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Atomic Sites of Dopants in Si Visualized by Spectro-Photoelectron Holography

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Abstract

Spectro-photoelectron holography method combined with first-principles simulations determined the local three-dimensional atomic structures of arsenic (As) atoms doped in a silicon (Si) crystal. Presence of the three types of As atomic structures were revealed; electrically active As occupying substitutional sites, electrically inactive As embedded in the As_nV (n = 2-4) type clusters, and electrically inactive As in locally disordered structures.

1. Introduction

Techniques for the electrical activation of impurities doped into semiconductors at high concentrations have always been an essential in semiconductor device technologies. However, the maximum concentration of an active dopant is limited. The limitations on active dopant concentrations result from the deactivation of excess dopant atoms by the formation of various types of clusters and other defect structures.

As such, an understanding of the atomic structures of dopants would assist in the development of new process technologies. However, direct observation of the three dimensional (3D) structures of dopant arrangements has been difficult. Since the dopants are not dispersed with a regular periodicity in the crystal, XAFS and high resolution STEM have been used, however, direct 3D imaging including vacancies is not easy. On the other hand, dopants having different chemical bonding states in Si have been examined using soft X-ray photoelectron spectroscopy [1], although their 3D atomic arrangements cannot be observed.

2. Photoelectron Holography

Photoelectron holography is a method of examining element specific local 3D atomic structures that is applicable to non-periodic structures [2, 3]. The principle of photoelectron holography is summarized in Fig. 1. Soft X-rays excite the core level electrons such that photoelectrons are emitted. A portion of each photoelectron wave is scattered by surrounding atoms and the scattered wave interferes with the original direct wave. The resulting interference pattern (that is, the photoelectron hologram) appears in the angular distribution of the photoelectrons.

Real space atomic arrangements are reconstructed from the photoelectron hologram by numerical calculations. Recently, the SPEA-MEM/SPEA-L1 (scattering pattern extraction algorithm using the maximum entropy method/L1 regularization) [4, 5] reconstruction algorithms have been improved. Furthermore, use of a high energy resolution electron analyzer has allowed visualization of local dopant atomic structures having different chemical bonding states.

In this work, the spectro-photoelectron holography method was applied to estimations of the 3D structures of As atoms arrangement doped in a Si(100) surface [6].

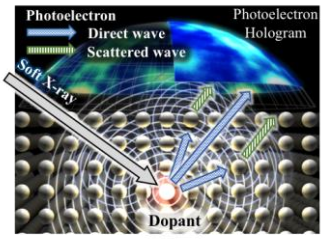

Fig. 1 Principle of photoelectron holography.

3. Experiments

As^+ ions were implanted (1.5×10^{15} cm^{-2}, 3 keV) into a p-type Si(001) wafer. Activation processes of spike-RTA at 1000°C and subsequent second RTA at 1050°C for 1 min were followed. Depth profiles of the As concentration determined by SIMS and carrier concentration determined by Hall effect measurement are shown in Fig. 2. Samples for the photoelectron holography were prepared using a step-by-step etching process [1] so that a new face that had been 36 nm under the original surface was exposed (Fig. 2).

The spectro-photoelectron holography measurements were performed at the BL25SU beamline at the SPring-8 synchrotron facility. A photoelectron hologram was cap-

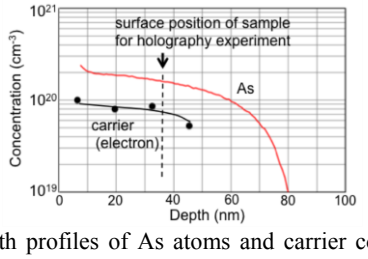

Fig. 2 Depth profiles of As atoms and carrier concentration for the samples used in this work.

tured with an electron analyzer capable of measuring the two-dimensional angular distribution. Entire holograms were obtained by stepwise angular variations of the sample.

Peak fitting was applied to all angle-resolved spectra to obtain the photoelectron hologram of individual atomic sites and the 3D atomic image was reconstructed [4, 5].

First-principles calculations were performed to evaluate As 3*d* binding energies for various As cluster structures [6], using the STATE-Senri (Simulation Tool for Atom TEchnology) program [7].

4. Results and Discussion

Figure 3(a) shows the experimental As 3*d* spectrum. It was found to contain three components labeled BEH, BEM, and BEL. The As atoms having three different chemical bonding states coexisted in the doped region.

