新博士紹介

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7. **要旨**

The current ultra large scale integration (ULSI) device technology demands the reduction of the gate-oxide film thickness down to about 1 nm. Therefore the chemical abruptness of the SiO_2/Si interface which largely affects the performance of MOS devices, and the control of oxide formation on an atomic scale are of great importance. However, an atomic-scale understanding of the interface structure and the initial oxidation features is still lacking, since it is difficult to analyze the interface structures with various oxidation states of Si, i.e., Si^{1+} (Si_2O), Si^{2+} (SiO), Si^{3+} (Si_2O_3) and Si^{4+} (SiO_2) components[1].

Although the incorporation of N atoms at the Si–SiO_2 interface proved to be very promising for high-quality uttra-thin gate dielectric in Si-based ULSIs with low leak current and impurity diffusion barrier, the detailed chemistry and structures of incorporated N atoms have not been elucidated yet.

In this study, we have investigated (i) the structure and the chemical abruptness of the SiO_2/Si(001) interface, (ii) the initial oxidation process, and (iii) the structure of nitrided Si–SiO_2 interfaces by high-resolution photoemission spectroscopy.

【High-resolution angle resolved photoemission spectroscopy (ARPES) beam-line BL–1C@KEK–PF】

A grazing incidence varied line spacing plane grating monochromator (VLS–PGM) has been designed and installed at the Photon Factory bending magnet beamline, BL–1C. The monochromator is designed to satisfy both high resolving power and high photon flux for a high-resolution angle-resolved photoemission study. The resolving power of the beam-line exceeds 10,000 at all the covered energy range of the monochromator with photon flux over 10^9 photons/sec[2]. This beam line is equipped with an angle-resolved photoemission spectroscopy system with a hemispherical electron analyzer mounted on a double axes goniometer. The total energy resolution of 70 meV at the 140 eV of photon energy is achieved for Si 2*p* from clean Si(111)–7×7 surface.

【Sample preparation & Measurements】

The ultra-thin SiO_2 films were grown by exposing clean Si(100)–2×1 substrates held at various temperatures to highly-pure O_2 gas at a pressure of 5×10^{-8} torr with changing the oxidation time (2 L～150 L: in total). The total-energy resolution was set to ～80 meV at photon energies of 130 and 140 eV and the angular resolution of ±2° for all measurements. The angle-resolved Si 2*p* photoemission spectra were measured by changing the polar emission angle (θ) from 0° to 70°.

In the case of the Si oxinitride, we have measured the Si 2*p* and N 1*s* at photon energies for the various samples; i) SiN film grown by the jet vapor deposition (JVD) method, ii) SiO_xN_y film grown by the rapid thermal nitridation method using NO and N_2O gases and iii) SiO_xN_y film grown by exposing 1000 L and 3000 L of NO gas.

【Structure of ultrathin SiO_2/Si(100) interfaces】

We measured the Si 2*p* core-level shifts of the various oxidation states (Si^{1+}, Si^{2+}, Si^{3+} and Si^{4+}) for ultrathin SiO_2/Si(100) interfaces using high-resolution angle-resolved photoemission and have investigated the depth distribution of the individual oxidation states by measuring the intensities of the different Si 2*p* components as a function of the polar emission angle. From these results, we constructed a non-abrupt SiO_2/Si(100) interface model. **Figure 1** shows high-resolution angle resolved Si 2*p* spectra of SiO_2/Si(100) (150 L at 600°C) taken at $\theta=0°$ and $\theta=60°$. These spectra were fitted by a standard curve fitting procedure using Voigt functions with the spin-orbit splitting of 0.60 eV for quantitative analyses. The core-level binding-energy shifts were determined accurately to be 1.00, 1.82, 2.62, and 3.67 eV for Si^{1+}–Si^{4+}, respectively.

Figure 2 shows the θ dependence of the intensities of the individual oxidation states (I_{x+}) normalized by the total intensities of the substrate-related components $I_{Si}=I_B+I_a+I_b$. The trend of the different θ-dependence of Si^{1+}/Si^{2+} and Si^{3+} suggests (i) that the Si^{1+} and Si^{2+} species have the same depth distribution, most probably at the first interfacial layer and (ii) that the Si^{3+} species are distributed in a wider region. The Si 2*p* intensity variation of each oxidation component (I_{x+}) then can be calculated using a simple electron damping scheme[3]. The solid lines shown in **Fig. 1** are obtained by fitting the experimental data. The optimized compositions of

