Three-dimensional atomic imaging of dopant sites in As-doped Si using spectro-photoelectron holography

A significant problem of the impurity doping techniques for semiconductor devices is the electrical activation of dopants with a high concentration. It is known that individual dopant atoms occupying a substitutional site in a crystal matrix provide carriers, making the dopant electrically active. However, in the doped regions with a high concentration, not all dopant atoms are active owing to the deactivation of excess dopant atoms by the formation of various clusters and other defect structures. With the aim of developing process technologies to overcome the problem, the atomic level dopant structures have been investigated by both theoretical and experimental approaches, although the direct observation of their three-dimensional (3D) structures has been difficult. As a different approach, dopants in Si have been examined using soft X-ray photoelectron spectroscopy (SXPES), in which particular chemical bonding states were correlated with electrical activity [1].

Photoelectron holography is a method of examining element-specific local 3D atomic structures applicable to nonperiodic structures [2]. Recently, the development of reconstruction algorithms has greatly improved the quality of reconstructed atomic images. Furthermore, a high energy resolution electron analyzer has allowed the visualization of local dopant atomic structures having different chemical bonding states. In this work, we report the 3D imaging of structures for As doped into a Si surface using spectro-photoelectron holography combined with first-principles simulations [3].

The sample was prepared by As^+ ion implantation followed by activation annealing and surface etching [3]. The As concentration and carrier concentration near the surface were evaluated as $1.5\times10^{20}\,cm^{-3}$ and $7.5\times10^{19}\,cm^{-3}$, respectively; thus, the activation rate was 50%. The spectro-photoelectron holography measurements were performed at SPring-8 **BL25SU**. Soft X-rays were incident to the sample at a 5° glancing angle, as shown in Fig. 1(a). The principle of photoelectron holography is summarized in Fig. 1(b). Part of each photoelectron wave emitted from the excited atom is scattered by surrounding atoms and the scattered wave interferes with the original direct photoelectron wave. The resulting interference pattern, i.e., the photoelectron hologram, appears in the angular distribution of the photoelectrons. An entire photoelectron hologram was obtained with an electron analyzer (Scienta-Omicron DA30) capable of measuring the angular distribution with high energy resolution. The 3D atomic image reconstruction was conducted using the SPEA-L1 algorithm [4]. First-principles calculations were performed to calculate the stability, core-level shifts, and dynamical properties of As doped in Si using the STATE-Senri program [5]. First-principles molecular dynamics (MD) simulations were carried out to evaluate atomic fluctuations at room temperature.

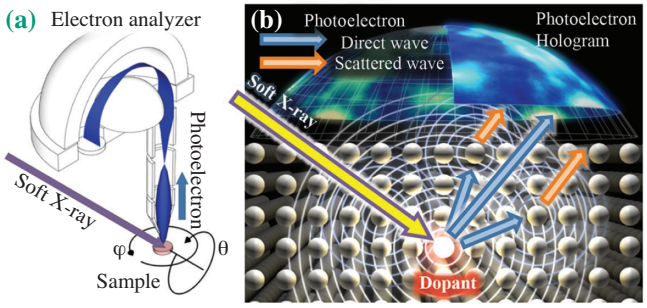

Fig. 1. **(a)** Experimental setup at BL25SU. **(b)** Schematic diagram summarizing the principles of photoelectron holography. [3]

Figure 2 shows the obtained As 3*d* spectrum containing three components labeled BEH, BEM, and BEL (Fig. 2(d)), which are attributed to three distinct atomic sites, and the corresponding photoelectron holograms (Figs. 2(a-c)). The hologram associated with the BEH peak is very clear and its pattern is similar to that of the Si 2*p* hologram (not shown here).

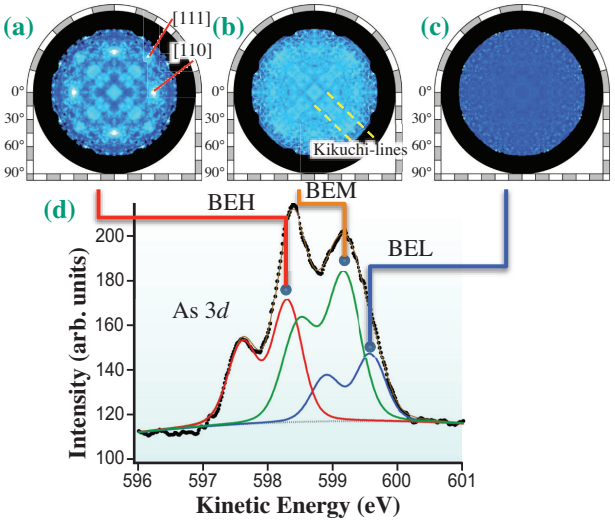

Fig. 2. Holograms generated from the spectra labeled **(a)** BEH, **(b)** BEM, and **(c)** BEL, and **(d)** As 3*d* core-level photoelectron spectra with labels. [3]

Although the pattern associated with the BEM peak is less intense, Kikuchi lines are clearly evident. The pattern from the BEL peak is unclear and has little structure.

