TOPICAL REVIEW

$^{11}$B nuclear magnetic resonance in boron-doped diamond

Miwa Murakami$^{1}$, Tadashi Shimizu$^{1}$, Masataka Tansho$^{1}$ and Yoshihiko Takano$^{2}$

$^{1}$ National Institute for Materials Science, 3-13 Sakura, Tsukuba, Ibaraki 305-0003, Japan
$^{2}$ International Center for Materials Nanoarchitectonics, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

E-mail: MURAKAMI.Miwa@nims.go.jp

Received 7 January 2009
Accepted for publication 10 February 2009
Published 24 April 2009
Online at stacks.iop.org/STAM/9/044103

Abstract

This review summarizes recent results obtained by $^{11}$B solid-state nuclear magnetic resonance (NMR) on boron-doped diamond, grown by the high-pressure high-temperature (HPHT) or chemical vapor deposition techniques. Simple single-pulse experiments as well as advanced two-dimensional NMR experiments were applied to the boron sites in diamond. It is shown that magic-angle spinning at magnetic fields above 10 T is suitable for observation of high-resolution $^{11}$B spectra of boron-doped diamond. For boron-doped HPHT diamonds, the existence of the excess boron that does not contribute to electrical conductivity was confirmed and its $^{11}$B NMR signal was characterized. The point-defect structures (B + H complexes and $-$B-$B-/B-C-B- clusters), postulated previously for the excess boron, were discarded and graphite-like structures were assigned instead.

Keywords: boron-doped diamond, $^{11}$B NMR, two-dimensional NMR

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In 2004, Ekimov et al discovered superconductivity in heavily boron-doped diamond [1]. So far, two major synthesis techniques of heavily boron-doped diamond are known: high-pressure high-temperature (HPHT) method and chemical vapor deposition (CVD). In contrast to the expectation of higher $T_C$ (the superconductivity transition temperature) for higher boron concentrations [B], Takano et al [2, 3] showed that $T_C$ of homoepitaxial (100) thin films, synthesized by the microwave plasma assisted CVD, increases with increasing [B] and reaches a maximum at [B] $\sim 1 \times 10^{22}$ cm$^{-3}$. They also pointed out that $T_C$ ([B]) dependences are similar for diamonds grown by the HPHT method and (100) CVD films. On the other hand, $T_C$ for (111) films increases with increasing [B] in the same concentration range, and those $T_C$ values are more than twice higher than those of the (100) films [2–4]. These findings indicate that not all boron atoms provide charge carriers.

Detailed studies have been reported on synthesis and characterization of heavily boron-doped diamond [5–9]. Despite the gained insights, the relation between the local structure around boron dopants and physical properties of boron-doped diamond has not been fully clarified. This may be attributed to the difficulty in applying many spectroscopic techniques because the doped boron sites lack a long-range order. Solid-state nuclear magnetic resonance (NMR) is particularly useful in analysis of amorphous inorganic solids without such long-range order; besides, NMR can determine site distributions of each atomic species. Due to the low natural abundance of $^{13}$C (1.1%), $^{11}$B is expected to be the most accessible nucleus in boron-doped diamond. In this review, we have summarized solid-state $^{11}$B NMR results on the disordered local structure in several boron-doped diamonds and, in particular, the structure of the excess boron which does not contribute to electrical conductivity.
2. Spectral analysis of $^{11}$B NMR

The first $^{11}$B NMR study on boron-doped diamond was reported by Mukuda et al. [10, 11]. They applied $^{11}$B solid-state NMR to boron-doped CVD diamond and found that $^{11}$B spectra observed in magnetic field of 2.554 T consist of two components—sharp and broad; the broad signal appearing at the lower-frequency side (figure 1). They assigned the sharp signal to boron at highly symmetrical site, that is, the substitutional position for the carbon site in the diamond lattice. They also showed that the carriers associated with this boron site are responsible for the superconductivity. Further, on the basis of $ab$ initio calculations and secondary ionization mass spectrometry (SIMS), the other, broad signal was assigned to a boron–hydrogen ($B + H$) complex, where the positively charged hydrogen compensates the carrier provided by the boron acceptor.

