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Chemical Bonding States of As in Si Shallow Junctions Detected by Soft X-ray Photoelectron Spectroscopy and their Profiles

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1. Introduction

For the continuous scaling down of complementary metal-oxide-semiconductor (CMOS) technology, ultrashallow junctions having sufficiently low sheet resistance are strongly anticipated. Various new doping process technologies are developed to meet this requirement. To develop process technology, electrical measurements such as sheet resistance and Hall effect measurement, and surface analyses such as secondary ion mass spectroscopy (SIMS) have been widely used. However, these measurements provide only transport properties, and concentrations of impurity atoms and their depth profiles. However, chemical bonding states of impurity atoms is also necessary to clarify the role of impurities in semiconductors under the various process conditions.

We succeeded in analyzing chemical bonding sates of B in Si shallow junction by soft X-ray photoelectron spectroscopy (SXPES)[1]. Excitation of photoelectrons by strong soft X-ray available in synchrotron radiation facilities is also desirable to detect As with high sensitivity and high energy resolution. In this study, we applied SXPES to clarify the chemical bonding states of As doped in Si shallow junctions.

2. Experimental

P-type Si wafers were doped with As by plasma doping up to a dose of 2×10^{15}cm^{-2} followed by spike-rapid thermal annealing at 1025 °C. The annealed samples were treated in dilute HF solution to remove native oxide. Then, the samples were etched to various depths by step-by-step etching. In each etching step of removing sub-nm-thick Si layer, oxidation of the sample in an atmosphere containing ozone at room temperature and removal of the oxidized layer by HF treatment were carried out. After each etching step the photoelectron spectra arising from As 3*d* and Si 2*p* core levels in the annealed sample were measured at a photon energy of 500 eV at BL27SU in SPring-8. The spectra were measured at a photoelectron take-off angle (TOA) of 55° with an energy resolution of 0.3eV.

Hall effect measurements based on the van der Pauw method were also carried out for the samples prepared at the same time for the SXPES measurements. From changes in the sheet resistance and the Hall coefficient produced by each etching step, depth profiles of electron concentration at each etching step were evaluated.

3. Results and Discussion

Figure 1 shows concentration depth profile of As measured by SIMS for the sample after the initial treatment in dilute HF and that after 10 cycles of the step-by-step etching. If the latter profile is shifted to 8.0nm in depth, the concentration depth profile of the sample in the depth larger than 12 nm agrees well with that before etching. Based on this observation, the etching rate was determined to be 0.80nm/step.

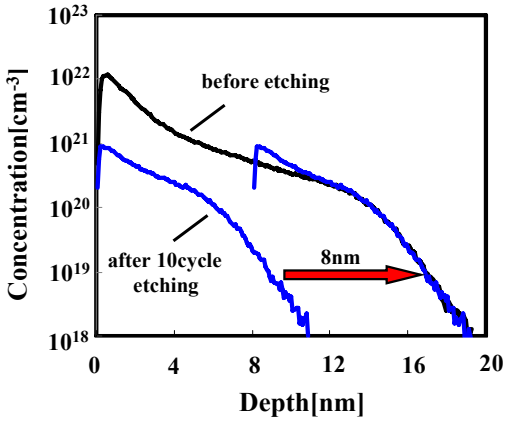

Fig. 1 Concentration depth profiles of As determined by SIMS for the sample before etching and the sample after 10 cycles of the step-by-step etching. The latter depth profile shifted in depth of 8.0nm is also shown.

Figure 2 shows the As $3d_{3/2}$ spectra with the depth as a parameter. The value of the depth is determined as sum of etched depth and a half of escape depth of photoelectrons. For all samples, As $3d_{3/2}$ spectra can be decomposed into three spectra, that is, a spectrum having the lowest BE of 40.9 eV (referred to hereafter as BEL), a spectrum with the middle BE of 41.5 eV (referred to hereafter as BEM), and a spectrum with the highest BE of 42.1 eV (referred to

hereafter as BEH). It was found that As atoms having three kinds of chemical bonding states coexist in the As doped layer, and concentration of these three kinds of As is dependent on the depth.

