Asymmetric phosphorus incorporation in homoepitaxial P-doped (111) diamond revealed by photoelectron holography

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ABSTRACT: Diamond has two crystallographically inequivalent sites in the unit cell. In doped diamond, dopant occupation in the two sites is expected to be equal. Nevertheless, preferential
dopant occupation during growth under non-equilibrium conditions is of fundamental importance, for example, to enhance the properties of nitrogen-vacancy (N-V) centres; therefore, this is a promising candidate for a qubit. However, the lack of suitable experimental techniques has made it difficult to study the crystal- and chemical-site-resolved local structures of dopants. Here, we confirm the identity of two chemical sites with asymmetric dopant incorporation in the diamond structure, via the photoelectron holography (PEH) of heavily phosphorus (P)-doped diamond prepared by chemical vapor deposition. One is substitutionally incorporated P with preferential site occupations and the other can be attributed to a PV split vacancy complex with preferential orientation. The present study shows that PEH is a valuable technique to study the local structures around dopants, with a resolution of crystallographically inequivalent but energetically equivalent sites/orientations. Such information provides strategies to improve the properties of dopant related-complexes in which alignment is crucial for sensing of magnetic field or quantum spin register using N-V centres in diamond.

**KEYWORDS:** Dopant local structure, asymmetric dopant incorporation, substitutional doping, dopant-vacancy complex, diamond, photoelectron holography

The incorporation of dopant atoms, vacancies, and dopant-related complexes (known as point defects) into semiconductors is a method to not only control conducting properties but also induce new functionalities, like optical properties, derived from dopant-vacancy complexes\(^1\). Diamond, due to its extraordinary properties that can be used for several applications, synthesis of high-quality single crystal diamond, by controlling the crystal orientation, synthesis process, and doping, has been a popular and important research subject in the field of the materials
Recently, the demand for understanding point defects, especially in diamond, is increasing, as nitrogen-vacancy (N-V) centres can be used for quantum technology, including quantum metrology and information processing and communications\textsuperscript{10-12}. Interestingly, control of the alignment of N-V centres for enhancing the properties has been reported in doped diamond synthesized by chemical vapour deposition (CVD)\textsuperscript{13-15}. In previous studies\textsuperscript{16}, the mechanism of the alignment has been explained theoretically based on the preferential incorporation of a nitrogen atom at one of the two crystallographically inequivalent sites\textsuperscript{17} in diamond during CVD.

However, experimental confirmation of the crystal site occupation of substitutionally incorporated dopants in the diamond structure is difficult because the two crystal sites are energetically equivalent. Optical spectroscopy and electron paramagnetic resonance spectroscopy are conventional techniques to study the characteristics of point defects in diamond\textsuperscript{18}, but are applicable for deducing local structures. Rutherford backscattering spectrometry using channelling techniques\textsuperscript{19} can provide the location of interstitial dopants, but not that of substitutional dopants. Extended X-ray absorption fine structure (EXAFS) analysis provides the bond length to and coordination number of neighbouring atoms around selected elements, but without information on the direction of neighbouring atoms\textsuperscript{20}. Scanning transmission electron microscopy can be used to detect the site in principle\textsuperscript{21}, because it can provide the three-dimensional (3D) local structure. However, it cannot be used for determining light elements or vacancies.

Photoelectron holography (PEH) is promising for determining the 3D local structure around a dopant atom\textsuperscript{22}, with chemical-site and crystal-site selectivity. In the core-level photoelectron angular distribution, i.e. the photoelectron hologram, an interference pattern between two types of photoelectron waves is involved, one of which comes directly from the atom (emitter) and the
other is scattered by neighbouring atoms (scatterer) (Fig. 1). Since the photoelectron hologram reflects the local crystal structure around the atom where photo-excitation takes place, a 3D atomic image can be directly reconstructed from the photoelectron hologram using a developed reconstruction algorithm\textsuperscript{23}. Recently, PEH using third-generation synchrotron light has facilitated the observation of the local structure of dopant atoms in impurity-doped semiconductors\textsuperscript{24,25}. For the preferential incorporation of dopant atoms, there is a pioneering study on the local structure of boron-doped sites in heavily B-doped diamond\textsuperscript{26}; however, it was a chemical-site-integrated study and the reconstruction of atomic images was not performed.

