

Multiple phosphorus chemical sites in heavily phosphorus-doped diamond

Hiroyuki Okazaki,^{1,2,a)} Rikiya Yoshida,¹ Takayuki Muro,³ Tetsuya Nakamura,³ Takanori Wakita,^{1,2,4} Yuji Muraoka,^{1,2,4} Masaaki Hirai,^{1,4} Hiromitsu Kato,⁵ Satoshi Yamasaki,⁵ Yoshihiko Takano,⁶ Satoshi Ishii,⁶ Tamio Oguchi,⁷ and Takayoshi Yokoya^{1,2,4}

¹The Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima-naka, Okayama 700-8530, Japan

²Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency, Okayama 700-8530, Japan

³Japan Synchrotron Radiation Research Institute (JASRI)/SPring-8, 1-1-1 Kouto, Sayo, Hyogo 679-5198, Japan

⁴Research Laboratory for Surface Science, Okayama University, 3-1-1 Tsushima-naka, Okayama 700-8530, Japan

⁵Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Center 2, Tsukuba, Ibaraki 305-8568, Japan

⁶National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

⁷Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

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We have performed high-resolution core level photoemission spectroscopy on a heavily phosphorus (P)-doped diamond film in order to elucidate the chemical sites of doped-phosphorus atoms in diamond. P $2p$ core level study shows two bulk components, providing spectroscopic evidence for multiple chemical sites of doped-phosphorus atoms. This indicates that only a part of doped-phosphorus atoms contribute to the formation of carriers. From a comparison with band calculations, possible origins for the chemical sites are discussed. © 2011 American Institute of Physics. [doi:10.1063/1.3554699]

Diamond is a semiconductor with remarkable physical properties such as a wide band gap, very high electric breakdown, and high thermal conductivity. Therefore, the investigation of p- and n-type diamonds is very important for electrical applications. A p-type diamond is obtained by boron (B) doping, and the acceptor level in light doping is located at about 0.37 eV from the valence band maximum.¹ On the other hand, an n-type diamond is obtained with doping of nitrogen or phosphorus (P). Nitrogen gives a deep donor level with an activation energy of 1.7 eV.^{2,3} This means that its application as a device is difficult because of the nearly zero excitation of electrons into the conduction band at room temperature. P gives a shallower donor level of 0.6 eV from the conduction band minimum.^{4,5} This is the reason for the success of making controlled carrier concentration in n-type diamond films by light P-doping.³

One of the possible research directions of P-doped diamond is to obtain metallic samples because of the possible occurrence of superconductivity as in heavily B-doped diamond.^{6,7} Recently, heavily P-doped diamond with P concentration (n_p) as high as $\sim 10^{20}$ cm⁻³ has been obtained by microwave plasma assisted CVD (MPCVD).⁸ While n_p near 10^{20} cm⁻³ is very close to the calculated critical concentration (1.2×10^{20} cm⁻³) of a metal-insulator transition (MIT),⁹ the resistivity shows semiconducting temperature dependence. This implies that carrier compensation plays a crucial role in P-doped diamond.¹⁰ Theoretical studies predict that P-hydrogen (P-H) and P-vacancy (P-V) complexes compensate electrons.^{11,12} However, multiple chemical sites of doped-phosphorus atoms have not been experimentally con-

firmed yet. Note that previous photoemission spectroscopy (PES) from a phosphorus ion irradiated diamond using monochromated Al $K\alpha$ x-ray radiation could not discuss P chemical sites because of a lower signal to noise ratio.¹³

In this study, we have performed high-resolution soft x-ray core-level PES to understand P chemical sites in a heavily P-doped diamond. In order to measure very weak signals, we used a very high intensity soft x-ray from a third-generation synchrotron radiation facility, SPring-8. From high-resolution core level PES, we succeeded to observe multiple P $2p$ core level signals. From the depth dependence of P $2p$ and spectral analysis, we confirmed the existence of at least two bulk chemical sites in this heavily P-doped diamond, indicating that only a part of doped-phosphorus atoms dopes carriers to the diamond. From the comparison between P $2p$ core level spectra and the first-principles density-functional calculations, we found that the observed energy separation between the two sites is similar to the calculated energy separation between substitutional P and P-H complex sites.

A homoepitaxial heavily P-doped (111) diamond film was made by microwave plasma assisted chemical vapor deposition (MPCVD).⁸ The sample, whose thickness is 2 μ m, was homoepitaxially grown on synthetic Ib diamond (111) substrate with dimensions of $2 \times 2 \times 0.5$ mm³. n_p of 1×10^{20} cm⁻³ (0.06 at. %) was determined by secondary ion mass spectroscopy (SIMS). Resistivity measurements showed nonmetallic temperature dependence and a value of ~ 200 Ω cm at room temperature. The sample was hydrogen-terminated in microwave hydrogen plasma at 800 °C for 10 min.¹⁴

^{a)}Electronic mail: yuzan@cc.okayama-u.ac.jp.