Figure 3 shows intensity ratio of spectra having BEL, BEM and BEH with the depth as a parameter. It can be seen from this figure that the intensity of spectrum having BEL decreases with depth while that having BEH increases with depth. The intensity of spectrum having BEM is almost independent on depth and always lower than those having BEH and BEM. Concentration of B was calculated from the As $3d_{3/2}$ spectral intensity normalized by Si $2p_{3/2}$ spectral intensity measured at the same time. Figure 4 shows the depth profiles of As having chemical bonding states of BEL, BEM, and BEH, total of these (All As), that determined by SIMS for the sample before etching, and carrier concentration profile evaluated by the Hall effect measurement.

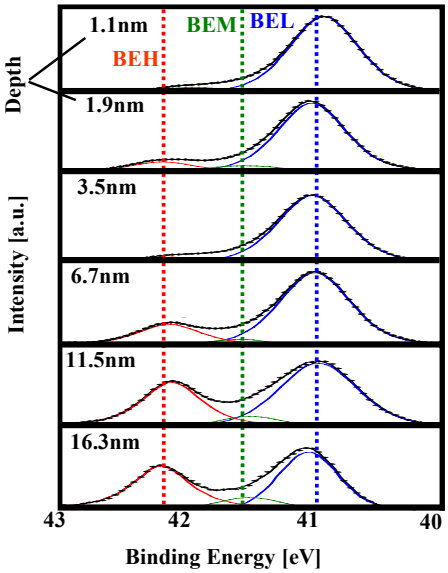

Fig. 2 As $3d_{3/2}$ spectra measured for samples with etching depth as a parameter. "Depth" in the figure denotes the sum of etching depth and a half of escape depth of photoelectrons.

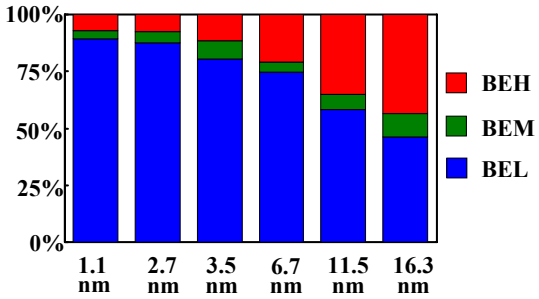

Fig. 3 Relative intensity ratio of spectra having BEL, BEM, and BEH for various etching depths.

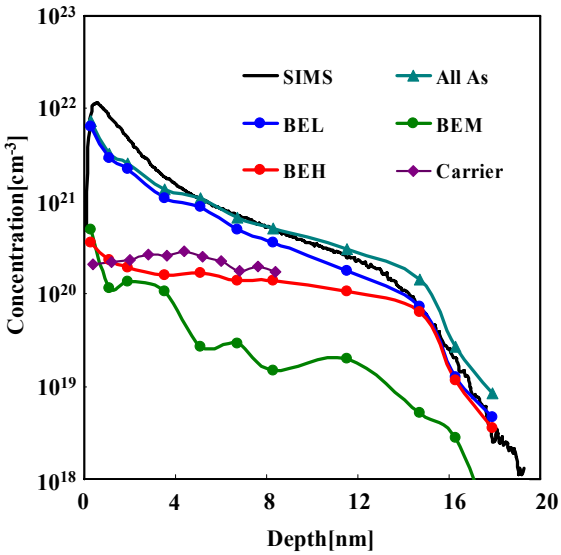

Fig. 4 Concentration depth profiles of As having three chemical bonding states (BEL, BEM, and BEH) and sum of these (All As). Concentration depth profile of carrier and that of As determined by SIMS are also shown.

The concentration depth profile of "All As" agrees with that determined by SIMS. It should be noted that, among the three chemical bonding states of As, the concentration depth profile of As having chemical bonding states characterized by BEH is quite close to that of carrier. This implies that As having chemical bonding states characterized by BEH can be correlated with electrically activated As, and that the other two kinds of As chemical bonding states characterized by BEM and BEL can be correlated with As cluster with different size. It is reasonable that As chemical bonding states characterized by the highest BE can be assigned as activated As since it is positively charged by donating an electron.

4. Conclusion

Chemical bonding states of As and their depth profiles in a Si shallow junction were studied by combining SXPES and Hall effect measurement with the step-by-step etching. As atoms having three different kinds of chemical bonding states were detected. Among them, As having the highest chemical bonding state characterized by BEH was correlated with electrically activated As, while As having the other two chemical bonding states characterized by BEL and BEM are correlated with As clusters with different sizes. This study must be useful in investigating chemical bonding states of As clusters for developing processes for ultra shallow junction with low resistivity.

References

[1] K. Tsutsui *et al.*, JAP, 104, 093709 (2008).