In this study, we performed the PEH of heavily phosphorous-doped diamond synthesized via microwave plasma-assisted chemical vapor deposition (MPCVD) to experimentally determine the local structure of two chemical sites.

The image on the left-hand side in Fig. 2(a) shows the measured C 1s photoelectron hologram of heavily P-doped homoepitaxial (111) diamond. There are intense regions around particular parts that correspond to the [111] and [110] directions, and also several dark and bright lines. The higher-intensity spots are forward focusing peaks (FFP), which indicate the directions of the scatterer with respect to the emitter, because the scatterer atoms play the role of a convex lens. The dark lines are Kikuchi lines that reflect long-range structural coherence. In the diamond structure (Fig. 2(f) (left)), there are two crystallographically inequivalent sites at (0,0,0) and (1/4,1/4,1/4), termed A and B sites, respectively. While a carbon atom in the B site has three bonds directed diagonally upward, a carbon atom in the A site has three bonds directed diagonally downward. The photoelectron hologram is the sum of the two holograms viewed from the A and B sites. The cross sections of the reconstructed atomic images cut by planes perpendicular to [001] at $z = 0, 0.89, 1.78$, and $2.67$ Å for the A site, which also correspond to the
planes for the B site (Fig. 2(f) (right)), are shown as [P1], [P2], [P3], and [P4], respectively, in Fig 2(b). The reconstructed images are located at the expected positions of carbon atoms (larger (smaller) circles viewed from A (B) site) in the diamond lattice. The calculated photoelectron hologram (right side of Fig. 2(a)) also reproduces the experiment reasonably well.

The measured P 2p core-level spectra are shown in Fig. 2(g). The spectra are reproduced with two components having a spin orbit partner (value of splitting is 0.84 eV). Here, higher and lower binding-energy components are labelled as $\alpha$ and $\beta$, respectively. We found that the two components exhibit similar angular dependence with a small variation, indicating that the two components may have a common depth profile. We also found good correspondence of the binding energies with those of two bulk components in a previous work.$^{27}$ The spectral ratio $\alpha$ to $\beta$ is 30:70, which is different from that obtained in a previous study.$^{27}$ Since we found that the ratio depends on surface treatments before photoemission measurements (surface treated with hydrogen plasma (present study) or as-deposited surface (previous study)), we attribute the different ratio to the difference in surface condition. Subsequently, all the angular-dependent P 2p spectra were fitted by the two components to obtain the holograms. The images on the left-hand side in Figs. 2 (c) and (d) show the photoelectron holograms of the $\alpha$ and $\beta$ components, respectively. The patterns are distinct, indicating that the local crystal structures around the P atoms of the two chemical sites are different.

The hologram pattern of component $\alpha$ rather resembles that of C 1s (Fig. 2(a)), suggesting that the P atoms of the chemical site are substitutionally incorporated into the diamond lattice. Indeed, in Fig. 2(e), the reconstructed 3D atomic images are observed at the locations expected for the carbon atoms in the diamond crystal. The substitutional incorporation of P atoms for P-doped diamond ($n_p \sim 4\times10^{19}$ cm$^{-3}$) was previously reported using Rutherford backscattering.$^{28}$
Interestingly, we found that the reconstructed atomic images are observed only at expected atomic positions viewed from the A site (larger circles of [P2] and [P4] of Fig. 2(e)). This indicates that the P atoms are preferentially incorporated into the A site of the diamond lattice, i.e., asymmetric dopant incorporation has occurred. We fitted the experimental hologram using two simulated holograms of the A and B sites, and found the occupancy to be 82% of the A site and 18% of the B site (Supporting Information). The simulated hologram obtained using the occupation ratio is shown in the right-hand-side image in Fig. 2(c); it reproduces the experimental hologram well. We will discuss the preferential incorporation later.

