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Three-dimensional atomic arrangement around active/inactive dopant sites in boron-doped diamond

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Boron-doped diamond has received significant attention as an advanced material for power devices owing to its high breakdown characteristics. To control the characteristics of diamond related to band conduction, it is essential to determine the atomic structure around dopants and to develop a method of controlling the atomic arrangement around dopants. We measured the photoelectron diffraction of a boron-doped diamond using a display-type ellipsoidal mesh analyzer to examine the dopant sites in heavily boron-doped diamond. The B 1s photoelectron spectrum shows two peaks for different chemical bonding sites. These two dopant sites were identified as the substitutional and interstitial sites in diamond.

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Boron-doped diamond has attracted considerable attention not only as a blue gem diamond but also as a more advanced material for power devices owing to its high breakdown voltage and high carrier mobility in high-temperature environments.1) The latest achievements in the development of diamond power devices are remarkable, for example, normally off performance at room temperature,2) fast switching capability at 250 °C,3) and stability above 400 °C.4)

When impurity atoms are able to supply electrons or holes, they act as dopant donors or acceptors in electronic materials. It is usually considered that impurity (donor/acceptor) atoms at the substitutional site supply carriers (electrons/holes) to the (conduction/valence) band. Boron is an effective acceptor with a ground state level of 0.37 eV above the valence band edge of diamond.5) High-concentration doping of impurities is necessary to achieve a high conductance. The carrier transport model of lightly boron-doped diamond, which is used as a semiconducting material, is described by band conduction. However, this band conductance saturates at a boron concentration of approximately 1018–1019 cm−3 because the increase in scattering of carriers by impurity atoms prevents an increase in mobility.

Recently, heavily boron-doped diamond has gathered attention. In a previous study,6) heavily boron-doped diamond with a boron concentration higher than 1 × 1020/cm3 was used as a conductive layer and achieved much higher conductance than the band conductance limit. The boron dopants in this sample, however, emitted only a small quantity of carriers.6,7) The high electrical conductivity was attributed not to band conduction but to hopping conduction.8,9) To develop high-concentration doping of impurities in diamond, a DIANA was used to take stereo photographs23) around the boron atom. In this study, we used a newly developed display-type ellipsoidal mirror analyzer (DELMA)24) that can detect a two-dimensional angular distribution of photoelectrons within ±50° with higher energy resolution than a DIANA.15

Recently, first-principles calculations suggested pairs of boron interstitials.10) If boron is located at these interstitial sites, it is not thought to act as an acceptor in band conduction. Therefore, the dopant sites in heavily boron-doped diamond are an important topic not only for fundamental research but also for device applications to develop a method of resistivity control for p-type conductive diamond. However, it is difficult to measure the atomic structure around the dopant because the X-ray diffraction of aperiodic structures such as dopants in the crystal cannot be measured.

X-ray photoelectron diffraction (XPD) has been a powerful tool for visualizing local atomic structures around a photoelectron emitter atom.11,12) The dopant atom can be selected as the photoelectron emitter by choosing the kinetic energy of the core-level photoelectrons from the dopant. An XPD pattern consists of several strong forward-focusing peaks (FFPs) and diffraction ring patterns created by interference between the direct photoelectron wave and the waves scattered by surrounding atoms. A scatterer atom located far from the emitter atom forms weak FFP and diffraction ring patterns. The FFP indicates the direction of the scatterer atom viewed from the emitter atom. The radius of the ring patterns around the FFP indicates the interatomic distance between the emitter and scatterer atoms. Thus, the XPD pattern provides a three-dimensional atomic image around a photoelectron emitter atom without requiring any initial model or phase information. To date, much effort has been made to study the structure at atomic resolution using XPD patterns13,14) and a display-type spherical mirror analyzer (DIANA).15–21) In a previous study22) of boron as a dopant in superconducting diamond, a DIANA was used to take stereo photographs23) around the boron atom. In this study, we used a newly developed display-type ellipsoidal mesh analyzer (DELMA)24–26) that can detect a two-dimensional angular distribution of photoelectrons within ±50° with higher energy resolution than a DIANA.

In this paper, we identified the dopant site of boron in heavily boron-doped diamond using XPD patterns by analyzing the emission angle dependence of the B 1s core-level-shifted peaks in the X-ray photoelectron spectra.

Epitaxial boron-doped diamond was grown on a type-Ib single-crystal diamond (001) plate (Sumitomo Electric
Fig. 1. (a) Observed XPD pattern of C 1s from heavily boron-doped diamond (001) at \( E_{\text{kin}} = 600 \) eV. This pattern was drawn using the orthographic projection method. (b) Simulated XPD pattern of diamond (001) at \( E_{\text{kin}} = 600 \) eV. The projection method is the same as in (a). (c) Structure of diamond unit cell illustrating the angles and distances between the emitter and scatterers. Red atom represents a photoelectron emitter. Atoms with other colors are photoelectron scatterers, which contribute to the FFPs in the PIAD pattern. (d) Arrangement of FFPs viewed from the (001) direction. Filled and open circles represent the FFPs of photoelectrons from emitter 1 at \((0,0,0)\) and emitter 2 at \((a/4,a/4,a/4)\), respectively, where \(a\) is the lattice constant, 3.567 Å. Inset shows the atomic cluster of diamond (001) used for the pattern calculation. Red sphere is the emitter, and other spheres are scatterers.