To improve spectral resolution, Murakami et al. applied magic-angle spinning (MAS) [12]. MAS has been widely applied in high-resolution solid-state NMR of spin-1/2 nuclei, such as $^{13}$C and $^{15}$N to remove the chemical-shift anisotropy. In this case, MAS removed not only the chemical-shift anisotropy, but also homonuclear $^{11}$B–$^{11}$B and heteronuclear $^{11}$B–$^{10}$B dipolar broadening. To show the effectiveness of MAS in the characterization of boron-doped diamond, Murakami et al. compared the $^{11}$B MAS NMR spectra of the following four boron-doped diamond samples. Three samples HPHT-1, 2, 3 were prepared with the HPHT method from different starting materials: HPHT-1 from naphthalene and boron, HPHT-2 from graphite and boron and HPHT-3 from boron-doped graphite. The fourth sample was grown by CVD from a dilute gas mixture of methane and trimethylboron in hydrogen. The transition temperatures are $T_C \sim 7.0$ K (onset) for the CVD, 3.8 K for HPHT-1, 4.5 K for HPHT-2 and 2.3 K for HPHT-3 samples.
sharp peak near 0 ppm is negligible in the CVD sample and the intensity of the broad signal is low in HPHT-3. Effects of the quadrupolar interaction on the $^{11}$B MAS spectra are appreciable in the observed pulse-width and magnetic-field dependences in figure 2; the effects are most prominent for the CVD and HPHT-1 samples, as discussed below. Comparison of the spectra of the HPHT-1,2,3 samples suggests that there are at least two signals at around 0 ppm. X-ray diffraction reveals $\text{B}_4\text{C}$ phase in HPHT-1 [5], which has a sharp $^{11}$B MAS NMR peak around 0 ppm. Hence, one of the two sharp components may be ascribed to $\text{B}_4\text{C}$ [12]. The other component at $\sim$0 ppm was tentatively assigned to $\text{B}_4\text{C}$ [12].

In the following, the relation is investigated between these spectral features and conductivity in three samples N1–N3 (N3 is identical to HPHT-1). These samples were prepared by the HPHT method with the same starting materials (naphthalene and amorphous boron) but with different initial boron ratios: $\text{B}/(\text{B + C}) = 0.75, 2.4$ and 5.0% for N1, N2 and N3, respectively.

Figure 3 shows the $^{11}$B MAS NMR spectra of the N1–N3 samples at 21.8 T [14]. The spectra mainly consist of four signals a–d. The signals a and b were assigned to boron and $\text{B}_4\text{C}$ inclusions and the signals c and d to boron dispersed in the diamond lattice [12]. All MAS spectra of figure 3 can be fitted by a sum of Gaussians (thin lines in figure 3) by taking the chemical shifts, the linewidths, and the relative intensities as fitting parameters. The best-fit chemical shifts for the signals a–d are $-4.3, 1.3, 28.5$ and 65.5 ppm, respectively. Note that these best-fit chemical-shift values are similar for the three spectra. Here, we used the term ‘chemical shift’. Other contributions, such as the Knight shift [15, 16], do contribute to the observed shift, as mentioned below. However, as the conductivity is small at room temperature, the contribution of the Knight shift should be relatively small.

Figure 4. Recovery-time dependence of the $^{11}$B signal intensities in sample HPHT-1/N3. The signal intensities at the four chemical shifts, determined in figure 3 as $-4.3$ ppm (a), 1.3 ppm (b), 28.5 ppm (c), 65.5 ppm (d), are normalized to those taken with the recovery time of 60 s. The solid lines are simulated ones with double exponents (see text). (Reproduced from [12] with permission of the Elsevier Ltd.)
~1.5–3 s, which may roughly explain the observed $T_1$ values for the signals c and d [12]. Hence, the sharper signal, found by Mukuda et al (B(1) in figure 1) for the CVD sample observed without MAS, corresponds to the signal-c; whereas the broader signal (B(2) in figure 1) was associated with the signal-d in figure 3 for the HPHT sample. Please note the different relative intensities of signals c and d in CVD (figure 2(a)) and HPHT samples that relates to the highest $T_c$ of the CVD sample ($\sim 7.0$ K) among those samples.

