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Charging and extra-atomic relaxation in SiO_2 films on Si studied by soft x-ray synchrotron-radiation photoemission spectroscopy

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Introduction

Over the past 30 years, the interface between SiO_2 and Si has been extensively investigated due to its technological importance in modern semiconductor devices. Atomic-scale understandings of the electronic structure and the charge distribution at the interface are important issues. Photoemission spectroscopy has widely been utilized to investigate the electronic structure such as band discontinuities and chemical states in thin SiO_2 films on Si. For SiO_2 insulating films, however, a charging effect is inevitably involved for precise detection of electronic structure during photoemission measurements, which yields extrinsic ambiguity. There remain some questions such as an uncertainty in Fermi level at the insulating surface and the relationship between charging and extra-atomic relaxation which is well known for final-state contribution in the chemical shifts. In this study, in order to elucidate the origin of photo-induced core-level shifts, thickness dependence of Si 2*p* core-level spectra in the device-quality SiO_2 films, which is free from Fermi level pinning, is systematically investigated using synchrotron-radiation time-dependent photoemission spectroscopy.

Experimental

The SiO_2/Si samples with various thicknesses were grown by dry oxidation using a pure O_2 gas on H-terminated Si(001) substrates at the substrate temperature of 850 ℃. We also prepared 2.0 nm TiN capped SiO_2 films in order to investigate effect of the metallic capping layer. Photoemission measurements were carried out at an undulator beam line BL-2C. The total energy resolution was about 0.15 eV at the photon energy of hν = 500 eV. Each Si 2*p* spectrum was recorded within the time interval of 6 sec.

Results and Discussion

Figure 1 shows the oxide thickness dependence of the energy shift for Si 2*p* core level ($\Delta E_{\mathrm{Si}2p}$) including both effects of the x-ray irradiation and the TiN-capping layer. Since x-ray irradiation effects are emphasized in thin films, the apparent difference between just after x-ray irradiation, i.e., $t \to 0$ and t ~ 30, that is the saturated condition, is observed in the range of the oxide thickness from 1.2 to 2.0 nm. By excluding x-ray irradiation effects, $\Delta E_{\mathrm{Si}2p}$ in this experiment is smoothly connected to that in the previously reported values on ultra-thin ~0.5 nm films [1]. We have found that there is a slight disagreement for the oxide thickness below 2.0 nm between the experimental data and theoretical curves including image charge contribution calculated with two photoelectron escape depths [2]. This disagreement indicates that other mechanisms of extra-atomic relaxation such as the polarization of the neighboring atoms and the screening from the substrate to the ionized Si atom make significant contributions [3]. In addition, the TiN capping layer drastically decreases the value of $\Delta E_{\mathrm{Si}2p}$ from ~4.4 eV to ~3.2 eV. Since time-dependent changes in $\Delta E_{\mathrm{Si}2p}$ are less than 0.2 eV for all the TiN capped samples (not shown), this significant decrease is meaningful. This behavior is qualitatively consistent with the previous report [4]. Therefore, it is considered that a dominant factor in $\Delta E_{\mathrm{Si}2p}$ is not the image charge contribution, which is only 0.4 eV in the range of the oxide thickness from 0.5 nm to 5.0 nm, but the core-hole screening effect from the Si substrates. These experimental facts suggest that the photo-induced hole in the SiO_2 layer was well screened by the electrons from the metallic layers, resulting in the decrease in $\Delta E_{\mathrm{Si}2p}$.

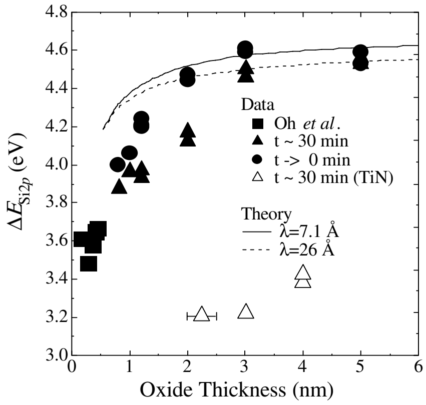

Fig. 1. Oxide thickness dependence of $\Delta E_{\mathrm{Si}2p}$ including effects of x-ray irradiati

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