

## Chemical Analyses of Heavily Doped Boron in Silicon-Based Shallow Junctions by Soft X-Ray Photoelectron Spectroscopy

Semiconductor device technology for large-scale integrated circuits has been advanced by pursuing aggressive scaling down of device feature sizes. The formation of an ultra-shallow junction, in which impurity atoms are heavily doped into a very shallow region near the surface of a single crystalline silicon (Si) wafer, is a key process in keeping this trend. An important impurity is boron (B), which produces holes in the doped region, forming Si-based p-n junctions. In up-to-date nanoscale transistors, the depth of the doped layer, the so-called junction depth, must be as small as a few tens of nm on the surface of a Si wafer. In actual doped layers, B concentration is excessively high in the near surface region, as shown in Fig.1. Some of the B atoms that occupy the lattice site in crystalline Si must be electrically activated. The rest of these B atoms that occupy the interstitial sites in the crystalline Si form clusters, particularly in the heavily doped region. Such B clusters do not contribute to electrical conduction, thereby degrading the electrical properties of devices. On the other hand, the thermal diffusion of B atoms during thermal annealing, which activates B atoms, should be suppressed in order to preserve the small junction depth. Thus, the development of process technology, which results in the high activation rate of B in a heavily doped shallow junction, is a significant challenge. To achieve such process technology, the chemical analysis of B atoms in shallow junctions is strongly required.

The detection of chemical bonding states of B, whose concentration in Si is in the order of 1% or less, using Al K $\alpha$  radiation excited photoelectron

spectroscopy (XPS) is difficult because the photoionization cross section of B is small. Thus, we performed soft X-ray photoelectron spectroscopy at beamline **BL27SU**, where intensive soft X-ray was available at a photon energy of 500 eV, in order to increase the photoionization cross section. In addition, we achieved concentration depth profiling of B having different chemical bonding states by using step-by-step etching. Figure 2 shows the B 1*s* spectra with the etched depth as a parameter for a heavily doped shallow layer. The B 1*s* spectra arising from unoxidized B can be decomposed into three spectra having binding energies of 187.1 eV (BEL), 188.3 eV (BEM) and 189.6 eV (BEH). Therefore, three different chemical bonding states of B exist in the doped layer.

The concentration of B related to each spectrum (with BEL, BEM or BEH) was evaluated from the B 1s spectral intensity normalized by the Si 2p spectral intensity obtained from the same sample, in which the concentration of B was calculated from the normalized spectral intensity by using the ratio of the photoionization cross section of B 1s to that of Si 2p, the ratio of the inelastic mean free path of B 1s to that of Si 2p and the concentration of Si  $(5.0 \times 10^{22})$ cm<sup>-3</sup>) [1]. Depth profiles of B concentrations evaluated from three spectra, BEL, BEM and BEH, and the total concentration of B including oxidized B denoted as "all boron" are shown in Fig. 3. The three different chemical bonding states of B exhibit different depth profiles. The depth profile of hole concentration evaluated by Hall effect measurement combined with step-by-step etching is also shown in Fig. 3.



Fig. 1. Schematic diagram of B-doped shallow junction formed on surface of crystalline Si and depth profile of B concentration. In the B-doped region, B atoms are incorporated into a Si crystal at interstitial sites to form clusters and at lattice sites.



Fig. 2. B 1s spectra are shown with various etching depths. Photoelectron spectra arising from B are decomposed into three spectra having different binding energies, denoted by BEL, BEM and BEH.

According to this figure, the carrier concentration profile agrees well with the B concentration profile of BEL. Therefore, the binding energy of BEL is assigned to electrically activated B, and binding energies of BEM and BEL are assigned to B clusters.



Fig. 3. Concentration depth profiles of B evaluated from BEL, BEM, BEH and total B including oxidized B. The profile of carrier concentration evaluated by Hall effect measurement is also shown. The depth profile of carrier concentration agrees well with the B concentration evaluated from BEL.

Present chemical analyses enabled the discrimination of three chemical bonding states of impurity atoms in the shallow junctions. The basic understanding of impurity activation in semiconductors for the development of new process technologies for future semiconductor devices is strongly anticipated.

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## References

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