

## Determination of 3D local structures of dopant in heavily phosphorus-doped diamond

Diamond is an important material not only for its beauty as a gem, but also for its excellent properties such as high hardness, high heat resistance, and good insulating performance. It is a promising material for realizing innovative devices, such as next-generation power devices and quantum sensors, because diamond becomes a high-performance semiconductor upon impurity doping. For device applications, it is necessary to introduce electron (n-type) or hole (p-type) carriers into diamond by adding other elements to make it conductive. Boron is an effective additive element for p-type diamond, whereas nitrogen has been found to be less effective owing to its high activation energy. Instead of nitrogen, phosphorus is used for obtaining n-type diamond and much effort has been devoted to improving the conducting properties of P-doped diamond [1].

When doped atoms are incorporated into substitution sites, electric conduction can be obtained. However, theoretical studies have predicted that some of the added phosphorus atoms, incorporated into the diamond crystal with an atomic arrangement, inhibit conduction [2]. Experimentally, high-resolution core-level photoemission spectroscopy demonstrated that there are two P chemical sites [3]. However, until now, the local structure of the P dopant has not been determined experimentally owing to the lack of appropriate research methods.

Photoelectron holography (PEH), performed with high-intensity/-resolution soft X-rays at SPring-8 and a high-resolution photoelectron analyzer, has made it possible to study the chemical-site-dependent local structure of impurity-doped semiconductors with low concentrations of impurity atoms. In the core-level photoelectron angular distribution, namely, the photoelectron hologram, there is an interference pattern between two types of photoelectron wave (Fig. 1): in one type, waves come directly from the atom (emitter) and in the other type, waves are

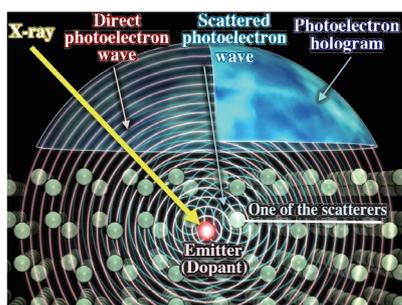


Fig. 1. Schematic illustration of photoelectron holography.

scattered by neighboring atoms (scatterer). Since the photoelectron hologram reflects the local crystal structure around the atom where photoexcitation takes place, a three-dimensional (3D) atomic image can be directly reconstructed from the photoelectron hologram. This is an excellent point of PEH, making it highly superior to conventional methods of local structure study, such as EXAFS. Moreover, PEH enables the detection of the locations of dopant atoms in crystallographically inequivalent sites of elemental samples and the orientation of dopant-related complexes.

A homoepitaxial heavily P-doped (111) diamond film was fabricated by microwave-plasma-assisted chemical vapor deposition (MPCVD). The P concentration was  $1 \times 10^{20} \text{ cm}^{-3}$  (0.06 at.%), which was determined by secondary ion mass spectroscopy. The film surface used for the PEH measurements was cleaned using  $\text{H}_2$  plasma, thereby providing a H-terminated film. To reduce the number of adsorbed molecules on the surface, the sample was annealed *in situ* at  $\sim 500^\circ\text{C}$  under ultrahigh vacuum before the measurements. PEH measurements for C 1s and P 2p were performed at SPring-8 BL25SU using a Scienta DA 30 electron analyzer with a photon energy of 700 eV. The energy resolution was set to approximately 200 meV. The base pressure of the PES chamber was better than  $5 \times 10^{-8} \text{ Pa}$ . The chemical potential of the sample was determined from the Fermi edge of the molybdenum substrate in electrical contact with the sample. All measurements were performed at room temperature to prevent charging.

Figure 2 shows photoelectron holograms for two phosphorous chemical sites (components  $\alpha$  and  $\beta$ ) of heavily P-doped diamond (yellow), together with simulated holograms obtained using theoretical local structure models. For component  $\alpha$ , 3D atomic images reconstructed using the scattering pattern extraction algorithm with  $L_1$ -linear regression [4] are also shown in Fig. 3. The reconstructed atomic images are located at the expected positions of the carbon atoms in the diamond crystal structure (large and small circles). This indicates that P atoms of component  $\alpha$  are located at substitution site of the diamond crystal. Diamond crystal contains two crystallographically inequivalent sites, which we call sites A and B (see Fig. 3(c)). The observed hologram is the sum of two holograms considering sites A and B to be emitters. Expected positions of carbon atoms viewed from sites A and B are denoted with the large and small circles,

