Stereophotographs of diamond and graphite

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Abstract

The direct imaging of atomic arrangement is essential for investigation of materials science. The rotation of forward focusing peaks in photoelectron intensity angular distribution (PIAD) pattern excited by circularly polarized light with the opposite helicities is found to be the same as the parallax in stereo view. Taking advantage of this phenomenon of PIAD circular dichroism, the three-dimensional atomic arrangement visualization of diamond and graphite crystal was realized. Taking a stereo picture around carbon atom, which has been thought difficult due to a small angular momentum and scattering cross section of photoelectron, proved that this method is applicable to various materials consisting of light elements. Furthermore, the local boron dopant site was concluded to be mainly substitutional one from the comparison of B 1s and C 1s PIAD patterns.

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1. Introduction

Up to now, there is no microscope for direct atomic arrangement imaging. Many kinds of scanning probe microscopes are developed, however, they provide only topographic corrugation of surfaces. A three-dimensional structure has been deduced from various diffraction techniques, and the Fourier transformation process of data is always required. The rotation of forward focusing peaks in photoelectron intensity angular distribution (PIAD) pattern obtained by clockwise (cw) and counterclockwise (ccw) helicity circularly polarized light are found to be the same as the parallax in stereo view. Taking advantage of this phenomenon of circularly polarized PIAD a stereo atomscope \cite{1,2}, and direct stereoscopic recognition of atomic arrangement around a specific atom has become possible. Furthermore, since photoelectrons are used for probing, this technique is element selective.

Dopant local site of heavily boron-doped diamond has been a key issue in the recent investigation on mechanism of its superconductivity \cite{3,4}. Substitutional site \cite{5–7} as well as interstitial site \cite{8} has been proposed for boron atom local structure. However, the direct determination method for local dopant site was lacking so far. Here we report the visualization of three-dimensional atomic arrangement of heavily boron-doped diamond and graphite crystal by a stereo atomscope. Firstly, it is proved that this method is applicable to various materials consisted of light elements by the success in taking a stereo picture around a carbon atom in graphite and diamond, which has been thought difficult due to a small angular momentum of the photoelectron. Secondly, we have
achieved in the measurement of PIAD from boron atom at a low concentration in the order of few percent. Finally, we show that the PIAD of dopant boron atom resembles that of carbon atom in the diamond crystal suggesting the local dopant site is substitutional.

2. Experimental

PIAD from sample at specific kinetic energy is most efficiently measured by a two dimensional display-type spherical mirror analyzer (DIANA) [9–15]. A schematic cross section of DIANA is shown in Fig. 1. A circularly polarized synchrotron radiation (SR) is introduced through a hole in the outer hemisphere of the analyzer. A spherical electric field between the obstacle rings and the main grid makes photoelectrons with a selected kinetic energy focus on the exit aperture. These photoelectrons are multiplied by a pair of microchannel plates and projected on a fluorescent screen with the emission angle preserved. Thus, the direction of the photoelectrons can be deduced directly from the position of the PIAD pattern on the screen. The energy resolution $\Delta E/E$ of this analyzer is 0.3% and the angular resolution is $\pm 0.5^\circ$.

DIANA, for a stereo atomscope, is installed at the soft X-ray solid-spectroscopy beamline BL25SU in SPring-8, Japan. Helicity of monochromatized circularly polarized soft X-ray was reversed by switching the gaps of twin helical undulators [16]. The circularly polarized SR was incident on the clean diamond and graphite surfaces $45^\circ$ off from the surface normal. The typical acquisition time for one PIAD measurement was 10 min. The forward focusing peak intensity distribution is in the order of 5–10% of photoelectron intensity. In order to extract them, PIAD patterns from the sample were divided by the image of photoelectron transmission factor. Here, PIAD pattern from polycrystalline graphite in the same condition was used for this purpose.

3. Results and discussions

When the photoelectrons are scattered by surrounding atoms, forward focusing peaks appear in a PIAD pattern along the directions connecting the emitter and the scatterer atoms [17]. In the case of the excitation by circularly polarized light, photoelectrons receive angular momentum from the light. As a result, positions of forward focusing peaks shift around the incident light axis. The rotation angle $\Delta \phi$ of the peak around the photon incident axis for the $1s$ initial state case is theoretically derived and expressed in a simple formula,

$$\Delta \phi = (kR \sin^2 \theta)^{-1},$$

where $k$ is the photoelectron wave number, $R$ the internuclear distance between the emitter atom and the scatterer atom, and $\theta$ is the angle between the photon incident direction and the outgoing photoelectron direction [1,14,18]. When the position vector of the scatterer viewed from the emitter is described as $(R, \theta, \phi)$, the peak positions observed by using circularly polarized light appear at $(\theta, \phi \pm \Delta \phi)$. Forward focusing peak rotates cw ($-\Delta \phi$) and ccw ($+\Delta \phi$) directions in the case of the cw and ccw helicity light excitations, respectively.

