Hafnium dioxide (HfO\(_2\)) has promising potential as an alternative material of silicon dioxide (SiO\(_2\)) used as a gate oxide film in metal-oxide-semiconductor field effect transistor (MOSFET) due to its high permittivity (\(k \approx 21\)), large bandgap (~5.7 eV), and thermal stability\(^1,2\). The application of ideal HfO\(_2\) film allows us to reduce the effective thickness of gate oxide film continuously without serious leakage current which happens through ultrathin SiO\(_2\) gate film. Therefore, to understand the oxidation dynamics at surface and interface of ultrathin hafnium (Hf) film composed on Si(100)-2\times1 [Hf/Si(100)] is one of the most significant issues for the sustainable development of Si semiconductor devices. In this study, we investigated Hf and silicon (Si) oxidation processes depending on different Hf chemical states by means of the Si 2p\(_{1/2, 3/2}\), Hf 4f\(_{5/2, 7/2}\), and O 1s core-level photoelectron spectroscopy combined with synchrotron radiation soft X-ray at BL23SU of SPring-8.

As our result, Hf and Si in Hf/Si(100) are immediately oxidized up to be HfO\(_2\) (Hf\(^{4+}\)) and SiO\(_2\) (Si\(^{4+}\)) by exposure to O\(_2\) molecules because metallic Hf component which generates just after Hf deposition works like oxidation enhanced catalysis\(^3\). On the other hand, the metallic Hf component could be turned into island Hf disilicide component [\(i\)-HfSi\(_2\)/Si(100)] after annealing around 1073 K. After exposure the \(i\)-HfSi\(_2\)/Si(100) to O\(_2\) molecules, the \(i\)-HfSi\(_2\) hardly reacts with O\(_2\) molecules because it doesn’t act as catalysis. Therefore, the oxidation of Si(100) substrate was suppressed drastically.

Our study indicates that the Hf chemical states have a major influence on Si oxidation dynamics.

**References**