

## CHARACTERIZING PROCESS SEMICONDUCTOR THIN FILMS WITH A CONFOCAL MICRO X-RAY FLUORESCENCE MICROSCOPE

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### ABSTRACT

The versatility of confocal micro X-ray fluorescence (MXRF) in analyzing thin films on semiconductor wafers is demonstrated. Unlike conventional MXRF, confocal MXRF can depth profile sample layers and reduce spectral background. Non-destructive quantification of the silicon dioxide (SiO<sub>2</sub>) concentration in hafnium silicate (HfSiO) thin films is an example of one application demonstrating the advantage of confocal MXRF. Additionally, the growth of titanium nitride (TiN) films on various high-*k* gate dielectric substrates was analyzed with confocal MXRF due to its ability to detect sub-nm film thickness changes.

### INTRODUCTION

To maintain the expectations of Moore's Law, the *International Technology Roadmap for Semiconductors* proposes that new materials replace traditional ones in semiconductor processing [1]. Hafnium silicate (HfSiO) is a potential gate dielectric candidate that has a higher dielectric constant than either silicon dioxide (SiO<sub>2</sub>) or silicon oxynitride (SiON) and may have suitable robust properties for maintaining favorable electrical characteristics under device processing conditions [2]. Currently, various deposition processes for HfSiO are being evaluated in ATDF's fab. One parameter being assessed is the SiO<sub>2</sub> concentration (mol %) in HfSiO films. To ensure reproducible deposition of the films, a rapid, in-line, non-destructive metrology technique is necessary.

X-ray fluorescence techniques are well known for their excellent sensitivity to elemental composition, are non-destructive, and, therefore, are ideal for thin film analysis. This paper demonstrates the applicability of confocal micro X-ray fluorescence (MXRF) in characterizing HfSiO thin films (~ 15 nm) with varying mol % SiO<sub>2</sub> concentrations.

Atomic layer deposition (ALD) is currently being investigated for highly conformal film deposition and precise thickness control over hafnium silicates. This type of film is grown layer by layer, and obtaining a depth profile of these layers provides another facet of the material's characterization process. Consequently, the non-destructive depth profiling capabilities of confocal MXRF on these thin films is also explored.

Due to undesirable properties that can adversely alter the effective electrical thickness of the gate dielectric [3], new materials are also being investigated for the gate electrode. Titanium nitride

is a potential gate electrode material, which may replace polysilicon when high- $k$  gate dielectrics replace the conventional SiO<sub>2</sub> or SiON. The growth of a TiN gate electrode deposited on various gate dielectrics is characterized in this study as well.

## EXPERIMENTAL

The confocal MXRF microscope used in this study was an in-house built system designed in a joint project between Los Alamos National Laboratory and X-Ray Optical Systems (XOS, Albany, NY). To create a confocal analysis volume, both the source and the detector were fitted with polycapillary optics. The X-ray and detection polycapillary optics were positioned so that the focal point of each beam overlapped, creating the confocal analysis spot. The confocal analysis volume was an ellipsoid (30 x 30 x 60  $\mu\text{m}$ ). A sealed Ag tube source operating at 0.5 mA and 50 kV was used as the source. Acquisition time for spectral data collection was 100 s on an AmpTek detector. The samples were placed as received into the microscope and analyzed under ambient conditions. A depth profile was collected to determine the surface position, and spectra were collected at the surface.

HfSiO was deposited by ALD onto 200 mm diameter Si (100) wafers to create a target 15 nm film. The HfSiO wafers were broken into 1-inch square pieces to fit easily into the microscope's sample area. Film uniformity across a wafer by ALD is excellent (< 1% deviation); therefore, the broken wafer pieces were a reasonable representation of the entire film. Table 1 lists the characterized HfSiO films based on mol % and film thickness. The concentration of SiO<sub>2</sub> (mol %) and thickness of the films were determined by Rutherford backscattering spectrometry [4], except for the pure HfO<sub>2</sub> film for which the thickness was determined by spectroscopic ellipsometry [4].

Film (%)	Thickness (nm)
100% HfO <sub>2</sub>	10.0
33% SiO <sub>2</sub>	13.7
45% SiO <sub>2</sub>	13.0
55% SiO <sub>2</sub>	13.5
67% SiO <sub>2</sub>	8.8

Table 1. List of HfSiO films used in the study with varying concentrations of SiO<sub>2</sub> (mol %).

In addition, a series of TiN films was also deposited by ALD on top of various dielectrics. The series included 5–100 deposition cycles, during which each cycle deposited 0.12 nm of material. The dielectrics used in this study were 10 nm films of SiO<sub>2</sub>, HfSiO (20 mol % SiO<sub>2</sub>), and HfO<sub>2</sub>.

