

## Fluorescence XAFS analysis of thermal stability for Ru/HfSiON/SiON/Si gate stack structure

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### 1. Introduction

Metal gate/high-dielectric metal oxide (high- $k$ ) gate stack technology has attracted considerable attention for the future scaling and performance improvement of complementary metal-oxide-semiconductor devices [1]. However, in high-temperature annealing processes for dopant activation the metal gate/high- $k$  stacks remains serious issues such as such as formation of metallic component and diffusion of metal, resulting increase of leakage current. It is important to resolve these problems in order to improve the device performance.

In this work, thermal stability of geometric structures for Ru/HfSiON/SiON/Si films was investigated by using fluorescence x-ray absorption fine structure (XAFS) measurement at Hf L- and Ru K-edge.

### 2. Experimental

Amorphous HfSiON ([N] = 10%) films with thickness of 2 nm were deposited on clean p-type Si (001) substrates by atomic layer deposition. There was a 0.7-nm-thick SiON interfacial layer between a Si substrate and the HfSiON film. Ru gate electrodes were deposited by magnetron sputtering. Each sample was annealed at 1050 °C for various annealing time in N<sub>2</sub> gas ambient. As reference, 100-nm-thick Ru film on glass and RuO<sub>2</sub> powder are also measured.

The XAFS measurements were performed at the bending-magnet beam line BL14B2 at the SPring-8 with a Si(111) double crystal monochromator using synchrotron radiation from the 8GeV storage ring. The XAFS spectra for the HfSiON films were measured in the fluorescence-detection mode. Intensity of incident X-ray beam was monitored by a nitrogen-filled ionization chamber, while the X-ray fluorescence signal was detected by an array of 19 elements of Ge solid state detectors. All the XAFS measurements were performed at room temperature. The XAFS spectra were analyzed by REX 2000 XAFS analysis package [2].

### 3. Results and discussion

Figure 1 represents Fourier transformed Hf L<sub>III</sub>-edge  $k^3\chi(k)$  extended x-ray absorption fine structure (EXAFS) spectra for the Ru/HfSiON films. For all

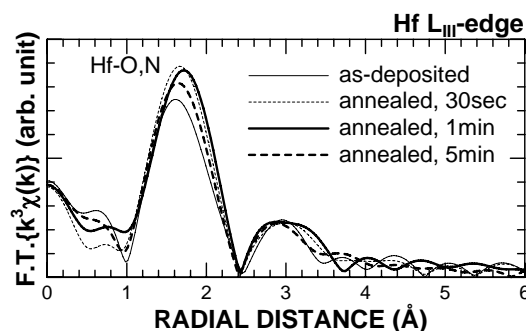


Fig.1 Fourier transform of Hf L<sub>III</sub>-edge EXAFS oscillation functions  $k^3\chi(k)$  spectra for Ru/HfSiON films. The Fourier transformation was performed in the  $k$  range of 3.0 – 9.0 Å<sup>-1</sup>.

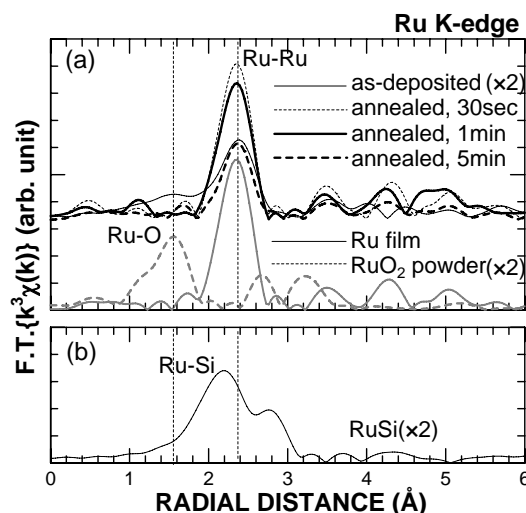


Fig.2 Fourier transform of Ru K-edge EXAFS oscillation functions  $k^3\chi(k)$  spectra for (a) Ru/HfSiON films, Ru film, and RuO<sub>2</sub> powder, and (b) theoretical EXAFS spectra for RuSi. The Fourier transformation was performed in the  $k$  range of 3.0 – 15.0 Å<sup>-1</sup>. Theoretical EXAFS spectrum was generated by FEFF8 [3].

