Surface and Interface

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Effect of nitrogen bonding states on dipole at the HfSiO/SiON interface studied by photoemission spectroscopy

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Introduction

Because SiON gate dielectrics have reached a physical thickness scaling limit of complementary metal-oxide-semiconductor (CMOS) devices, high dielectric (high-*k*) transition metal oxide materials such as ZrO_2, HfO_2, and their silicates have been utilized to reduce the leakage current from channel to gate. HfSiO and HfSiON are candidates for high-*k* materials due to appropriate band gap and dielectric constant. For understanding electrical characteristics such as leakage current and threshold voltage, band alignments of high-*k* gate stacked structures including the SiO_2 interfacial layer (I.L.) should be clarified. Recently, controllability of the threshold voltage (V_{th}) during high-temperature thermal annealing processes is widely investigated to improve the device performance. Several studies clearly show microscopic dipole model at high-*k*/I.L. interfaces for mechanism of the V_{th} shift and the mobility degradation is caused by dipole formation. However, there are few reports on the observation of the interface dipole formation itself at high-*k*/I.L. interfaces by photoemission spectroscopy, probably due to the experimental difficulty and ambiguity. In this study, we have demonstrated the formation of the interface dipole at the HfSiO/SiON interface and investigated effect of nitrogen bonding state in terms of in-depth profiles using photoemission spectroscopy.

Experimental

HfSiO films with thicknesses of 2.0 nm were deposited on 0.7 nm SiON interfacial layers using atomic layer deposition. The Hf/(Hf + Si) value in the HfSiON film and the N concentration in the SiON interfacial layer were 56% and approximately 10%, respectively. Annealing was performed at 850 °C and 1050 °C for 1 min in a nitrogen gas pressure of 760 Torr by the direct current flowing method through the Si substrate. Photoemission measurements were performed at BL-2C of the Photon Factory in High Energy Accelerator Research Organization (KEK). The total energy resolutions were estimated to be 0.20 eV for photon energy of $h\nu$ = 630 eV. The spectra were decomposed by Voigt functions that were obtained by convoluting Gaussian and Lorentzian functions. Rutherford backscattering spectroscopy (RBS) was performed to analyze changes upon annealing in in-depth profiles.

Results and Discussion

Figure 1 shows annealing-temperature dependence of the (a) Si 2*p* and (b) Hf 4*f* core-level photoemission spectra for HfSiO films. Spectral line shapes of the Hf 4*f* core-level spectra remain almost unchanged even after the annealing at 1050 ºC. Core-level shifts toward higher binding energy upon annealing are observed. In Fig. 1(b), the Si 2*p* spectra around a binding energy of 103 eV are derived from Si-oxide (Si^{4+}) components. Note that energy positions are shifted to higher binding energy, which can be strongly related to behaviors of the Hf 4*f* core-level spectra. Difference between Si 2*p* and Hf 4*f* core-level shifts can be interpreted as changes in the dipole at HfSiO/SiON [1]. In-depth profiles suggest that nitrogen atoms at the HfSiO/SiON interface diffuse to the Si substrate upon annealing, which is correlated to the increase in strength of the interface dipole due to the formation of the HfSiO/SiO_2 interface [2].

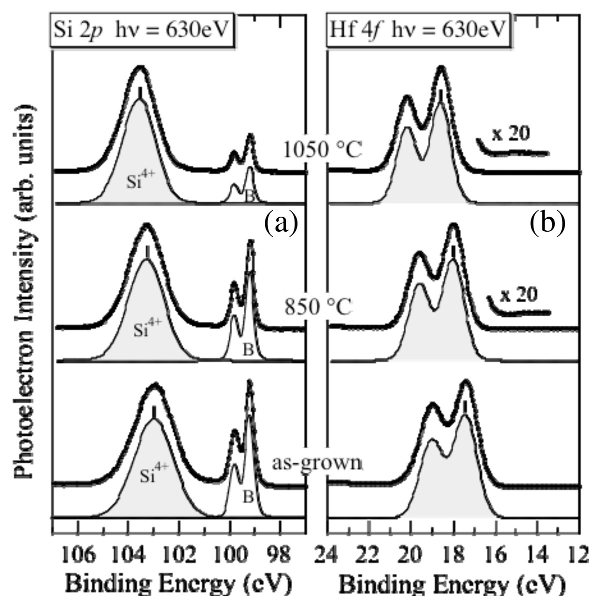

Fig. 1; Annealing-temperature dependence of (a) Si 2*p* and (b) Hf 4*f* core-level spectra for the HfSiO films.

References

[1] S. Toyoda *et al.*, Appl. Phys. Lett. **96**, 042905 (2010).
[2] S. Toyoda *et al.*, J. Appl. Phys. **107**, 124103 (2010).

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