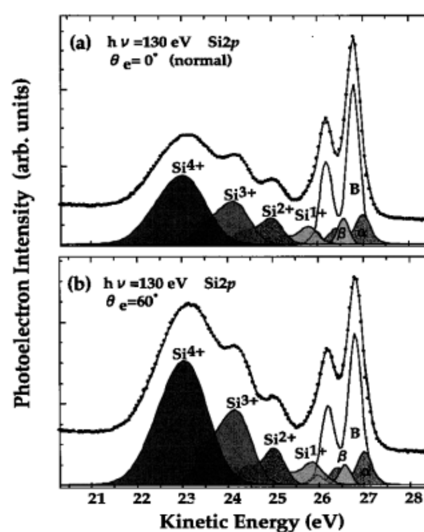

Figure 1. Si 2*p* core-level spectra taken from ultrathin SiO_2/Si(100) at (a) a polar emission angle θ of 0° and (b) of 60° with a photon energy of 130 eV. The ultrathin SiO_2 layer is formed by 150 L O_2 dose onto the Si(001) 2×1 surface held at 600°C.

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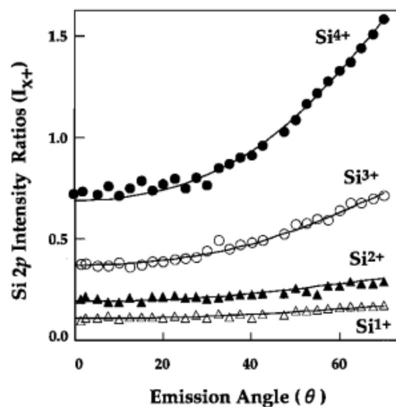

Figure 2. Intensity ratios of the Si 2p Si^{1+} ~ Si^{4+} components to the total intensity of the Si substrate-related components as a function of the polar emission angle (θ). The symbols represent experimental data, and the curves the results of fitting based on the interface structure model explained in the text.

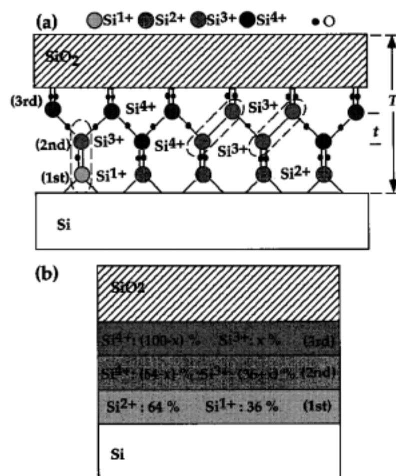

Figure 3. (a) Side-view of a simple chemically non-abrupt interface model for SiO_2/Si(100). (b) Schematic illustration of the chemical composition of the transition layers based on the model shown in (a).

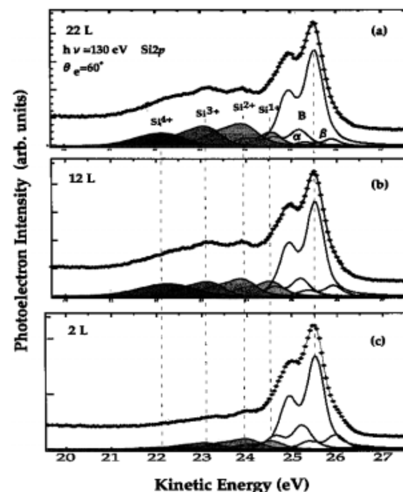

Figure 4. Si 2p photoemission spectra for 2 L, 12 L and 22 L oxygen-exposed Si(100) surfaces at room temperature. The photon energy was 130 eV, and the emission angle of photoelectrons was 60°.

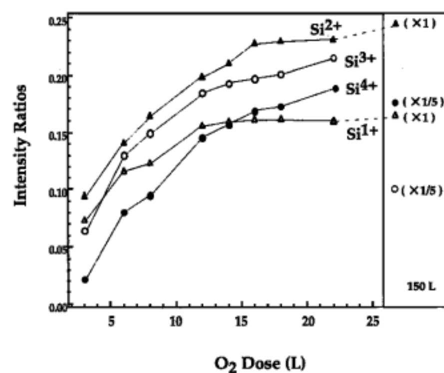

Figure 5. The peak intensity ratios of each sub-oxide component to the bulk component as a function of oxygen exposure (Langmuir) at room temperature on Si(100).

the transition layers are, 36% Si^{1+} and 64% Si^{2+}, 71% Si^{3+} and 29% Si^{4+}, and 35% Si^{3+} and 65% Si^{4+}, at the first, second and third interfacial layers from the Si substrate, respectively. This result thus indicates clearly a chemically non-abrupt interface, which is composed of three transition layers (**Fig. 3**)[4].