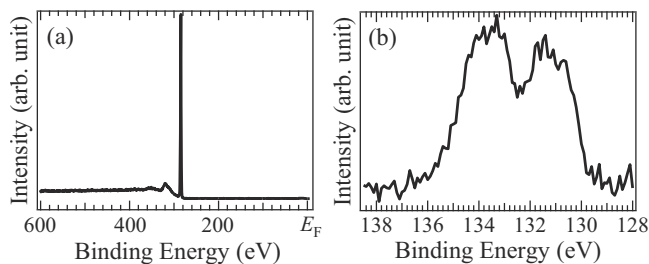


FIG. 1. (a) Photoemission spectrum of heavily P-doped homoepitaxially (111) diamond film for a wide energy range using photon energy of 1100 eV. (b) P $2p$ core level PES spectrum.

PES measurements have been performed at BL25SU, SPring-8, by using a Scienta SES200 electron analyzer. Photon energies of 460, 700, and 1100 eV were used in order to measure the depth dependence. The energy resolution was set to 80, 100, and 160 meV, respectively, depending on the photon energies. The base pressure of the PES chamber was better than 5×10^{-8} Pa. The Fermi level (E_F) of the sample was determined from the Fermi edge of a gold film evaporated onto the sample substrate. To clean the surface, the sample was annealed *in situ* at ~ 800 °C before the measurements. All measurements were done at room temperature to prevent a surface charging effect.

Figure 1(a) shows the PES spectrum of the heavily P-doped diamond film measured using photon energy with 1100 eV for a wide binding energy range. The intense peak around 285 eV is a C $1s$ core level. No oxygen signal around 530 eV indicates the cleanliness of the measured sample surface. In order to study the P $2p$ core levels, we measured the region of P $2p$ with a high signal to noise ratio and succeeded to observe signals from doped-phosphorus atoms of a very small concentration (0.06 at. %), as shown in Fig. 1(b). One can find two peaks at 131 and 134 eV with shoulder structures. Since the spin-orbit splitting of P $2p$ core level is 0.84 eV,¹⁵ the double-peak structure separated by 3 eV suggests that there are at least two P chemical sites in the heavily P-doped diamond.

To further investigate the number and nature (surface or bulk) of the chemical sites, we have measured the depth dependence of P $2p$ core level spectra with three different photon energies 460, 700, and 1100 eV, corresponding to the photoelectron escape depths $\lambda \sim 8, 12,$ and 20 Å, respectively,¹⁶ as shown in Fig. 2. These P $2p$ spectra are normalized by the area of the P $2p$ peaks. For the 1100 eV spectrum (bottom), we observe a broad peak with several structures around 130.6, 131.6, and 133.6 eV. In the 460 eV spectrum (top), the intensities around 131 eV are strongly enhanced. We have performed spectral fittings for these spectra in order to make quantitative estimations for each component, as indicated by green thin curves (A-C). These components at 130.6, 131.6, and 133.3 eV are necessary for describing the depth dependent spectra. From a comparison of the area of those components, the area of A is found to decrease, while those of B and C remain similar or increase as the photon energy increases (namely, bulk sensitive). Therefore, we assigned A to surface dominant components and B and C to bulk dominant components. This result indicates that there are two dominant P chemical sites, B and C, in the heavily P-doped diamond film, whose binding energy positions are separated by 1.7 eV. In heavily B-doped dia-

