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Effects of interlayer and annealing on chemical states of HfO_2 gate insulators studied by photoemission spectroscopy

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Introduction

High-dielectric constant (high-*k*) materials such as Ta_2O_5, $SrTiO_3$, ZrO_2 and HfO_2 have been extensively investigated as alternatives to SiO_2 in the downscaling of complementary metal-oxide-semiconductor (CMOS) field effect transistor dimensions resulting in increasing levels of leakage current. Especially, HfO_2 has a high potential for the next-generation device applications using merits as a considerably large energy-band gap, high dielectric constant and compatibility with conventional CMOS processes because of the thermal stability. However, there are several problems to be solved such as the Hf-silicate layer formation at the interface between the HfO_2 layer and the Si substrate, the formation of metallic Hf-silicide, and the crystallization in the HfO_2 layer after annealing for activation. To fabricate high-quality gate insulators where interlayer formation is well controlled, we have to investigate the change of chemical states due to the subsequent annealing systematically.

Experimental

We have performed photoemission spectroscopy of high-*k* gate insulators HfO_2/HfSiON/Si during ultra high vacuum (UHV) annealing process to investigate the Hf-silicide formation, which may cause the gate leak in C-MOS devices. The Hf-metal layer and the HfO_2 layer were deposited by DC sputtering using a Hf-metal target on the Si substrate at room temperature. We measured two films without (sample A: HfO_2 layer 1.6 nm, interlayer 2.8 nm) and with (sample B: HfO_2 layer 3.9 nm, interlayer 1.7 nm) the Hf-metal predeposition [1].

Results and Discussion

Figure 1 shows Hf 4*f* core-level spectra of as-grown and subsequently annealed samples at 800 ºC, 900 ºC, and 1000 ºC. Spectra were normalized at the peak height of Hf $4f_{7/2}$. Binding energies of Hf $4f_{7/2}$ were different between Sample A (17.4 eV) and Sample B (18.3 eV) due to the difference of the chemical environment. There are several reports on Hf 4*f* photoemission spectra which are deconvoluted into one or two components including the interlayer concerning the dip structures between the spin-orbit splitting of Hf $4f_{7/2}$ and $4f_{5/2}$ [2,3]. In this experiment, we conclude that Sample A contains mainly the Hf-silicate component and Sample B consists of HfO_2 with little Hf-silicate component. In the case of annealing at 900 ºC, a small peak for the metallic Hf and/or Hf-silicide component appeared in Sample A by 100 times expanding although such a structure never appeared in Sample B. This indicates that the Hf-metal predeposition can restrict the formation of the Hf-silicide and the segregation of the Hf metal at the interface even after 900 ºC annealing, probably playing a significant role of suppressing the gate leakage currents. After the annealing at 1000 ºC in UHV, Hf $4f_{7/2}$ peaks were located at 14.6 eV of binding energies for both films, which suggests that the Hf-O bonding is broken. The Hf-Si and Hf-Hf bondings appear, suggesting the formation of metallic Hf-silicide and Hf-cluster. In the spectra of the annealed sample at 1000 ºC, there are satellite structures at the higher binding energy side although the peak height is different. Asymmetric line shapes also reveal the metallic feature. Considering the spectra of 900 ºC and 1000 ºC annealing, we conclude that the main peak and the satellite structure are assigned as metallic Hf and Hf-silicide components, respectively [4]. Angular dependence in the spectra reveals that Hf-silicide is located in the more surface region after the annealing at 1000 ºC.

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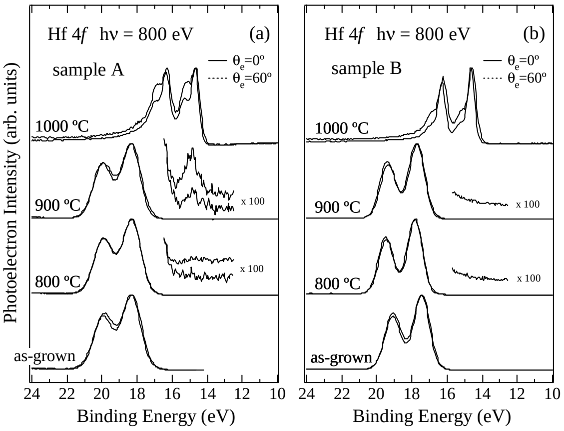

FIG. 1: Hf 4*f* core-level photoemission spectra in HfO_2 without (a) and with (b) the Hf-metal predeposition with angular dependence of 0º (solid curves) and 60º (dashed curves). Each panel shows the annealing-temperature dependence (as-grown, 800 ºC, 900 ºC, and 1000 ºC).

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