

High-resolution analysis of the HfO₂-SiO₂ interface by soft x-ray photoelectron spectroscopy

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The current trend to attempt integrating new high-permittivity dielectric oxides in advanced (sub-0.1 μm) CMOS technology in replacement of SiO₂ requires extremely fine control of the hetero-interface with the substrate. Promising dielectrics as HfO₂, when deposited by Atomic Layer Deposition (ALD), have usually to be grown onto an ultra-thin SiO₂ layer that is prone to re-growth upon subsequent treatments of the SiO₂/HfO₂ oxide gate stack. Using x-ray photoelectron spectroscopy it is possible to address the two important issues of interfacial layer re-growth metrology and precise chemical analysis of the SiO₂/HfO₂ interface. This latter goal is best achieved when bright soft x-rays of a synchrotron source are used, yielding enhanced surface sensitivity, high energy resolution and signal-to-noise ratio.

Such measurements were performed at the Super-ACO storage ring on beamline SA73, at an overall energy resolution of 0.15 eV, on SiO₂ 0.7 nm/Si (100) samples before and after *ex-situ* HfO₂ deposition by ALD [1]. SiO₂ layers were obtained by wet oxidation using ozonated deionized water after an HF-last step, and produce Si 2p spectra as shown in Fig. 1b, with typical features related to fully oxidized Si and sub-oxide species located at the Si/SiO₂ interface; the energy shift (table 1) of these features are in agreement with those reported for an in-situ grown, thermal SiO₂ film. After HfO₂ deposition, an additional oxidation state of Si clearly emerges between Si⁴⁺ and Si³⁺ (fig. 1a). We assign this extra-component to the spectral fingerprint of Hf-silicate bonds that form at the SiO₂-HfO₂ interface from interfacial Si⁴⁺, probably over 1-2 ML. The lower energy shift (table 1) of the silicate feature relative to the Si⁴⁺ one arises from enhanced charge transfer from the Hf atom to the silicate Si-O bond, compared to the Si-O-Si situation (i.e, this is a second-nearest neighbor effect). This view agrees well with the Hf 4f spectra (fig. 2), which also exhibit an extra component (fig. 2b) to higher energy assignable to Hf silicate, in the case of ultra-thin HfO₂. For thicker (fig. 2a), this interfacial component is no longer observed.

The identification of the spectral fingerprints of interfacial bonds in SiO₂-HfO₂ systems should allow further quantitative treatment of the intensities; this point will also be addressed in the presentation.

[1] O. Renault *et al.*, *Appl. Phys. Lett.* **81** (19) (in press).

[2] F. J. Himpsel *et al.*, *Phys. Rev. B* **38**, 6084 (1988).

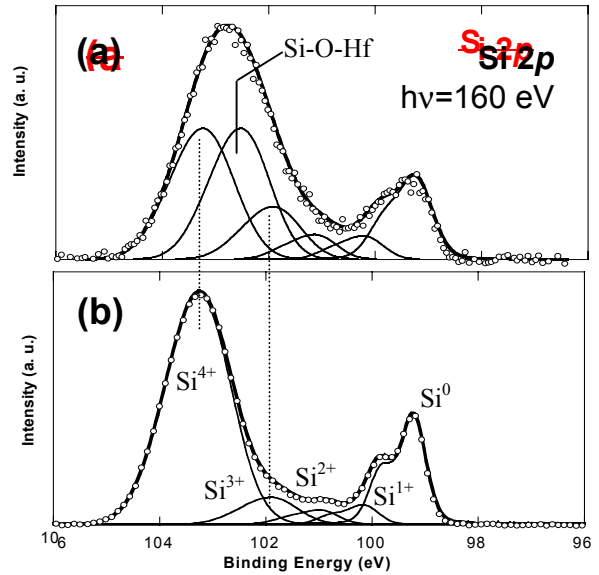


Fig. 1. High-resolution Si 2p spectra recorded at 160 eV photon energy of (a) 0.7 nm SiO₂/Si (before HfO₂ deposition); (b) 0.6 nm HfO₂/0.7 nm SiO₂/Si.

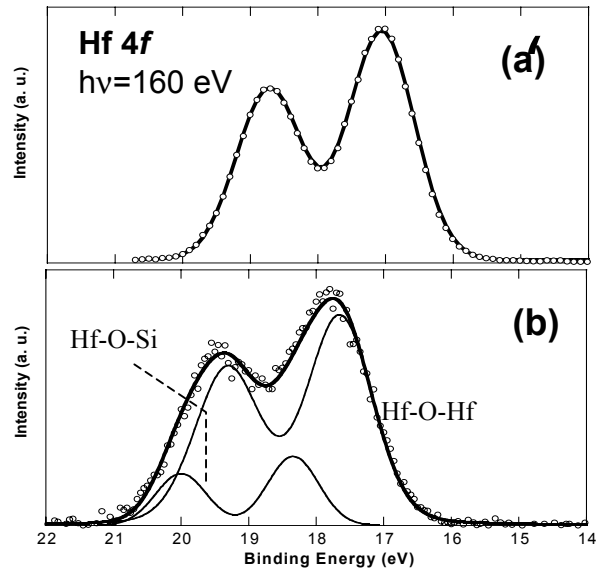


Fig. 2. High-resolution Hf 4f spectra at 160 eV of (a) 2.5 nm HfO₂/0.7 nm SiO₂/Si; (b) 0.6 nm HfO₂/0.7 nm SiO₂/Si (binding energies are referred to the Fermi level).

Oxidation state of Si	Energy shift (eV)		
	Ref. [2]	SiO ₂ /Si	HfO ₂ /SiO ₂ /Si
Si ¹⁺	0.95	0.93	0.94
Si ²⁺	1.75	1.73	1.83
Si ³⁺	2.48	2.56	2.56
Si-O-Hf	-	-	3.16
Si ⁴⁺	3.90	3.89	3.86

Table 1. Energy shift of each Si oxidation state extracted from spectra of fig. 1 after deconvolution.