## RESULTS AND DISCUSSION

With the polycapillary optics on the source, a high X-ray flux reaches the sample in a tightly focused beam. The polycapillary optics beam on the detector overlaps with the focused X-ray

beam creating a confocal volume, thus excluding all other spatial areas except for the confocal region. When used in a confocal arrangement the optics allow for an increase in spatial resolution and a reduction of background counts [5, 6].

Figure 1 is the background subtracted Hf- $L_{\alpha}$  (7.9 keV) signal from the 10 nm HfO<sub>2</sub> film showing the excellent signal-to-noise of confocal MXRF. Samples with increasing concentrations of SiO<sub>2</sub> in the HfSiO film were then analyzed to establish a correlation between the mol % SiO<sub>2</sub> and the Hf signal from the confocal MXRF. Overlays of the Hf- $L_{\alpha}$  signal from the series of HfSiO films, with increasing mol % SiO<sub>2</sub>, are shown in Figure 2. Based on Figure 2, the Hf- $L_{\alpha}$  peak intensity decreases with increasing mol % SiO<sub>2</sub>, indicating that the confocal MXRF is capable of discriminating between changes in composition of the HfSiO thin films.

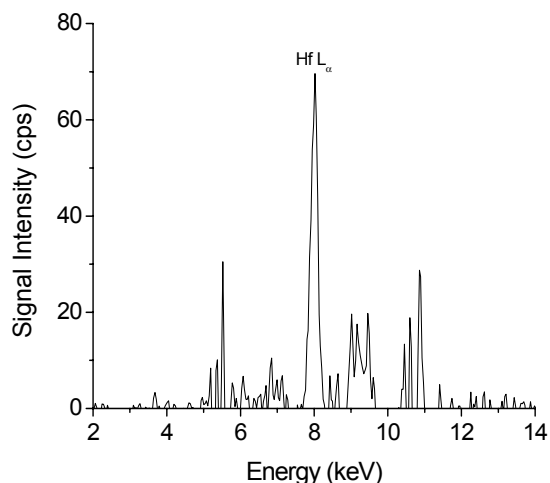


Figure 1: Background corrected Hf signal from a 10 nm HfO<sub>2</sub> film

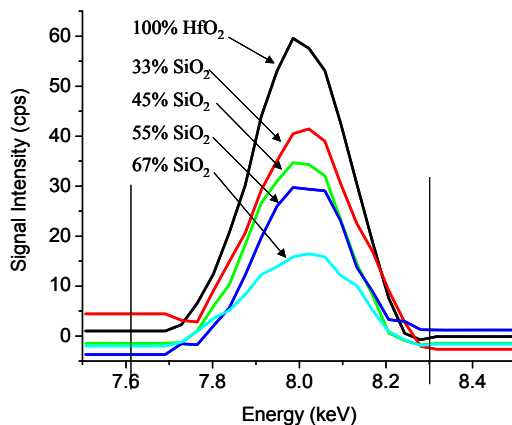


Figure 2: Overlays of Hf peak with increasing % SiO<sub>2</sub> in the deposited films

Calculating the area under the Hf- $L_{\alpha}$  peaks ( $\sim 7.6$ – $8.3$  keV as indicated by the vertical lines in Figure 2) and plotting it against the mol % SiO<sub>2</sub> in the films generates the relationship shown in Figure 3. The best-fit line has an  $R^2$  correlation value of 0.99, which is similar to the correlation to the same set of wafers measured by total reflection X-ray fluorescence (TXRF) [7]. The

TXRF used both a Ag anode operating at 600 W and a W anode operating at 400 W, while the MXRF's Ag anode was operating only at 25 W. The comparable sensitivity of both techniques to the compositional changes of the high- $k$  gate dielectric films with this large difference in power is a testament to the efficiency of the polycapillaries and the confocal arrangement of the optics of the confocal MXRF microscope. A future study will be to test how well the confocal MXRF can discriminate among different compositional 3 nm HfSiO films that are a closer representation of actual device process parameters.

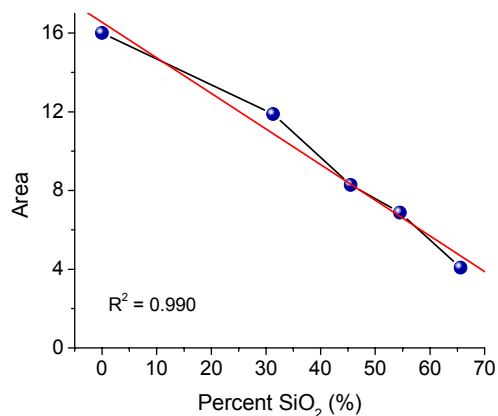


Figure 3. Relationship of the area under the Hf peaks to the mol % SiO<sub>2</sub> in the HfSiO films

