AN 400
Hafnium Oxide (HfO_2) Composition and Stoichiometry

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Discussion

Hafnium oxide and hafnium silicates are among the leading contenders for new high-κ gate dielectric films. Material properties need to be tested, and characterization of films is required to verify theory, ascertain best-candidates, delimit process conditions, etc. Tests with actual devices, i.e. transistors with high-κ gates, are too costly and time consuming (requires a nearly complete device production cycle). Earlier in-process tests and process control checks are desired such as thickness, composition, dopant diffusion, impurities, etc.

Standard measurement methods used for SiO_2 may not be able to provide sufficient information for correct composition or stoichiometry coefficients of high-κ materials. XPS has a depth of information (~30-90Å) and matrix-independent quantification that makes it ideal for high-κ dielectric films. Even so, a simple XPS measurement of total O and total Hf can result in an incorrect ratio of O:Hf (see first line in Table 1). A more correct analysis must measure and determine the O and Hf as HfOx and be able to report total composition (i.e. C, O, Hf, Zr, etc. in at%) and the stoichiometry of the films.

XPS can easily distinguish between O bound to HfO_2 and O bound to other sources (see Figure 1). Removing the contribution of O bound to other sources from the total O results in an O/Hf ratio much closer to the theoretical value of 2 (see second line in Table 1).

Table 1

	O1s		C1s	Hf4f	Ratio	
Total O Method	63.6at% (total)		11.7at%	24.8at%	Total O:Hf =	2.57 (~Hf_2O_5)
Corrected O Method	51.6at% (HfO_2)	12.0at% (Other O)	11.7at%	24.8at%	Corr. O:Hf =	2.09 (~HfO_2)

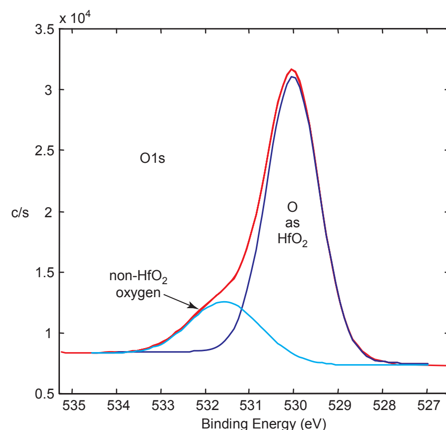

Figure 1. XPS Spectrum of HfO_2 O Window

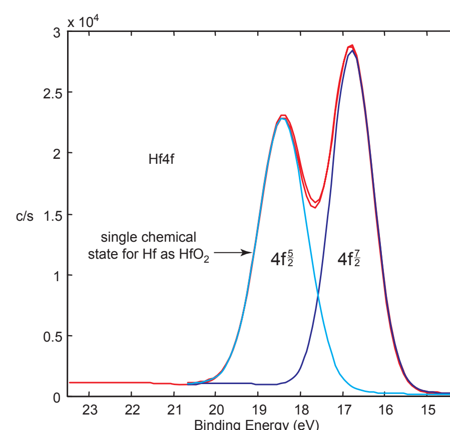

Figure 2. XPS Spectrum of HfO_2 Hf Window

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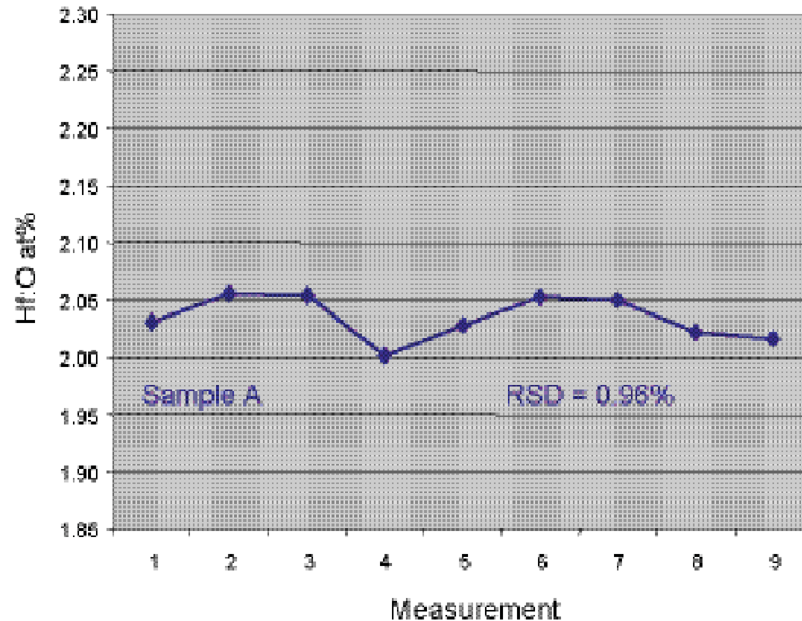

Figure 3. Reproducibility Hf:O Corrected

The reproducibility of this measurement by XPS is very good. Figure 3 shows the reproducibility of the Hf/O ratio using the Corrected O Method for a typical sample.

- 9 measurements each
- S/N set for <0.3% precision
- Largest error from O1s curve fit repeatability
- Data for films >9nm and pure HfO_2
- Precision decreases with interfacial oxides, silicates, and oxidized impurities
- Electron IMFP/EAL correction not applied

IMFP - Inelastic Mean Free Path
EAL - Effective Attenuation Length
S/N - Signal-to-Noise

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