AN 400
Hafnium Oxide (HfO_2) Composition and Stoichiometry

May 7, 2007 (Version 3.0)

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)

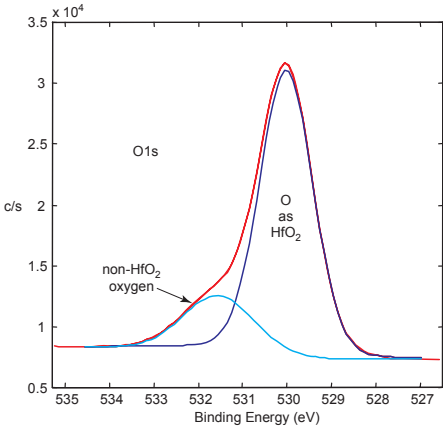

Figure 1. XPS Spectrum of HfO_2 O Window

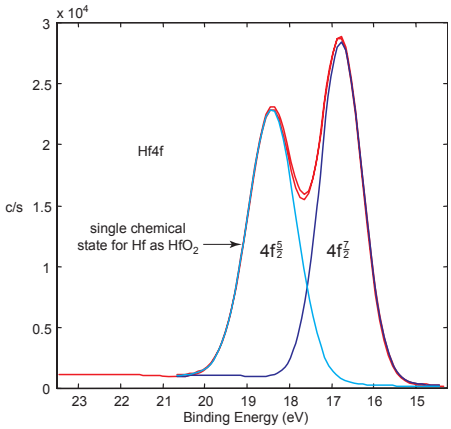

Figure 2. XPS Spectrum of HfO_2 Hf Window

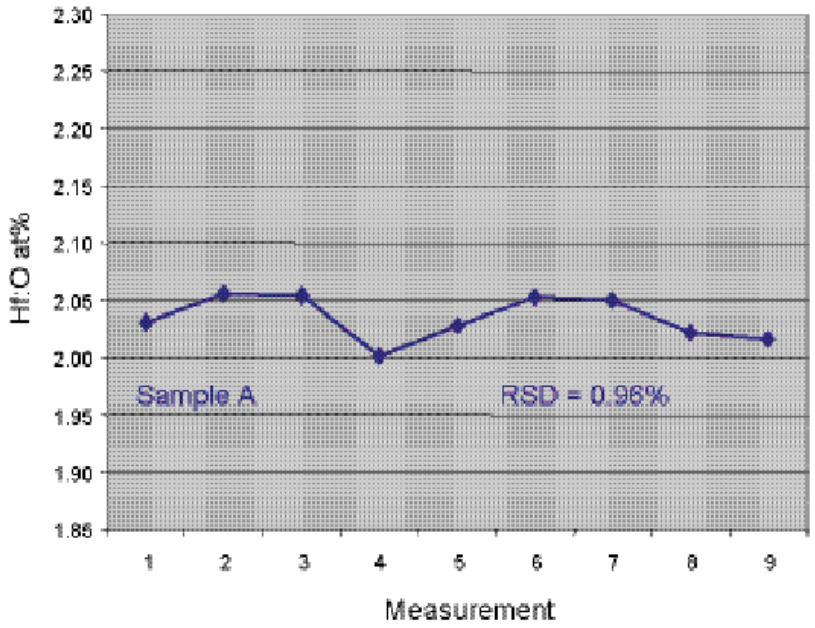

Figure 3. Reproducibility Hf:O Corrected

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 HfO2
- 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

United States Locations

Tempe, Arizona
+1 480 239 0602 info.az@eaglabs.com
+1 602 470 2655 fax

Sunnyvale, California
810 Kifer Road
+1 408 530 3500 info.ca@eaglabs.com
+1 408 530 3501 fax

1135 E Arques Avenue
+1 408 738 3033
+1 408 738 3035 fax

785 Lucerne Drive
+1 408 737 3892
+1 408 737 3916 fax

Peabody, Massachusetts
+1 978 278 9500 info.ma@eaglabs.com
+1 978 278 9501 fax

Chanhassen, Minnesota
+1 952 828 6411 info.mn@eaglabs.com
+1 952 828 6449 fax

East Windsor, New Jersey
+1 609 371 4800 info.nj@eaglabs.com
+1 609 371 5666 fax

Syracuse, New York
+1 315 431 9900 info.ny@eaglabs.com
+1 315 431 9800 fax

Raleigh, North Carolina
+1 919 829 7041 info.nc@eaglabs.com
+1 919 829 5518 fax

Round Rock, Texas
+1 512 671 9500 info.tx@eaglabs.com
+1 512 671 9501 fax

International Locations

Shanghai, China
+ 86 21 6879 6088 info.cn@eaglabs.com
+ 86 21 6879 9086 fax

Tournefeuille, France
+ 33 5 61 73 15 29 info.fr@eaglabs.com
+ 33 5 61 73 15 67 fax

Frankfurt, Germany
+ 49 (0) 693053213 info.de@eaglabs.com
+ 49 (0) 69307941 fax

Tokyo, Japan
+ 81 3 5396 0531 info.jp@eaglabs.com
+ 81 3 5396 1930 fax

HsinChu, Taiwan
+ 886 3 5632303 info.tw@eaglabs.com
+ 886 3 5632306 fax

Uxbridge, United Kingdom
+ 44 (0) 1895 811194 info.uk@eaglabs.com
+ 44 (0) 1895 810350 fax