11B-NMR study in boron-doped diamond films

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Abstract

We have investigated an origin of the superconductivity discovered in boron (B)-doped diamonds by means of 11B-NMR on heteroepitaxially grown (111) and (100) films and polycrystalline film. The characteristic difference of B-NMR spectral shape for the (111) and (100) thin films is demonstrated as arising from the difference in the concentration \( n_B(1) \) of boron substituted for carbon. It is revealed from a scaling between a superconducting transition temperature \( T_c \) and \( n_B(1) \) that the holes doped into diamond via the substitution of boron for carbon are responsible for the onset of superconductivity. The result suggests that the superconductivity in boron-doped diamond is mediated by the electron–phonon interaction brought about a high Debye temperature \( /C241860 \) K characteristic for the diamond structure.

1. Introduction

In 2004, Ekimov and coworkers discovered the superconductivity in heavily boron (B)-doped diamond synthesized by high-pressure and high-temperature technique, and found it to be superconductive in very low carrier concentration \( n_B \sim 4 \times 10^{21} \) cm\(^{-3} \) [1]. After this discovery it has been also reported on the B-doped diamond film synthesized by microwave plasma-assisted chemical vapor deposition (MPCVD) method [2]. One of the advantages of this method is that boron concentration can artificially tune over a wide range, which enables us to elucidate how a superconducting transition temperature \( T_c \) depends on a doping level of boron \( n_B \) [3,4]. Particularly, Umezawa et al. have performed the systematic study on homoepitaxially grown (111) and (100) films, and revealed that \( T_c \) for the (111) films is by more than two times higher than for the (100) films despite of an equivalent boron concentration for both films [4]. The discovery of superconductivity in a vicinity of metal–insulator transition for the B-doped diamond reminds us of the relevance with the exotic superconductivity in strongly correlated electron materials. Actually, Baskaran has theoretically pointed out the importance of the electron correlation effect in boron impurity band, which may lead to the formation of a resonating valence bond state [5,6]. However, several theoretical studies have stressed the similarity to MgB\(_2\) with a high-\( T_c \) value of 40 K where strong coupling of the holes at the top of the valence band with optical phonons plays an important role [7–9]. Thus, an understanding of the origin of superconductivity discovered in the B-doped diamonds is now underlying hot issue.

2. Experimental

The B-doped diamond films were deposited on substrates by means of MPCVD method described elsewhere [2,4]. As summarized in Table 1, we used four different heteroepitaxially grown diamonds, thick (111) film, and thin and thick (100) films, and thick polycrystalline diamond film, piled on appropriate substrates for each
The boron concentration $n_B$ is derived from secondary ion-mass spectroscopy (SIMS) measurement. $T_c$ of each sample is determined by an onset of superconducting diamagnetism under zero-field cooling as shown in Fig. 1, which coincides with an offset of zero resistance. In particular, it is noteworthy that $T_c = 5$ K for the $(111)$ film becomes higher than $T_c = 3.4$ K for the $(100)$ thin film, although $n_B$ for the former is smaller than for the latter. NMR spectra were obtained by fast Fourier transform (FFT) technique using a conventional phase-coherent-type NMR spectrometer. The Knight shift of $^{11}$B-NMR was determined by the relative shift from the resonance frequency of $\text{B(OH)}_3$ ($K[\text{B(OH)}_3] \approx 20$ ppm). NMR measurements were performed at a constant magnetic field $H = 2.554$ T, which is sufficiently lower than an upper critical field $H_c(0)$.

3. Results and discussions

Fig. 2 shows $^{11}$B-NMR spectra at 4.2 K for the $(111)$- and $(100)$-thin films, the $(100)$-thick and the polycrystalline films. For all of the samples, two spectra overlap with a narrow peak around $\Delta f = 0$ with a linewidth of 5 kHz and broad ones in the range $\Delta f = -40$ and 20 kHz. For the former, the Knight shift is approximately $-10$ ppm, and for the latter, their shifts are distributed over a wide range between $-1200$ and $+600$ ppm, both of which are independent of temperature from $T_c$ up to 200 K. The narrow spectrum originates from the most symmetric boron site, i.e. the substitutional position for the carbon site, the linewidth of which should be narrow due to the uniaxial symmetry along each [1 1 1] direction at the carbon site in the diamond structure. We denote it as B(1) site hereafter. However, the broader spectrum should arise from the borons in lower local symmetry, such as boron + hydrogen (B + H) complex site, the interstitial boron sites, B–B paired occupation sites, boron sites surrounded by lattice defects, and so on. We denote it as B(2) site. Among those possible boron sites, we consider that the boron

