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Analysis of x-ray irradiation effect in high-*k* gate dielectrics by time-dependent photoemission spectroscopy using synchrotron radiation

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Introduction

Among high-*k* materials as alternates to SiO_2, HfO_2-based dielectrics have one of the most desirable properties for gate insulators in complementary metal oxide semiconductor (CMOS) devices. However, since the barrier heights at the interface between HfO_2-based dielectric films and Si are relatively small, it is required to determine band offsets more precisely for accurate estimation of gate leakage current. Though photoemission spectroscopy (PES) is one of the most powerful methods to evaluate the band offsets of ultra thin films, x-ray irradiation itself for measurements hinders accurate determination of peak positions of PES spectra. For precise determination of band offsets, it is necessary to exclude the effect. In this study, we have performed x-ray irradiation time-dependent measurements of PES spectra with the temporal resolution of a few seconds using synchrotron radiation and accurately determined the band offsets of HfO_2, HfSiO and HfSiON by eliminating the x-ray irradiation effect.

Experimental

The HfO_2, HfSiO, and HfSiON layers were deposited on clean *p*-type Si (001) substrates by chemical vapour deposition (CVD). The thickness was estimated by the elipsometry to be 2 nm for the HfO_2 layer and 3.0 nm for the HfSiO and HfSiON layers. Poly-Si electrodes of 3 nm were deposited on HfO_2 gate stacks at room temperature by magnetron sputtering. Photoemission spectroscopy was carried out at an undulator beam line BL-2C of the Photon Factory in High-Energy Accelerator Research Organization (KEK).

Results and Discussion

Figure 1 shows x-ray irradiation time dependence of Si 2*p* core-level spectra in HfSiON/Si. Each spectrum was measured within a few seconds. It is observed that both oxide and substrate peaks are shifting toward lower binding energy with x-ray irradiation. However, a closer look at the initial stages reveals that peak positions shift toward higher binding energy for a few minutes. Figure 2 shows peak shifts of Si 2*p* core-level photoemission spectra from Si substrates as a function of x-ray irradiation time for HfO_2/Si, HfSiO/Si and HfSiON/Si. All samples shows peak shifts toward higher binding energy at first, and then toward lower binding energy. Hf 4*f* core-level photoemission spectra from thin oxide films also show the similar peak shift tendency to that for the Si 2*p* substrate component. Taking into consideration the time-dependence in peak width and the sample current, these phenomena can be explained as follows: At first, samples are positively charged due to photoemission. The holes in Si substrates are compensated immediately, and the band bending in Si occurs toward higher binding energy because of positive charge in the dielectrics. Then, the band bending is gradually relaxed with the increase of electrons supplied from the substrate. Finally, sample current and photoemission current reach equilibrium states.

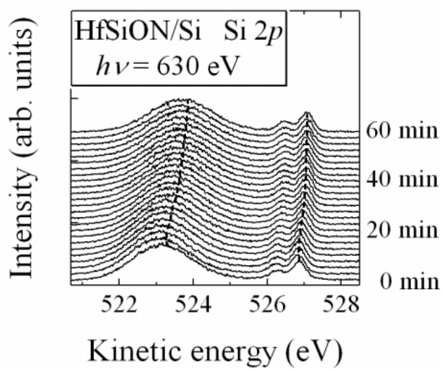

Fig. 1 Si 2*p* core-level spectra in HfSiON/Si as a function of x-ray irradiation time.

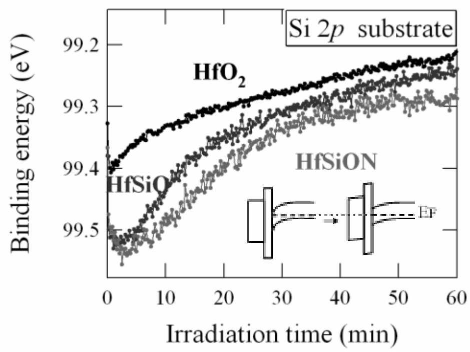

Fig. 2 Peak shifts of Si^0 2*p* core-level spectra for various high-*k* dielectrics as a function of x-ray irradiation time.

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