The atomic images of these sites were reconstructed, as shown in Figs. 3(a-c) and Figs. 2(e-g), which correspond to the BEH and BEM peaks, respectively. The atomic image for the BEH peak indicated that the As atoms were located at substitutional sites in the Si lattice. However, the atomic image of the first nearest neighbor (NB) was quite weak as shown in Fig. 3(b). Our first-principles MD simulations suggested that this is due to the slightly larger amplitude of thermal oscillations of As atoms relative to Si atoms, as shown in the structural image of Fig. 3(d). On the other hand, for the BEM peak, atomic images of (1/2, 1/2, 0) in Fig. 3(e) were elongated. On the basis of the result that atomic images of the first NB are visible (Fig. 3(f)), we conclude that As atoms occupy the substitutional sites, the same as in the BEH case, even though the positions of As atoms thermally fluctuate.

To investigate the structural difference between BEH and BEM, we observed electrical activation and chemical shifts. Comparing the relative peak intensity ratio (Fig. 2(d)) with electrical activation rate (~50%), and considering our previous work of SXPES indicating that electrically active As has a larger binding energy [1], the As giving the BEH peak was determined to be electrically active. On the other hand, As atoms giving the BEM peak are considered to form As cluster structures. We evaluated their binding energy shifts for As 3*d* core-levels by first-principles calculations. Comparing the theoretical values for candidate clusters reported so far with the experimental values, we concluded that the As atoms giving the BEM peak form $As_nV(n=2-4)$ cluster structures, as shown in Fig. 3(h) for the case of $n=2$. Based on the structureless hologram (Fig. 2(c)), the As atoms responsible for the BEL peak are thus considered to be located in either amorphous or disordered structures.

In conclusion, the 3D atomic structures of As doped into a Si crystal were successfully revealed. This work demonstrated the potential of spectro-photoelectron holography for the analysis of dopants in semiconductors.

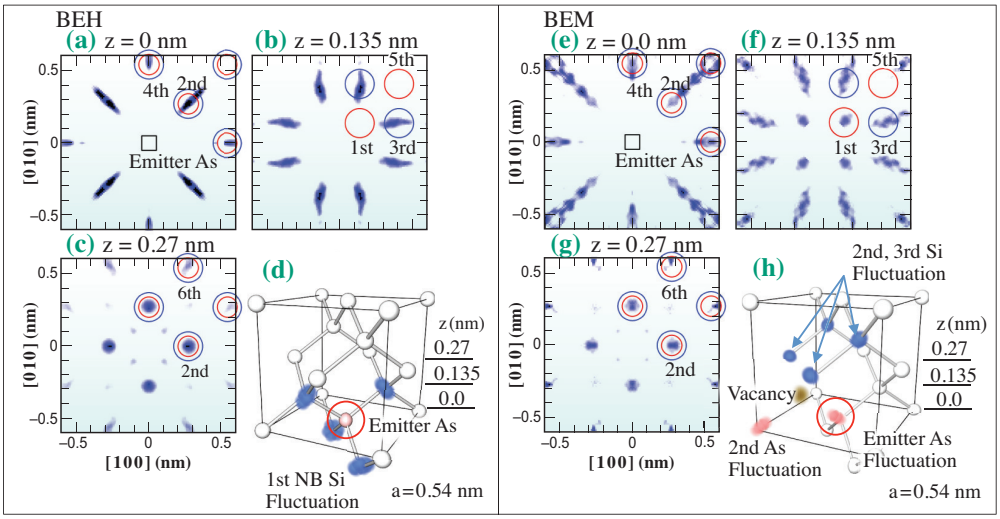

Fig. 3. Atomic images reconstructed from the holograms for the BEH and BEM spectra. The BEH cross sections are labeled as z = **(a)** 0, **(b)** 0.135 (= $a/4$), and **(c)** 0.27 nm (= $a/2$), a: lattice constant. The candidate structure is shown in **(d)**. Those for the BEM are shown in **(e)-(h)** in the same manner. In the structural images, (d) and (h), "emitter As" atoms are red, notable Si atoms and vacancies near the emitters are blue and brown, respectively, and fluctuating atoms appear blurry. [3]

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