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In-depth profiles of Hf-based gate insulator films on Si substrates studied by angle-resolved photoemission spectroscopy

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Introduction

High dielectric (high-*k*) transition metal oxide materials such as ZrO_2, HfO_2, and their silicates are widely investigated to reduce the leakage current from channel to gate, because SiON gate dielectrics have reached a physical thickness scaling limit of complementary metal-oxide-semiconductor (CMOS) devices. Among them, HfSiO and nitrided HfSiO are promising candidates due to appropriate band gap, soft reactivity to the Si substrate, and suppression of crystallization. Understandings of in-depth profiles and microscopic bonding states at the the high-*k*/SiO_2 interfaces are necessary after annealing since V_{th} of metal/high-*k* gate stack structures on the Si substrates readily change through dopant activation processes. In this study, we have demonstrated annealing effects on in-depth profiles and local structures in the HfSiO films by angle-resolved photoemission spectroscopy.

Experimental

HfSiO films with thicknesses of 2.0 nm were deposited on 0.7 nm SiON interfacial layers using atomic layer deposition. The physical thicknesses of the HfSiO films and the SiON interfacial layer were estimated by ellipsometry. Annealing was performed at 850 °C and 1050 °C for 1 min in a nitrogen gas of 1 atm. Photoemission measurements were performed at BL-2C of the Photon Factory. Photoelectron emission angles (θ_e) were changed from the surface normal to 60° for enhancement of surface sensitivity. To analyze in-depth profiles from angle-resolved core-level photoemission spectra, the maximum entropy method was utilized [1]. The validity of the in-depth profiles was confirmed by comparison with Rutherford backscattering spectrometry (RBS).

Results and Discussion

Figure 1 shows annealing temperature dependence of in-depth profiles in the HfSiO films. The in-depth profiles present a complicated layer structure even at the as-grown stage. Si concentrations are high in both surface and interface regions and nitrogen atoms are slightly distributed at the interfacial layer. Accumulation of Si atoms at the surface and interface is known by the ALD growth and the in-depth profile in the as-grown sample is quantitatively confirmed by RBS measurements. Changes in the in-depth profiles by annealing suggest that Si oxide components diffuse from the interfacial SiO_xN_y layer into the HfSiO layer and concentrations of Hf relatively decrease. It is possible that oxidation of the Si substrate occurs by residual oxygen in N_2 ambient [2]. These structural changes affect electrical properties of the gate insulator film such as capacitance, leakage current, and carrier motilities. These analyses consequently would be utilized to investigate the relationship between chemical structures and device characteristics.

References

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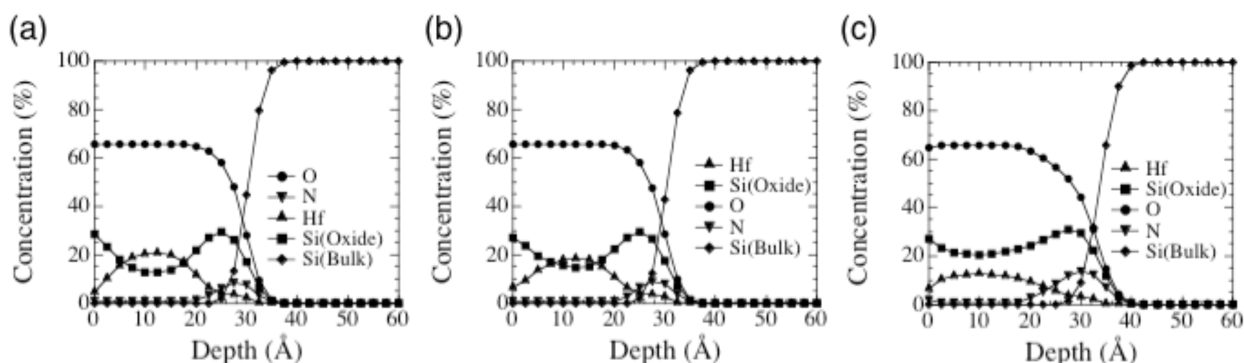

Fig. 1. Annealing-temperature dependence of in-depth profiles in the HfSiO films; (a) as-grown, (b) 850 °C and (c) 1050 °C.