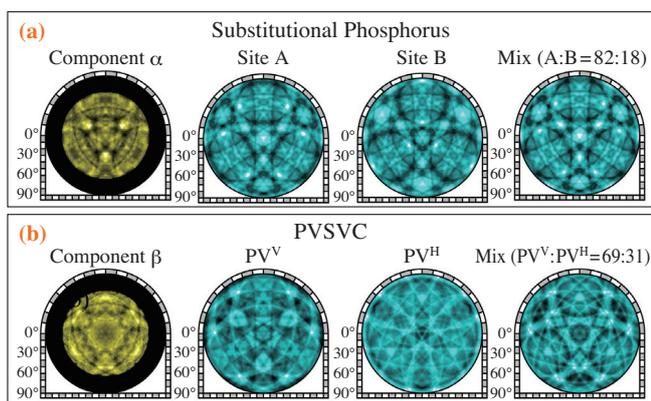


Fig. 2. Experimental (yellow) and simulated (blue) photoelectron holograms for components (a)  $\alpha$  and (b)  $\beta$  of P 2p core level spectra of heavily P-doped diamond. For the simulated holograms of substitutional P, holograms viewed from sites A and B as well as their weighted sum are shown. For the simulated holograms of PVSVC, holograms of different orientations ( $PV^V$  and  $PV^H$ ) and their weighted sum are shown.

respectively. Interestingly, the reconstructed images are observed mainly in the site A position, which is different from that in the C 1s reconstructed image (Fig. 3(b)). This indicates that doped P atoms are preferentially incorporated into site A of the diamond crystal (Fig. 4(a)). The ratio of site occupation can be obtained by reproducing the experimental hologram with the weighted sum of two simulated holograms for sites A and B (Fig. 2(a)). We obtained the ratio of 82:18 for sites A and B occupations. We speculate that this preferential occupation of site A stems from the CVD growth process.

For component  $\beta$  (Fig. 2(b)), we found that the experimental hologram looks very different from that of component  $\alpha$ , indicating that the P atoms in this chemical site are located differently from those in component  $\alpha$ . By considering the proposed local structure models, we found the phosphorus-vacancy (V) splitting vacancy complex (PVSVC) to be the most probable candidate. In PVSVC, a P atom is located in

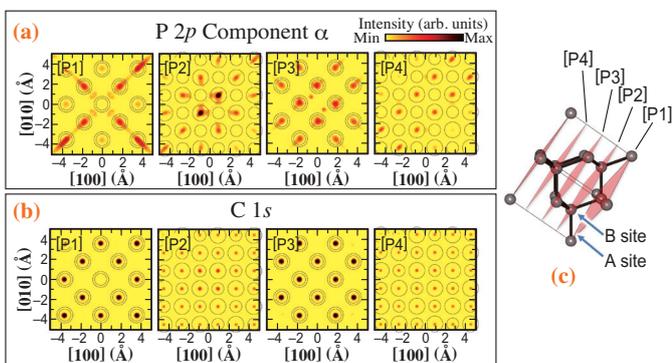


Fig.3. Cross sections of reconstructed atomic images at different z values for (a) component  $\alpha$  of P 2p and (b) C 1s. (c) The diamond crystal structure and the planes of reconstructed atomic images shown in (a) and (b).

the middle of the bond between two adjacent carbon atoms, but the two carbon atoms are removed to form vacant sites (Fig. 4(b)). This assignment is further confirmed from the similarity of the experimental and simulated holograms. To reproduce the experimental hologram, the sum of simulated holograms of  $PV^V$  and  $PV^H (=PV^{H1}+PV^{H2}+PV^{H3})$  (see Fig. 4(b) for geometrical configurations) with the ratio of 69:30 was used. This deviates from the expected value of 1:1, indicating the preferential orientation of the V-P-V direction parallel to [111].

Thus, the high-resolution PEH was used to determine the local structures of the two P chemical sites, with information on the crystal site of the substitutional P and the orientation of the PVSVC. Such information is valuable for understanding the atomistic mechanism of diamond thin-film growth during CVD and can be used to align the orientation of functional complexes.

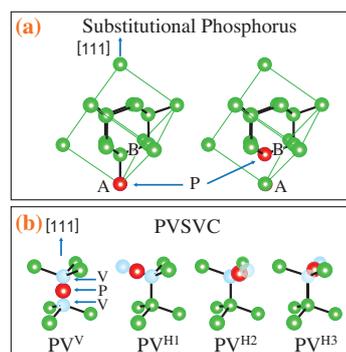


Fig. 4. (a) Crystal sites A and B in the diamond structure. (b) Local structures and orientations of PVSVC.

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