Regarding component $\beta$, we found that a simulated hologram considering contributions of $\text{PV}^V$ oriented to [111] and $\text{PV}^\text{H}$ oriented to other directions with occupancies of 69% and 31%, respectively, reproduces the experimental hologram (right side of Fig. 2(d)). This suggests that the PV split vacancy complex (PVSVVC), where a P atom occupies the centre of two vacancies (Fig. 3), is the most probable candidate. Notably, the occupancy deviates from the geometrically expected value ($\text{PV}^V:\text{PV}^\text{H}=50:50$), providing evidence for the preferential orientation of the P-V complex. Although a recent EXAFS study reported the interstitial site occupation of P atoms$^{29}$, the simulated hologram therein did not explain the main features of the experimental hologram (Supporting Information).

The possibility of the PVSVVC in P-doped diamond has been discussed theoretically$^{30}$. Since the PVSVVC forms empty in-gap states, the valence state should be $[\text{PV}]^1$ with spin $S = 0$, and no internal optical transitions are expected. This has made it difficult to reveal the identity from spectroscopic studies. The present PEH observed the ‘hidden’ P-complex in P-doped diamond by utilizing the characteristic ability of the method. Since the PVSVVC compensates the electron
carrier induced by substitutional P and thus reduces the doping efficiency, reducing the PVSVC is an appropriate strategy for improving the doping efficiency.

The present PEH study reveals asymmetric P dopant incorporation, i.e. the preferential incorporation of P atoms into the substitutional A site and the preferential orientation ($PV^v$) of the $PV_2$ complex. Since the two crystallographically inequivalent sites are energetically equivalent in the crystal, the asymmetry may stem from the CVD growth of (111) diamond. However, dopant incorporation in the step-flow mode of film growth\textsuperscript{31} is a complicated process, and theoretical studies on P doped diamond are limited. Here, we discuss the information that can be obtained from the present result, as well as a possible scenario for the preferential orientation of the PVSVC. For component $\alpha$, the difference in occupancy implies that the incorporation of P atoms at the A and B sites encounters different energy barriers during crystal growth. For component $\beta$, the preferential orientation may be related to the preferential incorporation of a substitutional P atom in the A site. In N-doped CVD (111) diamond, theoretical studies\textsuperscript{10} on N-V centres suggested preferential occupation of the A site during the step-flow mode of film growth, followed by the formation of vacancies leading to the [111]-oriented N-V centre. Herein we explained that the oriented N-V centre is formed because a lone pair of the N atom in the A site at the surface pointing to the vacuum increases the formation energy for another C atom located on top of the N atom. A similar mechanism can be considered for the formation of a PVSVC. However, the local structure of the PVSVC is different from that of the N-V centre, comprising a substitutional N atom and a vacancy on an adjacent lattice site\textsuperscript{12,14,15}. This suggests that the PV complex should transforms to the PVSVC via structural relaxation, indicating that the mechanism of formation of PVSVC is more complicated. We hope
that this study motivates further theoretical studies to elucidate the atomistic mechanism of preferential orientation of the PVSVC.

In conclusion, we confirmed asymmetric P dopant incorporation, i.e. the preferential incorporation of P atoms into one of the two substitutional sites and the preferential orientation of the PVSVC. The chemical- and crystal-site sensitive local structures of dopants can shed light on the mechanism of doping and provide strategies to control the orientation of dopant-related complexes. In the current situation of PEH, public-use experimental stations that are equipped with computer controlled sample manipulators and wide-acceptance angle electron analysers have been developed in SPring-8, and a data analysis tool with many functions has also been developed, so that measurements become easier. These progresses have enabled PEH study on diluted samples, like present study, too. Such efforts are in progress, and will make PEH a more popular and powerful technique in materials science in near future.

