Dopant-site effect in superconducting diamond (111) studied by atomic stereophotography

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We studied the cause of high $T_C$ of superconducting boron-doped diamond (111) when compared with that of (001) even at the same boron concentration. The atomic stereograph revealed that a disproportionate boron concentration is located at one of the two sites in (111). The distinction of the dopant site exists only in (111) surface and does not exist in (001) surface. Furthermore, there is a theoretical prediction of high density of state at Fermi level in ordered dopant diamonds. Therefore, this configuration should be the origin of the higher $T_C$ of (111) as compared with that of (001). © 2007 American Institute of Physics. [DOI: 10.1063/1.2824844]

Boron-doped diamond (B-diamond) has recently attracted much attention due to the discovery of its superconductive behavior. Because diamond has a high Debye temperature, it is expected to be a high-$T_C$ material. At present, the origin of its superconductivity has not been elucidated; hence there are several approaches to solve it. One unsolved issue is that of the contribution of the boron electrons in superconducting B-diamond. Yokoya et al. used photoelectron spectroscopy to find that the energy band of superconducting B-diamond has no impurity band and that the valence band top shifts across the Fermi energy ($E_F$) when the boron concentration increases. On the other hand, Bustarret et al. used calculations to show that there is an impurity state ($T_C$) increases with the density of state (DOS) near $E_F$. Saito et al. calculated that the density of B–B pair is inversely proportional to the DOS near $E_F$, which means that the impurity state does not contribute to the superconductivity of B-diamond. The present study is mainly concerned with the characteristics of dopant boron and its relation to $T_C$ in elucidating the electronic contribution of boron in the problem of high $T_C$ of (111). Mukuda et al. discussed various chemical states of boron in the atom pairs of B–C, B–B, and B–H. They suggested that B–H cancels the hole doping effect and that the percentage of B–H in (111) is lower than that of (001). Takano et al. suggested that the anisotropic lattice stretching in (111) is the primary origin of the superconductivity. However, until now, there has been no structure analysis of B-diamond which compares the boron dopant positions of (111) and (001).

Although it is known that the dopant position is substitutional in lightly doped semiconducting diamonds, there are interstitial dopants in heavily doped silicon and in germanium at concentrations up to about $1 \times 10^{19}$ cm$^{-3}$. In this study, the boron concentration of one sample determined by the peak ratio of carbon 1s (C1s) and boron 1s (B1s) in X-ray photoelectron spectroscopy spectra was about $5 \times 10^{19}$ cm$^{-3}$. When compared to the silicon and the germanium cases, the dopant site may be an interstitial site. Interstitial and substitutional positions have been predicted by calculation. The preferred method of local structure analysis is a direct measurement, but there have been no direct analyses on local dopant positions or atomic images around boron in superconducting B-diamond. We measured the photoelectron angular distribution (PEAD) of the superconducting B-diamond (111) using circularly polarized light in order to take atomic stereographs to directly reveal the local structure around dopant atoms. The samples used here are homoepitaxial B-diamond (111) surfaces grown by way of microwave chemical vapor deposition method. The $T_C$ measured for one of the samples was 4.2 K. PEAD from the sample is measured by a display-type spherical mirror analyzer at SPring-8 BL25SU. Photoelectrons from a core level of an atom at a kinetic energy higher than several hundred eV create forward focusing peaks (FFPs) in the directions of the neighboring atoms. This phenomenon can be used to analyze the directions at which nearby atoms will be found. Moreover, the PEADs for clockwise (cw) and counterclockwise (ccw) light can be used as a stereograph of atomic arrangement, which enables us to capture a direct image of the three dimensional arrangement of nearby atoms. PEAD patterns of C1s and B1s photoelectrons were measured at several kinetic energies $E_{\text{kin}}$ from 500 to 900 eV. Figures 1(a) and 1(b) are examples of a pair of PEAD patterns of C1s and B1s. These patterns are projected images of the three dimensional atomic arrangement around the emitter atoms. Nine peaks marked with red, yellow, green, and blue circles are the FFPs from the same-colored emitter-scatterer pairs. Each colored peak is named “Peak1,” “Peak2,” “Peak3,” and “Peak4,” respectively.

The atom marked by A sitting at (0, 0, 0) in Fig. 1(c) and the atom marked by B at (1/4, 1/4, 1/4) in Fig. 1(d) are not equivalent emitters in diamond unit cell composing two fcc sublattices. The atomic arrangements surrounding A-site and B-site are different, and both PEAD’s from A-site and B-site...
are included in the patterns of Figs. 1(a) and 1(b). Each peak in the PEAD pattern is denoted as “Scatterer-Scatterer pair” from the corresponding emitter-scatterer pair in Figs. 1(c) and 1(d). Peak1 \((\theta=0\,^\circ,\, \phi\) is an angle from the surface normal direction) is assigned to the atom \(B\) seen from the \(A\) site atom, \(B_A\) [the red atom in Fig. 1(e)], and also the atom \(A^*\) seen from the \(B\) site atom, \(A_B^*\) [the red atom in Fig. 1(d)]. The Peak2s \((\theta=35.3\,^\circ)\) are overlapped peaks of \(C_A\) and \(D_B\) in \{011\} directions. The Peak3s \((\theta=19.5\,^\circ)\) correspond to \(E_A\) and \(F_B\) in \{110\} directions. The Peak4s \((\theta=29.5\,^\circ)\) correspond to \(E_B\) in \{113\} directions.

