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Annealing-temperature dependence: Mechanism of Hf silicidation in HfO_2 gate insulators on Si by core-level photoemission spectroscopy

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Introduction

HfO_2 has a high potential for the next-generation ultra-large scale integration device applications using merits such as considerably large energy-band gap, high dielectric constant (high-k) and compatibility with conventional complementary metal–oxide-semiconductor (CMOS) processes. However, there remain serious problems to be solved such as low-dielectric-constant Hf-silicate layer formations at the interface, the formation of metallic Hf silicide ($HfSi_2$), and the crystallization in HfO_2 layers after annealing for the activation. In order to understand the silicidation mechanism, the changes in chemical states by annealing have to be clarified explicitly.

Experimental

HfO_2 layers were deposited in Ar/O_2 mixed atmosphere by dc sputtering using a Hf-metal target at room temperature. Photoemission spectroscopy using synchrotron radiation was performed at the undulator beam line BL-2C of the Photon Factory in High-Energy Accelerator Organization (KEK). Annealing was performed in ultra-high vacuum by the direct current flowing method through the samples. Using the sample-position dependence in annealing-temperature ranges of 10 ºC step, we performed the narrow range control of the annealing temperature around 920 ºC.

Results and Discussion

Figure 1 shows Si 2*p* and Hf 4*f* core-level spectra with the annealing-temperature dependence. Spectra at each panel are normalized at maxima of the peak height. Curve fitting for Hf 4*f* spectra was carried out by a least-squares-fitting procedure. By the annealing at 900 ºC, cross-sectional TEM images suggest that the layer structure remains unchanged [1,2]. With increasing the annealing temperature from 900 to 920 ºC, the intensity of Si 2*p* oxide components decreases drastically compared with that of the bulk components, suggesting the reduction of interfacial SiO_2-layer thickness. In Hf 4*f* spectra, the Hf-silicide component also increases compared with the oxide one. In addition, oxide components in Si 2*p* and Hf 4*f* spectra are shifted by about 1 eV toward lower binding energy. Annealing up to 940 ºC promotes the silicidation reaction. On the other hand, the oxide components in Si 2*p* and Hf 4*f* spectra are shifted by about 0.2 eV toward higher binding energy than those by the 920 ºC annealing. The oxide components in both Si 2*p* and Hf 4*f* spectra disappear completely by annealing up to 1000 ºC.

By the annealing at 900 ºC, it is considered that the Hf-silicide formations occur by the following two-step reactions,

$$SiO_2 + Si \rightarrow 2SiO\uparrow, \qquad (1)$$

$$HfO_2 + 6SiO\uparrow \rightarrow HfSi_2 + 4SiO_2. \qquad (2)$$

First, at the interface between the SiO_2 layer and the Si substrate, a SiO gas is generated by the reduction of the SiO_2 layer. The formation of the SiO gas by the reaction between SiO_2 and the Si substrate during annealing at higher temperature than 600 ºC in ultra-high vacuum, i.e., oxygen free ambient, is well known. Second, the diffusion of the SiO gas into the HfO_2 layer triggers the reduction of the HfO_2 top layer. According to the reaction (2), both $HfSi_2$ and SiO_2 are generated as products. By the reaction (1), the interfacial-layer thickness decreases and the HfO_2 layer is directly contacted with the Si substrate by the annealing at 920 ºC as shown in schematic views in Fig. 1.

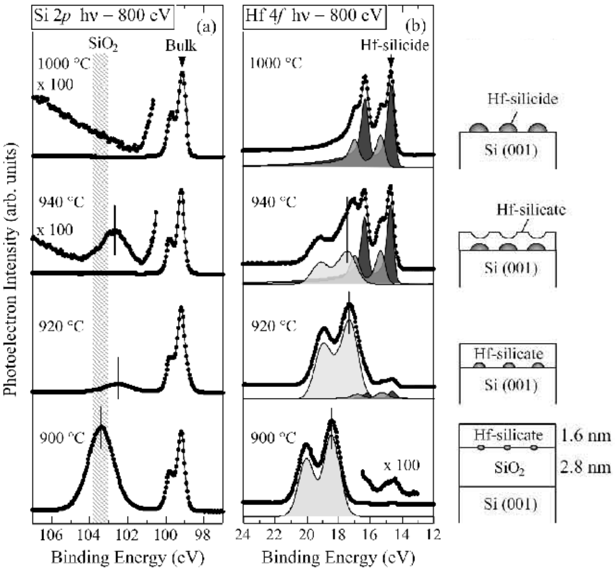

Fig. 1: Annealing-temperature dependence of (a) Si 2*p* and (b) Hf 4*f* core-level photoemission spectra. Hatched areas in (a) show the SiO_2 peak positions for several SiO_2 layer thicknesses [3].

Reference

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