the films, the main peaks were observed at 1.6 Å, which are due to Hf-O and Hf-N bonds. It is found that the feature of the main peak does not change by annealing. Figure 2 shows Fourier transformed Ru K-edge  $k^3\chi(k)$  EXAFS spectra for the Ru/HfSiON films. For the as-deposited and 5 min-annealed films, the height of the main peaks at 2.4 Å which are due to Ru-Ru bond in Ru metal becomes smaller than that for the 30 sec- and 1 min-annealed films. In addition, for the as-deposited film the additional peak was observed at 1.6 Å, which is due to Ru-O bond in RuO<sub>2</sub>. In order to investigate the details of the measured EXAFS spectra, parameter fitting for the EXAFS spectra in Fig.1 and 2 was conducted with the theoretically generated spectra. At Hf L<sub>III</sub>-edge, change of obtained parameter such as bond length and coordination number was not observed, which indicating that the local structures around Hf atom are not changed by annealing. On the contrary, it is found that at Ru K-edge each parameter changed by annealing. In the as-deposited film Ru-Ru and Ru-O bonds coexisted, and the Ru-O bond was not disappeared by the annealing, indicating that in the as-deposited film a part of Ru metal is oxidized, and the component of Ru oxide is fully reduced by annealing. In addition, coordination number of Ru atom for the annealed films decreased with annealing time, suggesting the local structures around Ru atom change with annealing time.

Figure 3 represents Ru K-edge x-ray absorption near edge structure (XANES) spectra for the Ru/HfSiON films. In Fig.3, intensities of white line around 22140 eV decreased and absorption edge at 22115 eV shifted toward lower energy by

annealing. Compared to the XANES spectra of Ru film and RuO<sub>2</sub> powder, it is considered that the change of XANES spectra is due to the reduction of Ru oxide in the as-deposited film, coinciding the result of EXAFS measurements. Although the intensities of white line increased with annealing time, the shift of the absorption edge was not observed for the increase of annealing time. Compared to the theoretically calculated XANES spectra for Ru and RuSi in Fig. 3(b), it is expected that the change of white line is due to the formation of RuSi. In Fig.2 (b), the EXAFS spectrum for RuSi is too small to identify that for the Ru/HfSiON films. Thus, it is considered that the decrease of coordination number with annealing time is due to the silicidation of Ru metal.

### 3. Conclusions

In this work, thermal stability of geometric structures for Ru/HfSiON/SiON/Si films was investigated by using fluorescence XAFS measurement. The XAFS analysis has revealed that in the as-deposited film a part of Ru metal is oxidized, and the component of Ru oxide is fully reduced by annealing. In addition, it is revealed that in the annealed films Ru silicide is formed partially, and the amount of the Ru silicide increases with annealing time. These results indicate that the appropriate annealing condition prevent the oxidation and silicidation of the metal gate Ru layer.

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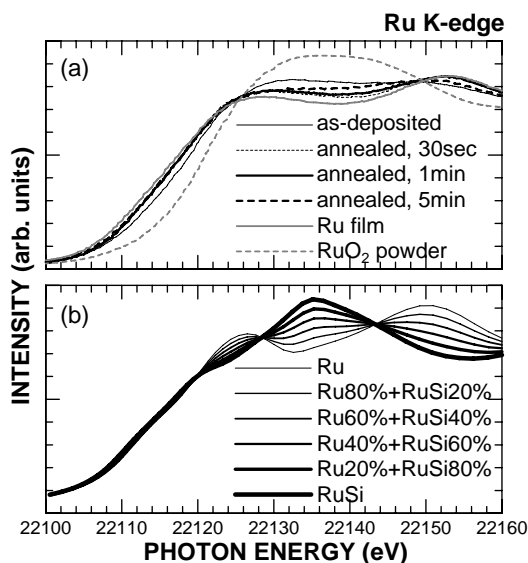


Fig.3 (a) Ru K-edge XANES spectra for Ru/HfSiON films, Ru film and RuO<sub>2</sub> powder, and (b) Ru K-edge XANES spectra for Ru and RuSi theoretically generated by FEFF8 [3].