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substituted as B + H complex is more dominant than others taking account of the MPCVD process using the mixed gas of CH₄, (CH₃)₃B and H₂ [10], suggested by result of ab initio calculation [11]. In this case, the presence of positively charged hydrogen makes the spectrum broader in association with the second order perturbation of nuclear quadrupolar interaction. Actually as shown in Fig. 3, the observed spectrum is well reproduced by the composition of the two different spectra from B(1) site and B(2) site dominated by B + H complex with reasonable parameters [12]. Thus, we identify the narrow and broad NMR spectra as arising from the substitutional boron site as single occupation (B(1) site) and as dominant B + H complex (B(2) site), respectively.

The comparison of NMR spectra for the (111)- and (100)-thin films gives some hints to understand the difference of $T_c$ between the growth facets [4], since $T_c = 5$ K for the (111) film becomes higher than $T_c = 3.4$ K for the (100)-thin film, although $n_{B(1)}$ for the former is smaller than for the latter (see Table 1). As indicated in Figs. 2 (a) and (b), it is remarkable that the intensity of the B(1) site is predominantly observed for the (111) film, whereas not for the (100)-thin film. Since the NMR intensity is proportional to the number of boron nucleus, we can estimate a fraction ($f_{B(1)}$) of B(1) site against nominal boron density, by means of evaluating a fraction of the narrow spectrum against an intensity integrated over a whole spectrum. The estimated values are about 49% for (111) film and 12% for (100)-thin film. Therefore, a reason why the $T_c$ for the (111) films is higher than for the (100)-thin films is that the doped borons in the former are predominantly substituted as B(1) site giving effective carriers for diamond as acceptor, whereas the B(2) site doped mainly as B + H complex does not contribute to carrier density due to that B + H complex is in the neutral charged state. With respect to the polycrystalline and the (100)-thick films, both of the narrow and broad spectra are observed with a comparable spectral intensity, as shown in Figs. 2(c) and (d). $f_{B(1)}$'s are estimated to be ~33% and ~44% for the polycrystalline and the (100)-thick films, as summarized in Table 1. In fact, the scanning electron microscopy (SEM) images for these samples revealed that the surfaces are not flat any longer due to the presence of the f_{111} facet as indicated in Fig. 4. As a result, for (100)-thick films more than 50 μm, it was evident that the (111) facet is preferentially grown with the substitution as B(1) site. On the other hand, for (100)-thin films less than 3 μm, borons tend to occupy at B(2) site mainly as B + H complex which does not contribute to giving carriers and then $T_c$ becomes relatively lower than others.

The boron-concentration dependence of $T_c$ is quite important to unravel an origin for the onset of superconductivity in the boron-doped diamond. We propose that $T_c$ should be plotted as the function of the boron concentration at B(1) site ($n_{B(1)}$) that introduces the carriers as acceptor effectively, instead of a nominal concentration.

Fig. 3. Calculated $^{11}$B-NMR spectrum (red curve) for the (111) film. The spectra shaded by blue and green denote the spectra arising from B(1) and B(2) sites, respectively.

Fig. 4. SEM images of (a) the (100)-thick film and (b) the polycrystalline film used in this work. The surfaces of both the films are dominated by the {111} growth facet.
4. Summary

In conclusion, the present $^{11}$B-NMR study on the boron-doped diamond revealed that borons are doped into the substitutional B(1) site as single occupation and as other low symmetric B(2) site as dominant B + H complex. This result has enabled us to extract the scaling behavior between $T_c$ and the boron concentration $n_B(1)$ at B(1) site. A clear evidence was presented that the charge carriers introduced into the intrinsic diamond bands are responsible for the superconductivity. These provides experimental support for the theoretical studies which suggest that the superconductivity realized in the boron-doped diamond is mediated by the strong electron–phonon interaction brought about the phonon vibration with the high Debye temperature ($\sim$1860 K) characteristic for the diamond structure. A route to make $T_c$ higher in the boron-doped diamond is to dissociate the hydrogens at B(2) site by annealing, and to find how it can be possible to make the boron concentration at B(1) site increase, keeping the diamond structure. This may also help developing diamond-based devices that make use of the unique properties of diamond.

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