Kundig, P.F. Meier, et al., Phys. Rev. A 25 (1982) 1272.

[15] T. Maki, S. Shikama, M. Komori, Y. Sakaguchi, K. Sakuta, T. Kobayashi, Jpn. J. Appl. Phys. 31 (1992) L1446.

[16] F. Fuchs, C. Wild, K. Schwarz, P. Koidl, Diamond Relat. Mater. 4 (1995) 652.

[17] A.M. Zaitsev, Properties, growth and applications of diamond, in: M.H. Nazare, A.J. Neves (Eds.), EMIS Datareviews Series no. 26, 2001, p. 155.

[18] C. Liao, Y. Wang, S. Yang, Diamond Relat. Mater. 8 (9) (1999) 1229.

[19] C. Haug, H. Gartner, J. Portmann, R. Samlenski, C. Wild, R. Brenn, Diamond Relat. Mater. 10 (2001) 411.

[20] I.Z. Machi, J.E. Butler, S.H. Connel, et al., Diamond Relat. Mater. 8 (1999) 1611.

[21] R. Zeisel, C.E. Nebel, M. Stutzmann, Appl. Phys. Lett. 74 (1999) 1875.

[22] R. Zeisel, C.E. Nebel, M. Stutzmann, Diamond Relat. Mater. 9 (2000) 413.

[23] C. Uzan-Saguy, C. Cyterman, B. Fizgeer, et al., Diamond Relat. Mater. 11 (2002) 316.

[24] J. Chevallier, Hydrogen diffusion and acceptor passivation in diamond, in: C. Nebel, J. Ristein (Eds.), Thin Film Diamond, Academic Press, 2002.

[25] D. Ballutaud, F. Jomard, J. Le Digou, et al., Diamond Relat. Mater. 9 (2000) 1171.

[26] A. Laikhtman, A. Hoffman, C. Cytermann, Appl. Phys. Lett. 79 (2001) 1115.

[27] J. Chevallier, F. Jomard, Z. Teukam, et al., Diamond Relat. Mater. 11 (2002) 1566.

[28] C. Uzan-Saguy, C. Cytermann, unpublished results.

[29] C. Uzan-Saguy, C. Cytermann, B. Fizgeer, et al., Phys. Stat. Sol. 193 (2002) 508.

[30] F. Fontaine, C. Uzan-Saguy, B. Philosoph, R. Kalish, Appl. Phys. Lett. 68 (1996) 2264.

[31] J. Prins, Phys. Rev. B 39 (1989) 1562.

[32] J.P. Biersack, L.G. Haggenark, Nucl. Instr. Phys. Res. 174 (1980) 257.

[33] G. Popovicci, T. Sung, S. Khasawinah, M.A. Prelas, J. Appl. Phys. 77 (1995) 5625.

[34] Z. Teukam, D. Ballutaud, F. Jomard, J. Chevallier, M. Bernard, A. Deneuville, Diamond Relat. Mater. 12 (2003).

[35] M. Tomita, F. Takahashi, Y. Homma, Nucl. Instr. Methods: Phys. Res. B 85 (1994) 399.