AN 415
Thin Film Hafnium Oxide (HfO_2) Thickness, Composition, and Uniformity Measurements by XPS

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Discussion

Fabrication of high-κ dielectrics such as HfO_2, used in semiconductor devices as a gate dielectric or capacitor dielectric, will require precise control of the film thickness, composition and stoichiometry, as well as film uniformity across a wafer and wafer-to-wafer. Failure to monitor and control any one of these factors will adversely affect the device performance and yield of the process. A HfO_2 *High Precision XPS Measurement* has been developed to characterize thin HfO_2 films on Si. Prior to this measurement, no one single technique could provide all of this information about the dielectric film in a rapid, precise, and cost-effective manner.

Semiconductor manufacturers, semiconductor process development groups, and deposition tool manufacturers need to control multiple properties of these ultra-thin dielectric films as early in the deposition process as possible to reduce costs and improve yields. Process development in particular requires feedback quickly and precisely in order to meet customer requirements for process tool design and performance. The deposition tool suppliers, be it MOCVD, PVD, or especially ALD, need to demonstrate the performance of their tools in depositing highly uniform ultra-thin films with constant composition and stoichiometry, and reliable thickness control.

As noted above, high-κ dielectric performance requires not only precise film thickness control, but because the dielectric constant is so high it is also very sensitive to compositional or stoichiometric changes. In the case of deposition of HfO_2 films on Si, the HfO_2 film has an interfacial layer of either SiO_2 or $Hf_xSi_{(1-x)}O_2$ (see Figure 1) that can substantially change the overall dielectric property of the film. (This is typically referred to as Equivalent Oxide Thickness, EOT, of an ideal equivalent SiO_2 film.) Therefore it is not only imperative to know the HfO_2 film thickness but also the interfacial silicate or SiO_2 film thickness. Thickness of both layers are possible with the HfO_2 *High Precision XPS Measurement*. For purposes of illustration, Table 1 shows the interfacial layer thickness and the HfO_2 thickness as determined by this measurement. The values in the first row of the table are the averages obtained from over 30 measurements across a Si wafer containing a thin HfO_2 layer.

Table 1. Layer Thicknesses and Stoichiometry of a thin HfO_2 film on Si

	Interfacial Layer Thickness (Å)	HfO_2 Thickness (Å)	Corrected O:Hf ratio
Avg.	12.14aa	39.95	2.50
Std. Dev. (1σ)	0.22	0.33	0.02
RSD%	1.83	0.83	0.85

Table 2. Composition of a thin HfO_2 film on Si

	Total Si^{4+} at%	Total Hf at%	Total O at%	Total C at%*	Uncorrected O:Hf ratio
Avg.	4.6	20.5	60.1	14.9	2.93
Std. Dev. (1σ)	0.11	0.24	0.37	0.56	-
RSD%	2.3	1.2	0.6	3.8	-

* Approximately 75% of the carbon is adsorbed C ('adventitious' C) on the surface and not in the layer. The remainder is within the film and/or the interface.

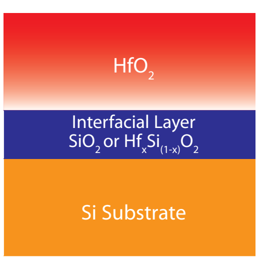

Figure 1. Schematic of HfO_2 film on Si substrate

Composition and stoichiometry of HfO_2 films can vary greatly depending on the process (i.e. MOCVD vs. ALD). Furthermore, the stoichiometry is not simply a measure of total O to total Hf concentrations. All thin HfO_2 films have some O associated with the interfacial layer that is not a part of the HfO_2 layer. In addition, all deposited films have surface-adsorbed O (in the form of carbon-oxygen functionalities, OH bonds, or H_2O) that is also not part of the HfO_2 film. Therefore a careful accounting of O as HfO_2 and non-HfO_2 composition is required to produce a meaningful O:Hf stoichiometry value. The third column in Table 1 shows the O:Hf stoichiometry corrected for O bonded to non-Hf species, whereas Table 2 shows the composition in atomic %. Again, the values in the tables are averages from multiple measurements on a single wafer. The total O:Hf ratio from the atomic concentrations is considerably higher than the corrected O:Hf ratio shown in Table 1. The excess O (Table 2) can be attributed to interfacial oxide, and surface-adsorbates, as noted above.

The corrected O:Hf ratio (Table 1) is higher than the theoretical value of '2' for HfO_2. While the calculated value for the corrected ratio is often 2 on many samples, the value of 2.5 on this film suggests that the film is O enriched.

As previously mentioned, determining the uniformity of the film thicknesses and compositions can be critical for process control. Figure 2 illustrates the capability of the HfO_2 *High Precision XPS Measurement* to determine uniformity of interfacial layer thickness, HfO_2 thickness and O:Hf ratio from a radial scan across a wafer. In this example, these parameters are uniform across the wafer.

The development of the HfO_2 *High Precision XPS Measurement* provides a single rapid acquisition and precise analysis that can yield critical information about HfO_2 dielectric films. This analysis provides a highly repeatable measurement of the thickness of the HfO_2 layer, the thickness of the interfacial layer, total film stack thickness (HfO_2 layer + interfacial layer), composition of the dielectric layer plus the interfacial layer, and the stoichiometry coefficient of the HfO_2 film.

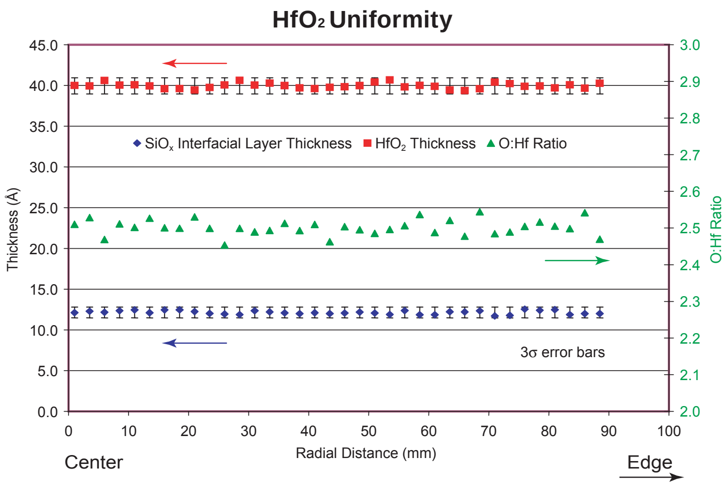

Figure 2. Uniformity of layer thickness and stoichiometry across a HfO2 film on a Si wafer

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