

## Thermal stability of TiN/HfSiON gate stack structures studied by synchrotron-radiation photoemission spectroscopy

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### Introduction

Aggressive scaling of nano-scale devices to improve performance has been pursued on the conventional poly-Si/SiO<sub>2</sub> system for complementary metal-oxide-semiconductor (CMOS) field effect transistors. TiN metal gate electrode on Hf-based high dielectric (high-*k*) materials is one of the promising candidates for next generation device applications, with the effective work function for *p*-type and *n*-type MOS appropriately controlled. In order to establish optimum device fabrication processes, the study of thermal stability during high temperature annealing in metal/high-*k* systems is of great importance, leading us to proper guidelines for degradation or improvement in device performance. Photoemission spectroscopy is one of the most powerful techniques to reveal chemical bonding states in metal gate on high-*k* gate insulator. In addition, non-destructive depth profiles during annealing processes can be derived by analysis of angle-resolved core-level photoemission spectra. In this study, we have investigated the thermal stability of TiN/HfSiON gate stack structures, using synchrotron-radiation photoemission spectroscopy.

### Experimental

HfSiON films with thicknesses of 2.0 nm were deposited on 0.7 nm SiON interfacial layers using atomic layer deposition. The physical thicknesses of HfSiON films and SiON interfacial layers were estimated by ellipsometry. TiN films were deposited by radio-frequency sputtering in an ambient gas mixture of N<sub>2</sub> and Ar, monitoring deposition rates by quartz crystal microbalance. After annealing the samples, *in situ* photoemission measurements were carried out at BL-2C of the Photon Factory in High Energy Accelerator Research Organization (KEK), which is equipped with a high performance photoelectron analyser (VGScienta SES2002). The total energy resolution was estimated to be about 0.15 eV for photon energy of  $h\nu = 630$  eV mainly used in this study. Photoelectron emission angles ( $\theta_e$ ) were changed from the surface normal to 60° for enhancement of surface sensitivity, to extract depth profiles from angle-resolved core-level photoemission spectra. We have used an algorithm based on the maximum entropy method, where the validity is

confirmed by comparison with depth profiles determined by Rutherford backscattering spectroscopy (RBS).

### Results and Discussion

Core-level photoemission spectra systematically show Ti-O bonding states change into SiO<sub>2</sub> compounds in the TiN/HfSiON system with increasing annealing temperature, which can be related to the degradation of thermal stability. [1]. In order to correlate with the mechanism of the interfacial reactions in the TiN/HfSiON gate stack structure, (a) atomic concentration and (b) chemical-state-resolved depth profiles are obtained by intensities of angle-resolved core-level photoemission spectra as shown in Fig. 1. Thicknesses and compositions of each layer coincide with the growth condition and TiN/HfSiON gate stack structures are well represented. Note that oxygen is distributed at the surface of the TiN metal gate layer, which may come from bond breaking of Hf-O and Si-O configurations in HfSiON films during the TiN growth. This is consistent with the results of the Ti 2*p* and O 1*s* core-level spectra. Chemical state resolved depth profiles are presented in Fig. 1(b), revealing that TiSi<sub>*x*</sub> and HfN<sub>*y*</sub> components are localized at the TiN/HfSiON interface. It is found that Si atoms move into the TiN layer on top of the HfSiON film and the formation of Ti-Si bonds occurs, which is closely related to the bond breaking of Si-O bonds and diffusion of Si atoms at the TiN surface.

### References

[1] S. Toyoda *et al.*, *J. Surf. Anal.* **15**, 299 (2009).  
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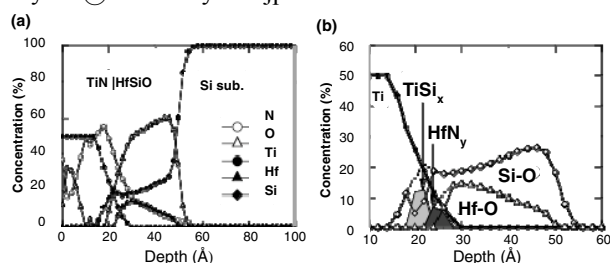


Fig. 1; (a) Atomic concentration and (b) chemical-state-resolved depth profiles are shown for TiN as-grown sample.