Local structure determination around copper adsorbed on the SiO_2/Si structure by the total reflection X-ray fluorescence-yield XAFS measurement

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For the currently produced devices, the contaminating Cu concentrations on the surface and in the Si bulk should be maintained to be less than 10^{10} atoms/cm^2 and 10^{11} atoms/cm^3, respectively, and for the next generation devices, these contamination levels should be reduced by one order. When the conventional RCA cleaning method is used, Cu contaminants are difficult to remove because Cu atoms form strong bonds with Si atoms. The information on the local structure and chemical states for metal contaminants is important to improve the semiconductor cleaning method. The present study has been conducted to measure XAFS spectra for these metal contaminants with extremely low concentrations using the total reflection X-ray fluorescence (TXRF) spectrometer with silicon drift detector installed at BL-16XU.

Boron-doped p-type Si (100) wafers with a ~10 cm resistivity and ~6 nm-thick SiO_2 layers formed by wet-oxidation of the Si (100) wafers at 850 °C were cleaned by use of the conventional RCA method. The Si wafers were contaminated with Cu by immersing in 100 ppm Cu^{2+} containing 3 % H_2O_2 solutions at 55 °C for 30 min and then rinsed twice with ultra-pure water for 10 min.

Prior to the XAFS measurements, TXRF spectra for the specimen were measured at the excitation energy of 9.5 keV. The incident angle with respect to the surface-parallel direction was set at 0.05 ° . A peak due to Cu $K\alpha$ radiation was clearly observed and the Cu concentration was estimated to be 2.5×10^{12} atoms/cm^2. The XAFS spectra were measured in this grazing incidence geometry and the standard EXAFS analyses have been performed using the XANADU program[1)]. Figure 1 shows the Fourier transforms for the Cu *K*-EXAFS oscillation extracted from the TXRF-XAFS spectrum. The first neighboring atoms around Cu are oxygen atoms with distance of 0.204 nm, which corresponds to the Cu-O distance in non-stoichiometric $Cu_{16}O_{14.15}$. Second and third peaks observed in Fig. 1 are also attributable to Cu and oxygen in $Cu_{16}O_{14.15}$. The results indicate that non-stoichiometric copper oxide species are formed over the SiO_2/Si structure. The detection limit of metals by the present TXRF apparatus is estimated to be 10^9 atoms/cm^2 and it is expected that the more improvement of the apparatus can reveal the chemical state and the local structure of trace contaminants.

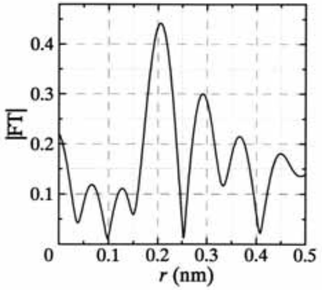

Fig. 1. The Fourier transformed Cu K-edge EXAFS spectrum.

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1) H. Sakane, T. Miyanaga, I. Watanabe, N. Matsubayashi, S. Ikeda, Y. Yokoyama, Jpn. J. Appl. Phys. 32 (1993) 4641.

X-ray reflectivity study of radical oxidized SiO_2 film.

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The density of SiO_2 film is one of the most important issues for the reliability of such as silicon MOS devices. X-ray reflectivity (XRR) is well-established method for the study of the density of thin films, however, we need more intense X-ray beams for investigation of ultra thin film, because the oscillation of the reflectivity curve has small amplitude and a few cycles. In this study, X-ray reflectivity study of radical oxidized SiO_2 film has been performed to investigate the density of the film using intense undulator beam.

SiO_2 films of about 6 nm thick were grown on Si (100) with radical oxidation in Ar/O_2 plasma excited by microwave at 673 K. XRR measurements were performed at BL16XU, using monochromatized x-rays of 0.154 nm.

Figure 1 shows experimental reflection curves of SiO_2 films. The oscillation amplitude depends on the difference of density between the film and substrate. The oscillation amplitude of pyrogenic SiO_2 film is small because the density of the film is close to that of the silicon substrate. The oscillation amplitude of CVD-SiO_2 film is large because the density of the film is smaller than the pyrogenic SiO_2 film. On the other hand, we could not fit the curve of radical oxidized film to any theoretical curves whose density is smaller than that of the silicon substrate.

In contrast, the curve fits the theoretical one satisfactorily with large density. It was reported that the mean free path of photoelectron in radical oxidized SiO_2 film is shorter than that in thermal oxidized SiO_2 film. [1] It would be caused by the large density of radical oxidized SiO_2 film. The stress of Si-O network with oxygen atom doping would not be relaxed because the radical oxidation is processed under low temperature.

[1] H. Okamoto and T. Hattori et al, Technical Report of IEICE. SDM2004-177 p23.

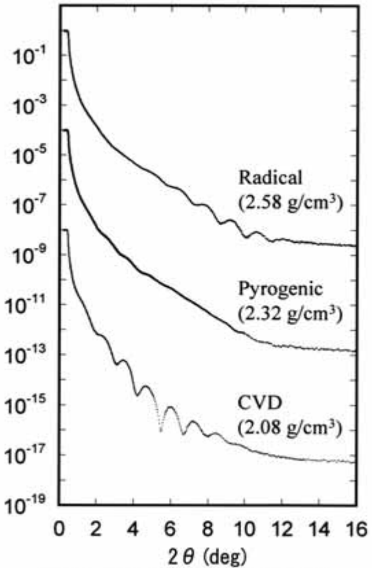

Fig. 1. X-ray reflectivity curves.