To examine how the $^{11}$B NMR spectra relate with electrical conductivity, the temperature dependence of the magnetization was measured for the N1–N3 samples (figure 5) [14]. Diamagnetic signals corresponding to superconductivity appeared for the N2 and N3 samples below 4 K. Further the transition temperature for N3 is slightly lower than that for N2, indicating that the increment of the initial amount of boron does not straightforwardly contribute to conductivity. The intensity of the signal-c (hereafter, boron-c) increases with the $B/(B+C)$ ratio in samples N1 and N2. Further increase in the $B/(B+C)$ ratio, however, does not straightforwardly contribute to the increase of boron-c in N3, but boron-d growth up. These results, together with the $T_1$ examination and the lineshape analysis, indicate that the boron-c contributes to the conductivity and the boron-d corresponds to the electrically inactive, ‘excess’ boron.

So far, two candidates for the excess boron have been postulated: (i) B + H and (ii) -B-B-/ -B-C-B- complexes. To test the B + H model, Murakami et al examined $^1$H-$^{11}$B dipolar broadening using a newly developed two-dimensional (2D) NMR technique (2D $^1$H on/off experiment) [14]. In a 2D spectrum, signal intensity is plotted as a contour in a plane spanned by two frequency axes. Figure 6(a) shows the contour plot of the 2D $^1$H on/off spectrum of borax under MAS [14], in which the projection on the horizontal frequency axis ($F_2$) corresponds to $^1$H-decoupled lineshape and the projection on the vertical axis ($F_1$) to $^1$H-coupled lineshape. Borax has two boron species B1 and B2 (see, the inset of figure 6).

From the neutron diffraction study [18], the shortest $^1$H-$^{11}$B distance is estimated as 0.2 nm. Figure 6(a) clearly shows

Figure 5. Temperature dependence of magnetization for samples N3 (a), N2 (b) and N1 (c). Field cooling (FC) and zero-field cooling (ZFC) results are shown. The vertical dotted line drawn at 4 K is for eye guidance. (Reproduced from [14].)

Figure 6. 2D $^1$H on/off spectra of borax (a) and HPHT diamond sample N3 (b) measured in 11.7 T. A structure of borax is given as the inset. (Reproduced from [14].)
1H-11B dipolar broadening in the $F_1$ dimension for the two boron species in borax. The 2D $^1$H on/off spectrum of the N3 sample (figure 6(b)), however exhibits only sharp diagonal components. There is no dipolar broadening, which should appear in the $F_1$ dimension if an appreciable amount of the $^1$H+$^{11}$B complexes existed. This observation ruled out the B + H model of the excess boron. Similar experimental results were obtained with static NMR (without MAS) [19].

The existence of the boron–boron (−B−B−/−B−C−B−) clusters has also been discarded [13, 17] by examining $^{11}$B−$^{11}$B 2D exchange NMR [20] and observing only diagonal peaks in the 2D exchange spectrum of the N3 sample [14]. Thus if neither the B + H nor -B-B- fit into the experiment then what is boron-d?

3. Two clues: chemical shift and quadrupolar coupling

In this section, the chemical shift and the quadrupolar coupling are used to unravel the structures of boron-c and especially boron-d. From the data for boron-containing organic compounds, it has been well established that $^{11}$B chemical shifts of tetrahedrally coordinated boron appear at frequencies ranging roughly from −20 ppm to 10 ppm [21]. The observed chemical shift of boron-c (∼28.5 ppm), which was assigned to the tetrahedrally coordinated boron in the diamond lattice, is therefore slightly shifted to higher frequencies. This could be due to the Knight shift contribution [15, 16].

On the other hand, the $^{11}$B chemical shifts of trigonally coordinated boron are found at higher frequencies ∼20–100 ppm [21]. Note the wider frequency range for trigonal boron compared to tetrahedral boron. The observed chemical shift of boron-d at ∼68.5 ppm thus suggests that boron-d is a trigonal boron. This is consistent with the assignment of boron-d to the electrically inactive boron—trigonal boron does not provide carriers in diamond. Hereafter we primarily concern with the quadrupolar interaction of $^{11}$B in boron-doped diamond.

