Multi-technique composition, coverage and band gap analysis of ALD-grown ultra thin films

Building on the success of the Thermo Scientific™ K-Alpha XPS System, the Thermo Scientific Nexsa XPS System adds the capability of multi-technique analysis to the already fully-automated and user-friendly instrument. In addition to XPS, the Nexsa XPS System can provide coincident analysis using UV photoelectron spectroscopy (UPS), ion scattering spectroscopy (ISS), reflected electron energy loss spectroscopy (REELS), and Raman spectroscopy.

This advantage of the Nexsa XPS System is used to investigate a series of samples consisting of thin layers of HfO₂ deposited by increasing numbers of atomic layer deposition (ALD) cycles. XPS is first used to quantify the amount of hafnium deposited onto the substrate and measure the thickness of the HfO₂ and SiO₂ layers. Subsequent analyses using ISS and REELS are then performed to provide surface coverage and band gap measurements, respectively.
Composition and film thickness analysis
First and foremost, the Nexsa XPS System is a high-performance XPS instrument, so this was the starting point of the investigation. In this case, XPS data was acquired not only to provide compositional information, but also to enable overlayer thickness measurements to be made. By acquiring XPS spectra from the HfO₂ on SiO₂/Si sample after each ALD cycle, the amount of deposited HfO₂ can be quantified over the duration of the ALD process.

The Thermo Scientific Avantage Data System is then capable of extracting thickness information from the XPS data. This is achieved using an equation derived from the Beer-Lambert law and requires only the material densities and band gap values from the user in order to calculate the attenuation lengths of the individual material layers. Using these attenuation lengths, the Avantage Data System is able to calculate layer thickness based on the relative intensities of the XPS signals. In this example, the relative intensities of Hf and Si signals are converted into Hf film thickness measurements between 0 and 10 nm. This information can provide a precise and valuable quality check to the thickness of the ALD film, assuming that the film coverage is uniform for all deposition cycles.

Coverage analysis
In practice, thin film coverage may not be completely uniform during deposition. Fortunately, the Nexsa XPS System can provide quality control in this aspect of sample production via measurements of sample coverage by ISS. In contrast to XPS, ISS extracts spectral information from only the top monolayer of the sample. This is because, during acquisition the beam of relatively low energy, He⁺ ions are scattered by the top surface atoms of the sample and do not interact with sub-surface atoms. The kinetic energy lost by the He⁺ ions after interaction with the surface atoms is related to the mass of both the ion and the sample atom and the scattering angle. As the mass of the He⁺ ion and the scattering angle does not change, the Nexsa XPS System is able to measure and analyze the energy of the scattered ions to reveal the elements present in the top monolayer of the sample. With this in mind, any Si signal acquired in the ISS spectra indicated incomplete surface coverage of HfO₂.

Figure 1: XPS survey spectra showing increasing HfO₂ composition as a function of ALD cycles.

Figure 2 shows that the intensity of the Si peak in the ISS spectrum reduces as the number of ALD cycles increases. After 50 cycles, the Si peak has been removed from the spectra completely; therefore, it can be deduced that the ALD process reaches full coverage between 20 and 50 cycles.

Figure 2: ISS spectra of the HfO₂ sample over 100 ALD cycles (top) and a plot indicating the level of surface coverage by ALD cycle (bottom).
Band gap measurements
One of the key properties of gate dielectric components, or high-k dielectric materials in general, is the band gap. This property, denoting the energy difference between the valence and conduction bands of a material, is the driving force behind many desirable material applications, such as LEDs, photovoltaics and solar cells. It is therefore essential that the band gap of such materials can be measured accurately. While band gap measurements can be routinely performed using XPS on most materials, when it comes to high-k dielectric materials like HfO₂, overlap of XPS peaks in the band gap energy region make measurements more difficult. Fortunately, with REELS, this is not a problem. Within seconds, the system is able to acquire a REELS spectrum from the same position on the sample surface. The Avantage Data System can then use the data to automatically calculate the band gap of the sample material by measuring the energy loss at which inelastic scattering of electrons begins to occur. This is achieved using the same dual source flood gun that is used for charge compensation, meaning that a second electron source is not required.

Summary
Alongside compositional and thickness information taken from XPS data, the Nexsa XPS System was used to provide coverage analysis via ISS and band gap measurements via REELS, producing a complete picture of properties vital to the development of ultra-thin film materials for semiconductor applications.

Figure 3: REELS spectrum of the HfO₂ sample after 100 ALD cycles with the band gap measurement illustrated.