Since ALD grows film in layers on top of the deposited layer, depth profile information is critical when characterizing new films or monitoring process control. There may be an interfacial region between the substrate (i.e., the Si wafer) and the bulk of the film material that will affect the electrical performance of the final semiconductor device. Standard laboratory sputtering techniques, for example, secondary ion mass spectrometry or Auger electron spectroscopy, while providing relevant data, are destructive techniques. A technique that could non-destructively depth profile thin films would provide valuable information to engineers developing a process if that characterized film could then be returned to the process line. Figure 4 shows the overlay of depth profiles for all of the HfSiO films. However, since the size of the

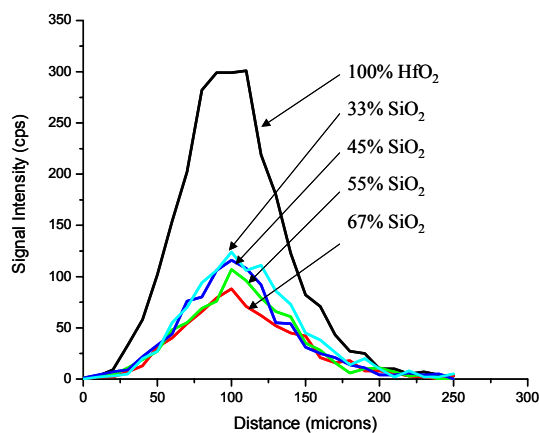


Figure 4. Depth profile of HfSiO films (Hf signal intensity)

probe beam and the z-axis step height are both much greater than the thickness of the films the figure is likely a representation of the height of optimum focus for the spectrometer instead of a true depth profile. Future studies will investigate whether a mathematical transformation would be able to extract accurate depth profile information from the raw data.

Confocal MXRF was also used to study the growth of TiN on three different gate dielectric materials. Figure 5 shows the area under the Ti- $K_{\alpha}$  (4.5 keV) peak for cycles of ALD TiN deposition (0, 5, 10, 20, 30, 50, 70, and 100 cycles) on the gate dielectric materials SiO<sub>2</sub>, HfSiO (20 mol % SiO<sub>2</sub>), and HfO<sub>2</sub>. The confocal MXRF is sensitive enough to detect an increase in the Ti signal on films that had five ALD cycles ( $\sim 0.6$  nm thick) on all three substrates. There was also a linear relationship between the number of deposition cycles and the area under the Ti- $K_{\alpha}$  peak; however, compared to a previous study using TXRF analysis on these films [8], there is less agreement between the confocal MXRF and the TXRF data. Both techniques have linear relationships but when examining the TXRF data, the slope from the TiN growth on the HfO<sub>2</sub> film is greater than that of the HfSiO, which is greater than that of the SiO<sub>2</sub>. Conversely, Figure 5 illustrates that confocal MXRF data for the slope of the TiN growth on all three substrates are practically the same. This difference may arise from the TXRF being a more surface-sensitive instrument than the confocal MXRF. As the films become thicker with additional ALD cycles, the confocal MXRF still samples well into the substrate with its micrometer sampling beam while the TXRF samples a greater percentage of the TiN film and less of the substrate. Therefore, the subtler slope changes may be more difficult to pull out using the confocal MXRF.

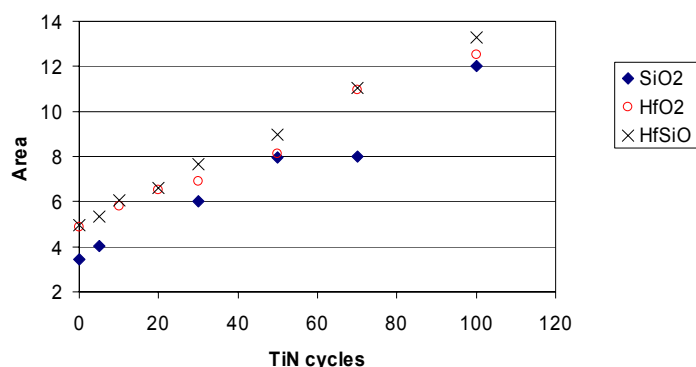


Figure 5: Area of the Ti signal vs. cycles of ALD TiN deposited on SiO<sub>2</sub>, HfO<sub>2</sub>, and HfSiO

## CONCLUSIONS

Confocal MXRF has the capability to quantitatively measure thin HfSiO films with increasing concentrations of SiO<sub>2</sub>. There is a linear relationship between the Hf- $L_{\alpha}$  signal and the mol % SiO<sub>2</sub>. By using a non-destructive technique, these films (once measured) could be returned to the line for further processing and remeasurement. More development is needed to take advantage of the non-destructive depth profiling capability of confocal MXRF, which would be an extremely useful application for the semiconductor manufacturing industry if it works for thin

films. Sensitivity to sub-nm TiN film growth was shown as well as a linear relationship of the ALD cycles to the Ti signal measured on the confocal MXRF.

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