Figures 1(a) and 1(b) are stereophotographs, and the atomic arrangements around the carbon and boron atoms can be captured separately by photoelectron spectroscopy. \(^{20,21}\)

From the equation
\[
R = \frac{m^*}{k\Delta \sin^2 \theta_p}
\]
and the peak shifts \(\Delta\) in Fig. 1(a), the atomic arrangement around the emitter was estimated, as shown in Fig. 2. Here \(R\) is the distance between the emitter and the scatterer, \(m^*\) is the effective magnetic quantum number of the photoelectron, \(k\) is its wave number, and \(\theta_p\) is the angle between the photon incident direction and the emitter-scatterer direction. When the position vector of the scatterer viewed from the emitter is described as \((R, \theta, \phi)\), the peak position observed by using circularly polarized light appears at \((\theta, \phi, \theta \pm \Delta)\). The ratios of the experimental and the actual structural data are \(R_{\text{exp}} / R_{\text{act}} = 1.08 \pm 0.004\) in distance \(R\), \(\theta_{\text{exp}} / \theta_{\text{act}} = 0.97 \pm 0.02\) in angle \(\theta\), and \(\phi_{\text{exp}} / \phi_{\text{act}} = 0.98 \pm 0.02\) in angle \(\phi\). From the similarity between the PEAD patterns from carbon and from boron, as shown in Figs. 1(a) and 1(b), and from the fact that the surrounding structure displays the elements of a diamond structure, as shown in Fig. 2, we can conclude that the boron dopant site is substitutional despite the heavy dopant concentration. This supports the prediction of the substitutional site. \(^{15-17}\) We could not detect any FFP from the interstitial atom. \(^{14}\) This conclusion of “only at the substitutional site” may look contradictory to the NMR result by Mukuda et al., which suggested that there are several species of boron. We suggest that most species of boron are “different species at the substitutional site.” We do not think this difference comes from the fact that the present method is more sensitive to surface than NMR. Although the probing depth is limited to several nanometers, the detected structure is similar to the bulk because the sample is homoepitaxially grown layer by layer.

To reveal the origin of the difference of \(T_C\) between (111) and (001) B-diamond, we examined the difference between two atomic sites, \(A\)-site and \(B\)-site. These sites have equivalent energy in the bulk, but the total energies of \(A\)-site and \(B\)-site are different during the growth process of (111) since the number of dangling bonds and configurations is different. We noticed that the relative intensities of the peaks from boron in Fig. 1(b) are different from those of carbon in Fig. 1(a). This difference is considered to be caused by the difference in the dopant occupation ratio between \(A\)-site and \(B\)-site, which is analyzed below.

We analyzed the relationships of each site to the FFPs. The intensity of the FFP in direction \(j, j\) is considered to be the sum of the FFPs \((F_A + F_B)\), from the two emitters \(A\) and \(B\) in the same scatterer direction \(j\). Each FFP intensity is considered to be inversely proportional to the square of the distance \(R\) neglecting multiple scattering or the photoelectron diffraction effect. The contribution of \(B\)-site to peak intensity \(x_B\) is defined as
\[
x_B = \frac{F_B}{F_A + F_B}.
\]
The horizontal axis of Fig. 3 is \(x_B\) of each peak. The vertical axis shows the intensity of each peak in B1s image divided by that in B1s image, where the site occupancy ratio \(r_{AB}\) \(= A\)-site/\(B\)-site = 1. \(r_{AB}\) of boron can be calculated by the ratio of the intercept values at \(x_B = 0\) and \(x_B = 1\) for the line...
fitted by using the least-squares method, which are 1:0.6 in sample I, and 1:0.8 in sample II. In the case of the approximately 3% boron doped diamond used in this study, the B-site boron concentration ratio is roughly two-thirds of that of the A-site. This difference of the boron occupation at A-site and B-site suggests that there is a difference in the energy barriers ($\Delta E$) during growth in [111] direction. By the equation, 

$$r_{A:B} = \exp(\Delta E / k_B T)$$

with the Boltzmann constant $k_B$, $\Delta E$ was estimated to be 80 meV at the substrate temperature $T$ of 1200 K during growth assuming the preexponent factors are the same. In other words, the energy height at the top of the reaction path to A-site is 80 meV lower than that of the B-site. This unbalanced site occupation between A-site and B-site can be explained because the A-site boron saturates the dangling bond in the diamond (111) surface during growth whereas B-site boron cannot saturate.

It was revealed in this paper that boron in a superconducting diamond is doped at the substitutional site and located in greater at the A-site than the B-site. This preferential occupation of one kind of dopant site increases the order of the boron site. Recently, Shirakawa et al.,[5] Fukuyama,[6] and Ohta et al.[11] calculated the dependence of $T_C$ on the disorderly nature of boron on the superconducting B-diamond. According to their results, boron ion disorder induces the broadening of the density of states at Fermi level, as well as the very short lifetime and mean free path due to the large imaginary part of the self-energy. Because the increased order of the dopant site has been suggested in this study, and because the distinction between A-site and B-site is characteristic only in (111) surface [they are equivalent in (001) surface], we can conclude that this increased order is the origin of the higher $T_C$ in (111) than (001).

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6. H. Fukuyama (private communication).