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Interfacial reactions for Ru metal-electrode/HfSiON gate stack structures studied by synchrotron-radiation photoemission spectroscopy

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Introduction

To integrate the performance of complementary metal-oxide-semiconductor (CMOS) devices, the physical thickness of SiO_2 dielectrics has correspondingly dropped below 2 nm. Metal/high-k gate stack structure is one of the candidates for alternatives to conventional poly-Si/SiO_2 system. However, high-temperature annealing above 1000 °C is needed for the metal/high-k gate stack structure when a conventional device-fabrication process is employed. Chemical reaction and atomic diffusion can easily occur at the metal/high-k interface during high temperature annealing process. Thus it is necessary to control or suppress such reactions to maintain the physical and electrical properties of the gate stack. Elemental Ru metal or its oxide, RuO_2, has been studied as a potential gate electrode material for p-MOS devices due to its appropriate work-function value. In this study, we have performed an analysis of interfacial reactions between metal electrode and high-k dielectric for the sample annealed under a controlled ambient condition.

Experimental

2-nm-thick HfSiO layers were deposited on clean p-type Si (001) substrates by atomic layer deposition followed by plasma-nitridation and post-nitridation annealing to incorporate N into dielectrics. 1.5-nm-thick Ru was deposited by radio-frequency sputtering in Ar gas ambient, monitoring deposition rates by quartz crystal microbalance. Subsequently, the samples with and without Ru deposition were annealed in the same chamber at various temperatures for 1 min at N_2 partial pressure of 50 Torr by the direct current flowing method through the samples. *In situ* photoelectron measurements were carried out at the undulator beamline BL-2C of the Photon Factory in High Energy Accelerator Research Organization (KEK).

Results and Discussion

Figure 1 shows the photoelectron spectra of Si 2p (a) and Hf 4f (b) core levels obtained from as-grown and annealed samples with Ru metal, respectively. An increase in the Si-oxide component compared to the as-grown sample is observed for the sample annealed at 850 °C. This is related to the surface Ru layer, which is expected to have a catalytic effect to enhance adhesion and diffusion of O_2 molecules. Oxygen species would diffuse through Ru to the Ru/HfSiON interface, resulting in the pile-up of oxygen at the interface [1]. In contrast, the intensity of Si-oxide began to decrease above 950 °C. Since thermal Si oxide formed at low temperature is less stable than that formed at high temperature, unstable Si-oxide layer would be decomposed into volatile SiO species. A portion of SiO gas would react with Ru and the following silicidation reaction would occur:

$$\mathrm{Ru} + 2x\mathrm{SiO} \rightarrow \mathrm{RuSi}_x + x\mathrm{SiO}_2 \qquad (1)$$

Gibbs free energy of above formula is estimated to be approximately –290 kJ/mol (at 900 °C) when x is equal to 1.5. Thus, some SiO molecules would return to SiO_2 with the silicidation of Ru metal, and other SiO species would desorb from the dielectrics. As these reactions proceed, the thickness of the dielectric layer is thin enough to diffuse Ru toward the bottom interface of SiON/Si. After Ru atoms reach the Si substrate, further silicidation reactions take place immediately.

References

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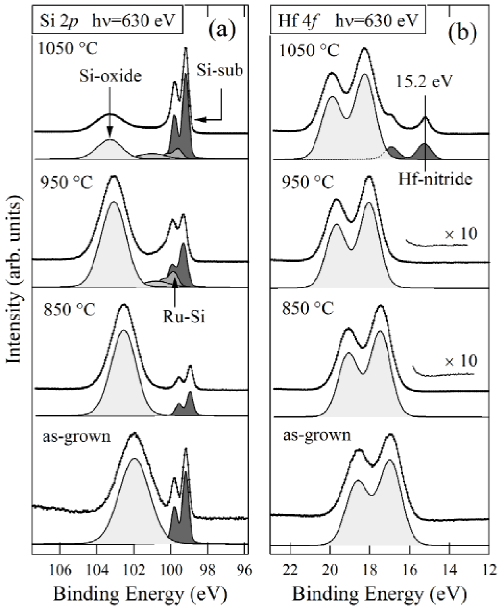

Fig. 1. Photoelectron spectra of Si 2p (a) and Hf 4f (b) core levels obtained from as-grown and annealed samples with Ru metal, respectively.