**Methods:** A homoepitaxial heavily P-doped (111) diamond film was prepared by MPCVD\textsuperscript{32}. \( n_p \) is \( 1 \times 10^{20} \) cm\(^{-3} \) (0.06 at.%), as determined by secondary ion mass spectroscopy. The thickness of the P-doped layer is estimated to be ~2 \( \mu \)m using a relation between growth rate and growth time\textsuperscript{33}. Resistivity measurements showed a semiconducting temperature dependence and a value of ~200 \( \Omega \) cm (\( 5 \times 10^{-3} \) S cm\(^{-1} \)) at ~27 °C. The film surface used for the PEH measurements was cleaned using H\(_2\) plasma, and was therefore a H-terminated film. To reduce adsorbed molecules on the surface, the sample was annealed \textit{in situ} at ~500 °C for 10 min under ultrahigh vacuum before the measurements.

PEH measurements for C 1s and P 2p were performed at BL25SU, SPring-8, using a Scienta Omicron DA30 electron analyser with a photon energy of 700 eV (1.8 nm). The energy resolution was set to ~170 meV (\( 4.3 \times 10^{-4} \) nm). The proving depth of the present PEH is of the
order of 1 nm, as estimated from the inelastic mean free path of the photoelectron having kinetic energy ~500 eV. The base pressure of the measurement chamber was better than $5 \times 10^{-8}$ Pa. The chemical potential of the sample was determined from the Fermi edge of a molybdenum substrate electrically contacted with the sample. All the measurements were performed at room temperature to prevent charging. A map of the photoelectron angular distribution, which is the photoelectron hologram, was acquired from a series of measured data (angular regions of $\pm 6^\circ$ and $\pm 10^\circ$) using the three-fold symmetry operation and mirror symmetry operation according to the symmetry of the (111) surface. 3D atomic images were reconstructed with the scattering pattern extraction algorithm using $L_1$-linear regression (SPEA-L1)$^{23}$. Simulated photoelectron holograms were obtained using the TMSP code$^{23}$, with an atomic cluster of radius 3 nm and mean free path 1 nm, based on the calculated positions of P and C atoms. The site symmetry of the substitutionally incorporated P atoms used was $T_d$. Although this is different from the previously reported $D_{2d}$ symmetry$^{35}$, the difference of local structure around a P atom between $T_d$ and $D_{2d}$ is small; hence, the simulated photoelectron hologram patterns may be identical (for detailed information on the PEH technique, see Supporting Information).
Figure 1. Illustration of photoelectron holography system.
**Figure 2.** (a) Experimental (left) and simulated (right) images of C1s photoelectron hologram of P-doped diamond (111). The centre of the hologram corresponds to the [111] direction and the angle with respect to the centre represents the polar angle. (b) Slices of the reconstructed 3D atomic image from the observed hologram. Planes [P1-P4] in (b) correspond to the planes perpendicular to [001] at \(z = 0, 0.89, 1.78,\) and 2.67 Å, respectively. Mark E indicates the photoelectron emitter. Large and small circles indicate the expected positions of carbon atoms as viewed from the A and B sites, respectively. (c) and (d) are the same as (a), but show P 2p holograms for components α and β, respectively. (e) is the same as (b), but for the component α of P 2p. (f) Diamond crystal structure (left) and a superposition of atomic structures, as viewed from the A and B sites as emitters (right). The observed hologram provides information from
both structures. (g) Angular dependence of the core-level spectra of P 2p with respect to the surface normal. The two components $\alpha$ and $\beta$ are labelled.

**Figure 3.** The structure of the PV split vacancy complex (PV SVC) in diamond. There are four candidate directions in diamond. Vertical PV SVC is denoted as $PV^V$ and others are $PV^H_x$ ($x = 1, 2, \text{ and } 3$).

**ASSOCIATED CONTENT**
Supporting Information. I. Simulated photoelectron holograms for substitutional P, PVVSC, and interstitial P, and II. details of PEH technique (file type: PDF).

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Notes

The authors declare no competing financial interests.

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