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ELEMENTAL QUANTIFICATION OF HAFNIUM–SILICATES BY ELECTRON ENERGY LOSS SPECTROSCOPY

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Hafnium-silicate thin films are potential candidates to replace SiO_2 as the gate-dielectric in semiconductor devices [1]. Elemental analysis of the gate-dielectric composition is necessary to understand relationships between processing conditions and electrical performance. Electron energy loss spectroscopy (EELS) recorded in a scanning transmission electron microscope (STEM) has been used for spatially resolved quantification of traditional gate dielectric stacks [2]. However, previous characterization of hafnium-silicates has been limited to qualitative elemental analysis [3], in part due to complications from plural scattering. In this work the composition of hafnium-silicate films is quantified using Hartree-Slater partial ionization cross-sections.

EEL spectra were recorded for hafnium-silicate films, as deposited by atomic layer deposition (ALD), with concentrations ranging from 30 to 63 mol.% SiO_2 as verified by Rutherford backscatter spectrometry (RBS), (Table 1). TEM cross-sections were prepared by focused ion beam (FIB) [4], as this technique provided a more planar surface than ion milling, which tended to make the hafnium-silicate layer bulbous due to differential milling (Figure 1). Both high and low energy-loss spectra were acquired at 1eV/pixel and stitched together (Figure 2). Elemental quantification was performed using commercially available software [5] to analyze the O-K, Hf-$M_{4,5}$ and Si-K. Sample thicknesses less than $0.3t/\lambda_{Si}$ (<60nm) were necessary to minimize plural scattering effects that otherwise hindered accurate quantification [6].

Elemental compositions of ALD hafnium-silicate films quantified by comparing core-loss intensities using Hartree-Slater determined partial ionization cross-sections are in good agreement with RBS data (Table 1). However, the success of this approach required long acquisition times of the low intensity Hf-$M_{4,5}$ and Si-K signals, while rastering a small probe over a large area to prevent beam-induced sample damage. For dielectric thin film process development, it would be desirable to measure changes in stoichiometry across a 3-4 nm thick dielectric film with sub-nanometer spatial resolution. To this end, multiple least squares (MLS) fitting of low-loss spectra, acquired with low probe current and short spectral acquisition time, is used for quantification at high spatial resolution.

[1] G. D. Wilk, R. M. Wallace, and J. M. Anthony, J. Appl. Phys. **89**, 5243 (2001).
[2] H. Stegmann and E. Zschech, Appl. Phys. Lett. **83**, 5017 (2003)
[3] B. Foran, J. Barnett, P. S. Lysaght, M. P. Agustin and S. Stemmer, J. of Electron Spectroscopy and Related Phenomena **143**, 151 (2005).

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[4] Sample preparation was performed by Maria Hall and Charlene Johnson at ATDF.
[5] Digital Micrograph V. 3.7.1. Gatan Inc. http://www.gatan.com
[6] N. Zaluzec, 41st Ann. Proc. Electron Microsc. Soc. Am., 388 (1983).

TABLE 1. ALD hafnium-silicate film compositions as quantified by RBS and EELS.

	RBS (at.%)			**EELS (at.%)**		
mol.% SiO_2	Hf	Si	O	Hf	Si	O
30	22	10	68	22	9	67
45	18	15	67	17	16	67
54	15	18	67	14	19	67
63	11	21	68	10	22	68
Uncertainty	*1*	*1*	*4*	*1*	*1*	*3*

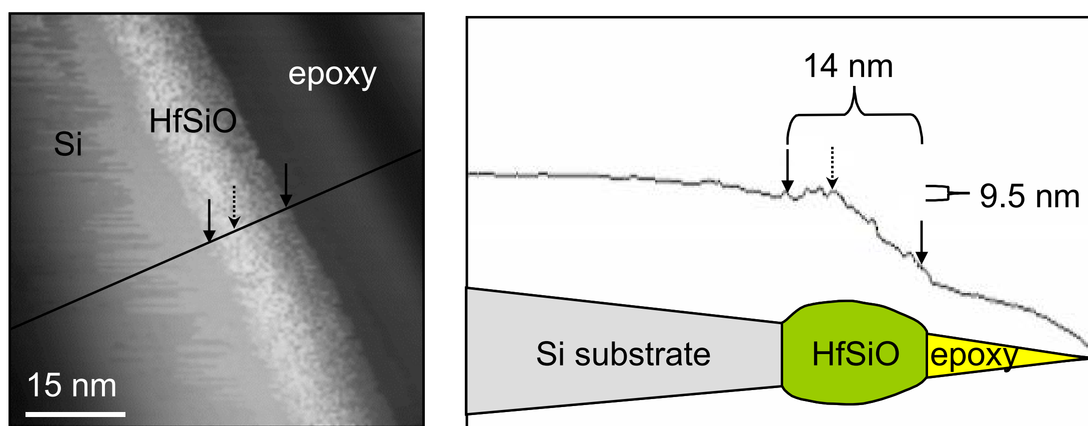

Fig 1. Atomic force microscopy (AFM) image of a 63 mol.% SiO_2 sample prepared in cross-section by ion milling and corresponding surface profile and cartoon.

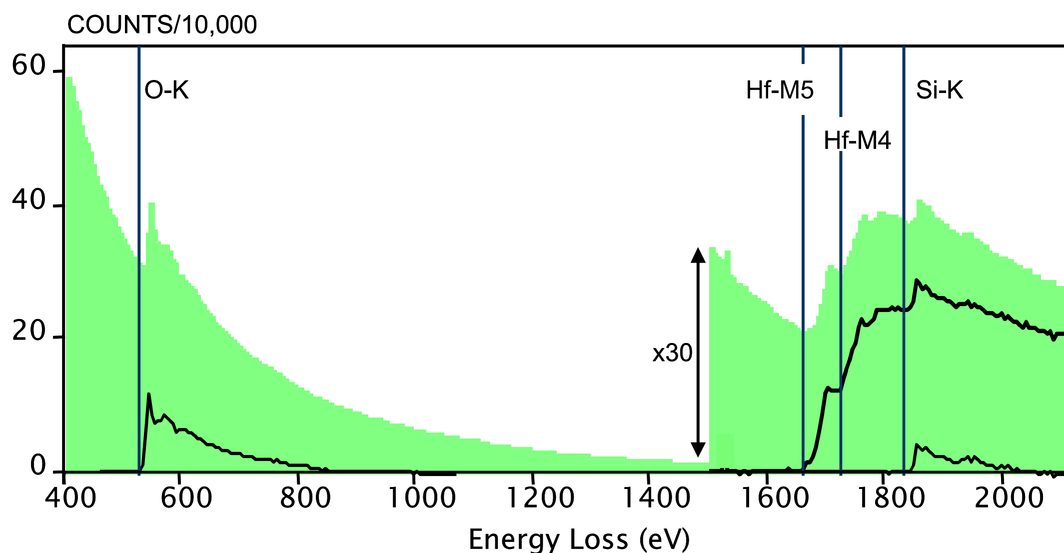

Fig 2. Electron energy loss spectra from a 40 mol.% SiO_2 ALD hafnium silicate were acquired at a dispersion of 1.0 eV/pixel. The integration windows were from 640 to 670 eV for O-K, 1790 to 1820 eV for Hf-$M_{4,5}$ and 1899 to 1929 for Si-K.

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