Trigonal coordinated $^{11}$B has appreciable quadrupolar coupling. For example, the quadrupolar coupling of trimesitylborane is 4.75 MHz and that of triphenyl borate is 2.32 MHz [22]. Mukuda et al reported the magnitude of the boron quadrupolar coupling in boron-doped CVD diamond as 1.6 MHz [10, 11]. Therefore it is worthy to examine the quadrupolar coupling of boron-d.

If quadrupolar coupling is large, the second-order quadrupolar interaction should be appreciable too. To examine whether the broad lineshape of boron-d can be reproduced by taking into account the second-order quadrupolar interaction, Murakami et al compared the calculated second-order quadrupolar MAS lineshape [23] with the observed lineshape in figure 2 [12]. The sharp signals e1 and e2 in figure 2 are simulated using the reported values for the CVD sample [10, 11] of the quadrupole coupling constant ($e^2Q/h$ = 1.6 MHz) and the asymmetry parameter ($\eta = 0$).

Clearly, the quadrupolar coupling constant used in calculation is too small to explain the observed large linewidth. Figure 7 shows magnetic field dependence of the calculated MAS lineshape, calculated taking $e^2Q/h = 5$ MHz (a and c) or 2 MHz (b and d); $\eta = 0$ for the magnetic field of 20 T (a and b) or 10 T (c and d). Figure 7 shows that $e^2Q/h \geq 5$ MHz is required to explain the large width of the boron-d signal at 11.7 T. For such large values, the lineshape dependence on the magnetic field should be apparent. However, the spectral features of the two $^{11}$B MAS NMR spectra of sample N3, measured at 21.8 T and at 11.7 T (figure 2; b1 and b2), are similar. This weak dependence on the static field indicates small quadrupolar couplings.
concluded that the quadrupolar coupling constant of the $^{11}\text{B}$ nuclei in diamond is $\lesssim 100$ kHz, and some boron atoms have much smaller quadrupolar coupling [14]. The smaller one should correspond to boron-c, which has been assigned to the tetrahedrally coordinated boron in the diamond structure, and the relatively larger one is boron-d.

4. The assignment of signal-d

Chemical shift suggests that boron-d is trigonally coordinated. The observed large chemical shift distribution can be attributed to variation in the local environment. As for a possible structure, we note that graphite formation is an intermediate stage of the HPHT synthesis [29]. Presence of disordered graphite in HPHT samples was inferred by Ekimov et al from the broadening of x-ray diffraction and Raman peaks [5]. Hence, it is suggested [14] that boron-d is trigonally coordinated boron in disordered graphite-like structures. This assignment may contradict the observed small quadrupolar coupling, because trigonally coordinated boron in a flat graphite structure should have a large quadrupolar coupling of $3.36$ MHz [30]. However, Murakami et al pointed out [14] that the small quadrupolar interaction merely indicates better ‘local’ symmetry of the electric field gradient around boron. They also pointed out these boron-containing graphite structures should be relatively small, otherwise distinct x-ray diffraction lines would have been observed. In summary, the excess boron is the trigonally coordinated boron in non-diamond phase; its local symmetry is high enough to produce small electric field gradient.

Acknowledgments

The diamond samples N1, N2, HPHT-1 (N3) and HPHT-2 were kindly supplied by Dr E A Ekimov and Dr V A Sidorov (Russian Academy of Science). The sample HPHT-3 was prepared by Dr H Sumiya (Sumitomo Electric Industries Ltd.) and CVD films were supplied by Dr H Kawarada (Waseda University). We thank all these co-workers and Professor K Takegoshi at Kyoto University for his general advice on NMR measurements.

MM appreciates support from the ‘Nanotechnology Support Project’ of the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan. TS thanks support from World Premier International Research Center Initiative (WPI Initiative) on Materials Nanoarchitronics (MANA) at NIMS, from MEXT of Japan. YT acknowledges support from the Grant-in-Aid for Science Research of MEXT. We also acknowledge technical support from Tsukuba Magnet Laboratory, NIMS.