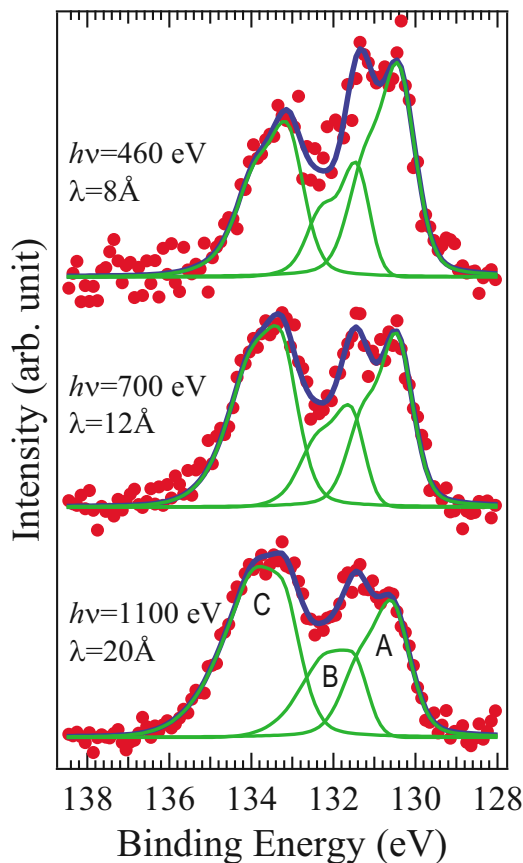


FIG. 2. (Color online) Results of curve fitting for the depth dependence of P $2p$ core level spectra of the heavily P-doped diamond film. Circles are the experimental data, thick lines are the fitting results and thin lines are the functions used for the fittings. Photon energy was set at 460, 700, and 1100 eV, corresponding to the photoelectron escape depth $\lambda \sim 8$ – 20 Å.

mond, multiple chemical sites of doped-boron atoms have been reported from high-resolution core level PES¹⁷ and NMR¹⁸ studies, and its relation to effective carrier concentration has been discussed. On the other hand, the fact that multiple chemical sites are observed both for heavily B- and P-doped diamond suggests that heavy doping induces several chemical sites of doped atoms in diamond other than the substitutional site.

In the more lightly P-doped diamond ($n_P \approx 10^{19}$ cm⁻³), it is reported that doped-phosphorus atoms are almost located at the substitutional site.¹⁹ Thus, the present observation of two P chemical sites for the heavily P-doped diamond suggests that a part of doped-phosphorus atoms in a heavily P-doped diamond are incorporated into other chemical sites different from the substitutional site. In a diamond lattice, the formation energy of the interstitial P site is larger by 22 eV than that of the substitutional P site, suggesting that numbers of the interstitially doped-phosphorus atoms are negligibly small. For CVD diamond films, H atoms and vacancies have been known as the most common grown-in defects, and therefore, possibilities of formations of P-H and P-V complexes have been discussed theoretically.¹¹ Indeed, a SIMS study for a P-doped diamond film synthesized with the same condition as the one for the present film shows that a dominant impurity is hydrogen, whose concentration is almost the same as the P concentration.⁸

To investigate the chemical sites of doped-phosphorus atoms in a heavily P-doped diamond, it is useful to compare the experimental energy positions of core level P $2p$ with the calculated energy positions. The first-principles calculations predict the P $2p$ energy positions of different chemical sites relative to the substitutional site: P-H complexes with C_{2v} (-0.527 eV), C_{3v} (-0.949 eV), and BC (-1.682 eV); P-P pair (-0.591 eV); and P-V complex (-0.169 eV), where C_{2v} , C_{3v} , and BC denote substitutional P and interstitial H at C_{2v} , C_{3v} symmetry, and substitutional P and H at the bond-center (BC) site between the P and C atoms, respectively. These calculations present that the P $2p$ binding energy of the substitutional P site is the highest in the sites. This indicates that component C is probably the peak due to the substitutional site. However, since the energy position of a P-V complex is close to that of a substitutional site, the existence of a P-V complex cannot be totally ruled out. Regarding component B, the experimental energy separation of component B from component C, which equals to -1.7 eV, is very close to the calculated energy separation of the P-H complex at the BC site from the substitutional site. This suggests that component B originates from the P-H pair. This result is consistent with the SIMS study, which shows the existence of many hydrogen atoms in P-doped diamond.⁸ Note that it is not possible to know how much the fraction of bonded impurity such as H and P is, since SIMS measures all H and P impurities in diamond films, including free and bonded H and P. Theoretical studies reported compensation of carriers due to P-H pair formation.¹¹ The existence of multiple P chemical sites other than the substitutional sites may reduce the carrier doping efficiency. In fact, despite the n_p of this sample near the calculated MIT concentration (1.2×10^{20} cm⁻³), the resistivity of this sample is still much higher than that of a heavily B-doped diamond with the B concentration near the MIT. These results imply that metallic and even superconducting properties in heavily P-doped diamond are realized by the increase of the substitutional P site and the decrease of the P-H site in heavily P-doped diamond. Thus, in order to further understand the incorporation mechanism behind this, it is necessary to prepare more P-doped diamond samples and study the incorporation form or chemical sites of P impurity with the growth conditions.

In summary, we have performed high-resolution core level PES of a heavily P-doped (111) diamond film to study P chemical sites. We observed that the P $2p$ core level consists of several peaks indicative of several chemical sites. Spectral analyses show that P $2p$ consists of two bulks and

one surface component, indicating that a part of doped-phosphorus creates carriers in the heavily P-doped diamond. A comparison between observed and calculated P $2p$ core levels suggests that the two bulk sites can be assigned as substitutional and P-H complex sites.

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