【Initial oxidation process of Si (100)】

We have measured the intensities of the different Si 2p components (Si^{1+}, Si^{2+}, Si^{3+} and Si^{4+}) as a function of the oxidation time, and discussed the initial oxidation process using a two-dimensional island model based on the experimental results. **Figure 4** shows high-resolution Si 2p spectra for (a) 2 L, (b) 12 L and (c) 22 L. The spectra have been decomposed with seven components, one bulk (B), two surface components of Si substrate (α, β) and four sub-oxide components (Si^{1+}, Si^{2+}, Si^{3+} and Si^{4+}). For the thermal oxidation of Si(100), the intensities of oxidation states are in the order of $Si^{4+} > Si^{3+} > Si^{2+} > Si^{1+}$ (see **Fig. 2**).

However, for initial oxidation of Si(100), the intensity of Si^{2+} species is the largest. The differences of intensity distribution between thermal oxidation and room temperature (RT) initial oxidation of Si(100) suggest that the concentration of suboxide components during initial oxidation is significantly different from that for typical thermal oxidation processes. **Figure 5** shows the intensity ratios as a function of the oxidation time. An important result to explain the initial oxidation process is the saturation of Si^{1+} and Si^{2+} intensities and the continuous increase of Si^{3+} and Si^{4+} intensities with increasing the oxidation time. In the case of Si^{3+} and Si^{4+} species, it is possible to assume that the area of the islands containing Si^{3+} and Si^{4+} are expanding horizontally on the initial oxide layer. We interpret this result as a sign of the initial oxidation caused by the two-dimensional island nucleation[5].

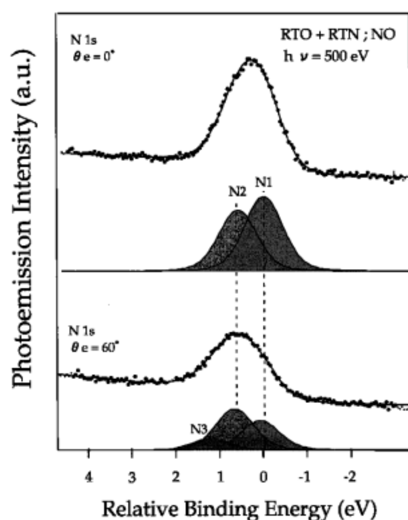

Figure 6. N1s photoelectron spectra and fitted results of the NO gas RTN SiON film. The photon energy was 500 eV and the emission angles of photoelectron were $\theta = 0°$ (a) and $\theta = 60°$ (b).

【The ultrathin oxynitride/Si(100) interface: Relation between N1s core-level shift and structure】

We have measured high-resolution N1s spectra to investigate the structures of Si–N–O bonding at the nitrided Si–SiO_2 interfaces, and clearly decomposed the N1s peak with two components corresponding to Si_3N_4 state based on the core-hole relaxation and second neighbor effects[6] for the first time.

Figure 6 shows N1s spectra of the RTN (using NO gas) sample taken at $\theta = 0°$ and $\theta = 60°$. The N1s spectrum has been decomposed with N1, N2 and N3, respectively. Taking into account above mentioned effects, we assigned N1, N2 and N3 as N bonded to three nonoxidizied Si atoms, N bonded to fully oxidized Si atoms $N[Si(O-)_3]_3$, and N bonded to two Si atoms and one O atom[7]. Thus, it is suggested (i) that two kinds of Si_3N_4 species exist at the double interfacial layers and (ii) that the NSi_2O species are distributed in the region which is closer to the surface.

【Conclusions】

From the results of high-resolution photoemission spectroscopy, we constructed a non-abrupt SiO_2/Si(100) interface model for thermal oxidation. For initial oxidation on Si(100), the oxidation process at R. T could be explained based on the two-dimensional island nucleation model. We also found the possibility of the presence of metastable molecular species on the Si(111) surface at low temperature. In the case of Si oxynitride, we succeeded in decomposing the N1s peak into two components corresponding to Si_3N^4 state based on the core-hole relaxation and second neighbor effects. In the near future, for Si oxynitride, we will investigate the annealing dependence of each Si–O–N bonding configurations and the difference of structure between RTO (NO gas) and RTO (N_2O gas) sample using high resolution photoemission spectroscopy.

REFERENCE

1) F. J. Himpsel et al.: Phys. Rev. **B 38**, 6084 (1988).
2) K. Ono, J. H. Oh et al.: Nucl. Instrum. Methods in press.
3) D. A. Luth et al.: Phys. Rev. Lett **79**, 3014 (1997).
4) J. H. Oh et al.: Phys. Rev. B in press.
5) J. H. Oh et al.: J. Electron Spectro. Rel. Phenom. in press.
6) G.-M. Rignanese et al.: Phys. Rev. Lett **79**, 5174 (1997).
7) M. Oshima, J. H. Oh et al.: J. Appl. Phys. Submitted.

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