References

[1] Ekimov E A, Sidorov V A, Bauer E D, Mel’nik N N, Curro N J, Thompson J D and Stishov S M 2004 Nature 428 542
[2] Takano Y, Takenouchi T, Ishii S, Ueda S, Okutsu T, Sakaguchi I, Umezawa H, Kawarada H and Tachiki M 2007 Diamond Relat. Mater. 16 911
[3] Takano Y, Nagao M, Sakaguchi I, Tachiki M, Hatano T, Kobayashi K, Umezawa H and Kawarada H 2004 Appl. Phys. Lett. 85 2851
[4] Umezawa H, Takenouchi T, Takano Y, Kobayashi K, Nagao M, Sakaguchi I, Tachiki M, Hatano T, Zhong G and Kawarada H 2005 arXiv:cond-mat/0503303
[5] Ekimov E A, Sidorov V A, Rakhmanina A V, Mel’nik N N, Sadykov R A and Thompson J D 2006 Sci. Technol. Adv. Mater. 7 S2
[6] Sidorov V A, Ekimov E A, Rakhmanina A V, Stishov S M, Bauer E D and Thompson J D 2006 Sci. Technol. Adv. Mater. 7 S7
[7] Yoshii T et al 2006 Sci. Technol. Adv. Mater. 7 S12
[8] Ishizaka K et al 2006 Sci. Technol. Adv. Mater. 7 S17
[9] Nishizaki T, Takano Y, Nagao M, Takenouchi T, Kawarada H and Kobayashi N 2006 Sci. Technol. Adv. Mater. 7 S22
[10] Mukuda H, Tsuchida T, Harada A, Kitaoaka Y, Takenouchi T, Takano Y, Nagao M, Sakaguchi I, Oguchi T and Kawarada H 2007 Phys. Rev. B 75 033301
[11] Mukuda H, Tsuchida T, Harada A, Kitaoaka Y, Takenouchi T, Takano Y, Nagao M, Sakaguchi I and Kawarada H 2006 Sci. Technol. Adv. Mater. 7 S37
[12] Murakami M, Shimizu T, Tansho M, Takano Y, Ishii S, Ekimov E A, Sidorov V A, Sumiya H, Kawarada H and Takegoshi K 2008 Diamond Relat. Mater. 17 1835
[13] Fenzke D, Freude D, Frohlich T and Haase J 1984 Chem. Phys. Lett. 111 171
[14] Murakami M, Shimizu T, Tansho M, Takano Y, Ishii S, Ekimov E A, Sidorov V A and Takegoshi K 2009 Diamond Relat. Mater. submitted
[15] Knight W D 1956 Solid State Physics vol 2, ed F Seitz and D Turnbull (New York: Academic) p 93
[16] Korringa J 1950 Physica 16 601
[17] Woessner D E and Timken H K C 1990 J. Magn. Reson. 90 411
[18] Levy H A and Lisensky G C 1978 Acta Crystallogr. B 34 3502
[19] Murakami M, Shimizu T, Tansho M, Takano Y, Ishii S, Ekimov E A, Sidorov V A, Kawarada H and Takegoshi K 2007 Japan. J. Appl. Phys. 46 L1138
[20] Murakami M, Shimizu T, Tansho M, Vinu A, Ariga K, Mori T and Takegoshi K 2007 Solid State Nucl. Magn. Reson. 31 193
[21] Reed D 1996 Encyclopedia of Nuclear Magnetic Resonance vol 2, ed D M Grant and R K Harris (Chichester, UK: Wiley) p 1002
[22] Bryce D L, Wasylishen R E and Gee M 2001 J. Phys. Chem. A 105 3655
[23] Kentgens A P M, Scholle K F M G and Veeman W S 1983 J. Phys. Chem. 87 4357
[24] Frydman L and Harwood J S 1995 J. Am. Chem. Soc. 117 5367
[25] Samoson A and Lippmaa E 1983 Phys. Rev. B 28 6567
[26] Samoson A and Lippmaa E 1983 Chem. Phys. Lett. 100 205
[27] Samoson A and Lippmaa E 1988 J. Magn. Reson. 79 255
[28] Kentgens A P M, Lemmens J J M, Geurts F M M and Veeman W S 1987 J. Magn. Reson. 71 62
[29] Voronov O A and Rakhmanina A V 1992 Inorg. Mater. 28 1408 (in Russian)
[30] Lee Y, Han D-Y, Lee D, Woo A J, Lee S H and Kim Y K 2002 Carbon 40 403