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Suppression of silicidation and crystallization by atmosphere controlled annealing for poly-Si/HfO_2/SiO_2/Si gate stack structures

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Introduction

For the shrinking of ultra-large scale integration (ULSI) device size, high dielectric constant (high-*k*) materials are utilized for gate dielectrics. HfO_2 is one of the most promising candidates because of its high dielectric constant and wide band gap. However, there are several problems to be solved such as Hf silicide (Si alloy) formation and crystallization during a dopant activation annealing, since silicidation and crystallization cause an increase in gate leakage current and instability of the threshold voltage, respectively. For this purpose, precise optimization of annealing atmosphere to prevent both silicidation and crystallization is necessary. In this study, we have used a mixture gas consisting of high-purity nitrogen gas with a small amount of high-purity oxygen gas.

Experimental

2 nm HfO_2 gate dielectrics and 3 nm poly-Si gate electrodes were deposited on clean *p*-type Si substrates by sputtering. After the deposition, we performed surface cleaning by a diluted HF solution and annealing at 800 °C for 1 min by a direct current flowing method in various atmospheres such as a mixture gas (nitrogen: oxygen = 19: 1), nitrogen, and oxygen. After annealing, synchrotron radiation photoemission spectroscopy and XAS measurements were carried out at BL-2C of the Photon Factory in High-Energy Accelerator Research Organization (KEK). In the measurements of photoemission spectroscopy, the photon energy was set to be 800 eV. The total energy resolution at room temperature was about 0.35 eV. XAS measurements were performed by a total-electron-yield mode.

Results and Discussion

Figures 1 (a) and (b) show the total gas pressure dependence of Hf 4*f* core-level photoemission and O *K*-edge absorption spectra for the mixture gas annealing. By annealing at the low total gas pressure ($P_{total} = 2\times10^{-4}$ Torr), a Hf silicide peak component is clearly observed in Hf 4*f* core-level photoemission spectrum at the binding energy around 14.5 eV. In the O *K*-edge absorption spectrum, there are peak components marked by the solid triangles in the high photon-energy region, indicating that the HfO_2 layer has been crystallized.[1] By annealing at the higher total gas pressure ($P_{total} = 4\times10^{-4}$ Torr), the silicide peak component disappears, while crystallization of the HfO_2 layer occurs. It is confirmed by the results of Hf 4*f* core-level photoemission and O *K*-edge absorption spectra that both silicidation and crystallization are suppressed by the annealing in $P_{total} = 1\times10^{-3}$ Torr. Subsequently, we performed the single gas annealing using only nitrogen ($P_{N_2} = 9.5\times10^{-4}$ Torr) or oxygen ($P_{O_2} = 5\times10^{-5}$ Torr) in order to investigate the annealing effect of each gas. Both silicidation and crystallization occur in the case of the nitrogen annealing, while silicidation does not occur but crystallization occurs by the oxygen annealing. Considering that the mixture gas annealing suppresses both silicidation and crystallization, nitrogen and oxygen may have different effects on the suppression each other. Thus, we conclude that the mixture gas can suppress both silicidation and crystallization, and that the suppression itself depends on the total pressure of the mixture gas.

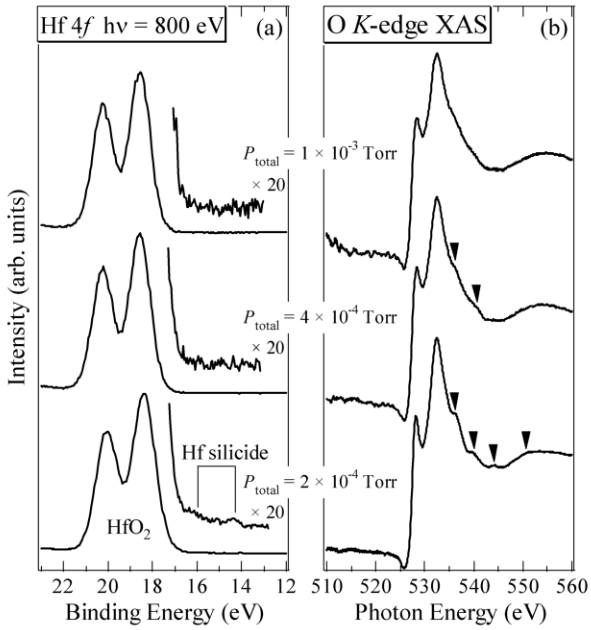

Fig. 1. Total gas pressure dependence for the mixture gas annealing in (a) Hf 4*f* core-level spectra and (b) O *K*-edge absorption spectra.

Reference

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