In investigating the atomic arrangement of the B-doped system, we start with the peak assignment of the FFPs seen in the photoelectron intensity angular distribution (PIAD) pattern of the C 1s core level. The observed C 1s PIAD pattern is shown in Fig. 1(a), and the multiple-scattering simulation pattern is shown in Fig. 1(b). The kinetic energy \( E_{\text{kin}} \) of the photoelectrons was set to 600 eV. The C 1s PIAD in Fig. 1(a) shows a clear four-fold symmetric pattern and emits good agreement with the calculation, suggesting that the heavily boron-doped diamond grew homoeptaxially on the diamond (001) substrate. This result is in good agreement with previous reports, which demonstrated homoeptaxial growth of boron-doped diamond (001). Because the lattice constant increases in proportion to the boron concentration in boron-doped diamond, the lattice is strained when the growth direction is (001). Thus, the average interatomic distances increase, although the crystal symmetry is unchanged. Figure 1(c) shows the atomic structure of diamond to illustrate the observed XPD pattern. Figure 1(d) is a projection image of the atomic distribution around the emitter atom. Because the diamond has two inequivalent sites in the unit cell, the observed XPD pattern is a superimposed image from two types of emitter atoms, called emitters 1 and 2 in this paper. The directions of each scatterer around emitter 1 are indicated by spheres of the corresponding color in Fig. 1(d).

Fig. 2. (a) Emission directions of photoelectrons. The colors of the atoms are the same as those in (c) and (d). (b) B 1s photoelectron spectra. Two peaks are observed in all the spectra: one peak at high binding energy, labeled peak A, and another peak at low binding energy, labeled peak B. (c) Simulated XPD pattern of boron at the interstitial site, which is the center of the unit cell. The green, blue, and pink open circles indicate the (001), (101), and (111) FFPs, respectively. (d) Simulated XPD pattern of boron at the substitutional site. Open circles have the same meaning as in (c).
of boron sites. Furthermore, a comparison of the core-level spectra for different emission directions clearly shows that the spectral weight in the low-binding-energy peak, peak B, decreases significantly in the [001] direction when we normalize the spectra at peak A. The intensity ratios of peaks A and B in the three directions, $B/A_{[001]}$, $B/A_{[101]}$, and $B/A_{[111]}$, are 0.7, 1.0, and 1.1, respectively.

To discuss the origin of the two observed peaks, we calculated the XPD patterns using two models (i.e., the interstitial and substitutional doping models). We note that, because the atomic radius of boron (0.82 Å) is larger than that of carbon (0.77 Å), the interstitial sites of boron in diamond are limited, and only tetrahedral interstitial doping seems to be possible, as shown by the X in Fig. 2(a). The XPD pattern simulated using the tetrahedral interstitial doping model is shown in Fig. 2(c). In this case, an FFP along the [001] direction, indicated by a green circle, appeared because there is a second-nearest-neighbor atom just above the interstitial boron atom. This FFP does not appear when boron is doped at the substitutional site of diamond, as shown in Fig. 2(d). We therefore can firmly conclude that peak A is caused by boron at an interstitial dopant site, and peak B is from a substitutional boron dopant site. This is consistent with the idea that the binding energy of interstitial boron (with a valence number of 0) should be higher than that of substitutional boron (with a valence number of −1).

This shows that boron at the substitutional site is an active dopant acting as an acceptor, because it is negatively charged and produces holes. On the other hand, the interstitial boron is an inactive impurity that causes band conductance without producing carriers, but it should be responsible for the hopping conductance when the concentration becomes high enough for hopping conductance to occur.

Hence, we could elucidate experimentally that there are two types of dopant boron at a concentration of $2 \times 10^{19} \text{ cm}^{-3}$: one is located at a substitutional site with a lower binding energy and produces carriers, and the other is located at a tetrahedral interstitial site and does not produce conductance for band conductance.

In this paper, the local atomic structure of the dopant sites in high-quality homoepitaxial heavily boron-doped diamond was investigated by XPD measurement. The emission angle dependence of the B 1s spectra was measured and analyzed by a multiple-scattering simulation. In particular, we found two peak structures in the B 1s XPS spectra originating from two types of boron atomic sites, which exhibit a strong photoelectron emission angle dependence. Using a multiple-scattering simulation, we found that these two peaks are caused by interstitial and substitutional dopant boron. The peak at a higher binding energy corresponds to the interstitial boron, and that at a lower binding energy corresponds to the substitutional boron. The binding energies of these peaks suggest that boron at the substitutional site is an active dopant acting as an acceptor because it is negatively charged and produces holes. On the other hand, the interstitial boron is an inactive impurity that causes band conductance without producing carriers, but contributes to hopping conductance when the distance between boron atoms decreases at high concentrations.

Hence, we have obtained a clue to optimizing the growth conditions for the development of ideal heavily boron-doped diamond for use as a high-conductance layer in diamond power devices. To realize the optimization, the B 1s peaks at lower and higher binding energies will be adopted as indicators of how many boron atoms act as acceptors in band conduction and which ones are responsible for hopping conduction. In the future, we will estimate the boron concentration dependence of the B 1s peaks at lower and higher binding energies to confirm this conclusion more strongly.

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