Obtained photoelectron holograms for the three different states of As 3*d* are shown in Fig. 3(b)-(d). The hologram associated with the BEH peak is very clear and its pattern is quite similar to that of the Si 2*p* hologram. Although the pattern associated with the BEM peak is less intense, Kikuchi-lines are clearly evident and the <111> forward focusing peaks are still present. In contrast, the pattern from the BEL peak is unclear and has little structure.

Fig. 4 shows atomic images reconstructed from holograms of BEH (Fig. 4(a)-(c)) and BEM (Fig. 4(d)-(f)), respectively. The atomic image for the BEH peak was similar to the Si structure, indicating that the As atoms were located

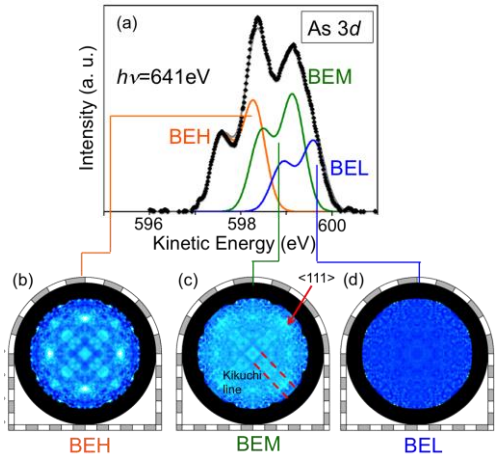

Fig. 3 (a) As 3*d* core-level photoelectron spectra. Photoelectron holograms obtained from separated peaks of (b) BEH, (c) BEM, and (d) BEL.

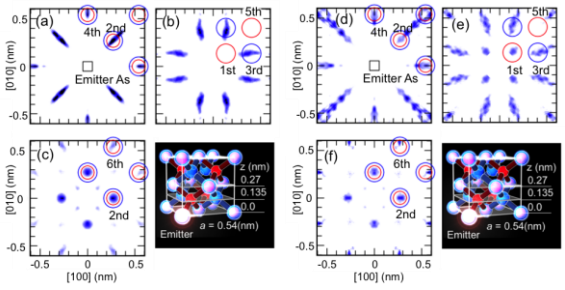

Fig. 4 Atomic images reconstructed form holograms of BEH at *z*= (a) 0 nm, (b) 0.135 nm, (c) 0.27 nm, and BEM at *z*= (d) 0 nm, (e) 0.135 nm, (f) 0.27 nm.

at substitutional sites in the Si lattice. However, the image of the first nearest neighbor (NB) was quite weak due to their significant fluctuation. The 3D atomic arrangement speculated from the discussion is shown in Fig. 5(a).

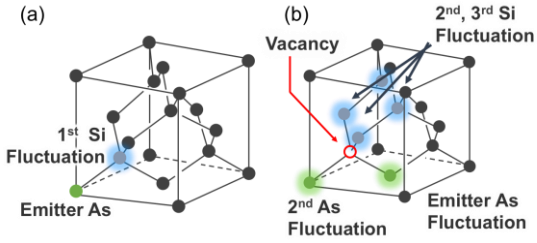

Fig. 5 3D atomic arrangements speculated form the atomic images shown in Fig. 4, for (a) BEH and (b) BEM.

As for the BEM peak, the reconstructed atomic image on *z*=0 plane was elongated, while those of the 1st NB are visible. Based on these results, we conclude that As atoms occupied the substitutional sites, and that As atoms occupy the 2nd NB sites and they fluctuate significantly. We performed first-principles calculations to find the binding energy shifts for As 3*d* core levels [6]. As a result, we concluded that the As atoms are assigned to As_nV (n=2~4) cluster structures. A candidate structure is shown in Fig. 5(b), as a case of n=2.

The As atoms responsible for the BEL peak are considered to be located in disordered structures, such as in zones of precipitated Si-As [8] within the Si crystal.

Comparing the relative peak intensities derived from the As 3*d* spectrum (Fig. 3(a)), to the electrical activation rate (Fig.2), and considering the structural features discussed above, we determined that BEH is electrically active and BEM and BEL are electrically inactive.

5. Conclusion

The 3D atomic structures of As doped into a Si crystal were successfully revealed using spectro-photoelectron holography. Electrically active substitutional As, electrically inactive As forming As_nV(n=2~4) clusters or embedded in disordered structures are revealed.

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