Fig. 2(a) is a set of $C\,1s$ PIAD patterns from the diamond(111) surface at the photon and photoelectron energies of 789.3 and 500.0 eV, respectively. The rotation direction of the electric vector of the photon used for the excitation in the left patterns was cw, and in the right patterns was ccw in the figure. This pair of PIAD patterns

![Fig. 2. (a) Set of two-dimensional photoelectron angular distribution patterns of C 1s from the diamond(111) surface excited by cw (left) and ccw (right) helicity light. The kinetic energies was set to 500 eV. Light incident direction is at the bottom of these figures. Three-dimensional image appears if one sees right and left figures with right and left eyes, respectively; (b) the crystal structure of the single-crystal diamond. Incident light is indicated by two arrows pointing to the emitter atoms A and B; (c) assignments of forward focusing peaks in (a)-right. Notation Bi indicates the forward focusing peak of emitter atom A and scatterer atom B, for example.](image-url)
excited by cw and ccw helicity light forms a stereo photograph of atomic arrangements for left and right eye, respectively.

Diamond crystal structure is depicted in Fig. 2(b). There are two types of carbon atoms; the atoms A and B. Diamond PIAD pattern is made up of the contributions from these two types of atoms.

Direction of peak observed at the center of screen corresponds to surface normal direction. This peak is assigned to the forward focusing peak of emitter atom A and scatterer atom B. Here, notation $B_A$ is used for such forward focusing peak. Three prominent peaks marked with open circle appear at about $35^\circ$ off from surface normal which coincide with [011], [101] and [110] directions. They are assigned to the forward focusing peaks of $C_A$ and $D_B$. Finally, features indicated by solid circles are assigned to the forward focusing peaks of $E_A$ and $E_B$. Schematic diagram of forward focusing peak distribution is depicted in Fig. 2(c). Large circles corresponding to the forward focusing peaks from first and second nearest neighbor atoms show shifts in their positions. In the left pattern, they are shifted to the right, while in the right pattern, they are shifted to the left. When looking at the left pattern with the left eye, and the right pattern with the right eye, simultaneously, large circles pop out and appear nearer compared to small circles.

Fig. 3(a) is a set of C 1s PIAD patterns from the graphite surface at the photon and photoelectron energies of 800.0 and 509.0 eV, respectively. The rotation direction of the electric vector of the photon used for the excitation in the left patterns was cw, and in the right patterns was ccw in the figure.

Graphite crystal consists of stacked carbon honeycomb sheets as shown in Fig. 3(b). There are also two types of carbon atoms in graphite unit cell; the atom A is bound to six atoms forming a hexagon above, while B is bonded to three atoms and one on-top atom.

Six prominent features at the direction of about $23^\circ$ off from surface normal and the one in the center, marked with solid circle are assigned to the forward focusing peaks of first layer carbon atoms. Other features indicated with open circle are assigned to the diffraction structures and the forward focusing peaks by other layer atoms [14]. All the solid circles in the left pattern are shifted to the right, while those in the right pattern shifted to the left. Solid circles pop out and appear nearer compared to open circles. By applying present method, the stereoscopic crystal structure around excited atom is directly visualized.

In order to clarify the local structure around boron dopant atom in diamond, photoelectron angular distribution of B 1s was compared to that of C 1s. Fig. 4(a) is the summed pattern of C 1s photoelectron angular distribution from the diamond(111) surface excited by cw and ccw helicity light. The kinetic energies was set to 500 eV. Dotted circles indicate $h_{102}$ directions where forward focusing peaks are expected if an extra atom existed at the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ site which is not the case for diamond structure. Fig. 4(b) shows B 1s photoelectron pattern at the same kinetic energy. The position of forward focusing peaks resemble that of C 1s pattern. Moreover the forward focusing peak at the $(102)$ direction is lacking also in the B 1s pattern. These observations clearly indicate that the main dopant site for boron atom is the substitutional one.

4. Conclusions

In conclusion, the atomic stereophotographs of diamond and graphite single crystal were obtained by DIANA successfully. The stereoscopic arrangements of the atoms can be imaged directly without any aid of computational analysis when looking at the pattern with each eye individually. Since photoelectron is used as a probe, this technique is element selective. We have also applied this technique to the local dopant site analysis of boron in diamond [19]. Absence of the forward focusing peak at the
(102) direction indicates that the main dopant site for boron atom is the substitutional one.

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