

Atomic Scale Materials Characterization Challenges in Advanced CMOS Gate Stacks

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In nanoscale Si-based CMOS electronics, interface and ultrathin film composition and structure determine critical electrical properties. Several major changes in transistor gate stack materials are being pursued including the replacement of SiO₂ and SiON dielectrics by high-k oxides, and doped polycrystalline Si gate electrodes by metals (or metal compounds or alloys). Eventually even the Si channel will likely be replaced by higher mobility semiconductors. High resolution microscopic and spectroscopic methods are central in facilitating new materials integration. In addition to traditional and advanced electrical characterization tools, researchers are utilizing a range of sophisticated novel physical and chemical methods to examine composition, structure, bonding, and electronic properties of next-generation gate stacks.[1,2] This article briefly reviews several high resolution electron, ion and photon-based tools currently utilized to examine nanoscale films and interfaces (see Table I). *In-situ* (and *in-vacuo*) growth and analysis are also discussed, necessitated by devices in which a fraction of a monolayer of an impurity would impact performance.

There are a host of scientific and engineering issues such as thermal diffusion between layers and charge defect minimization that must be addressed in order to permit new materials to be integrated and to continue scaling. The uncertainty and the debate over the exact identification of the physical and/or chemical configurations contributing to threshold voltage instabilities emphasize the need for complementary high spatial resolution techniques. A clear consensus on the atomic scale origin of these defects and the resulting performance degradation

remains elusive and proposed models have rarely been verified. Another issue pertains to diffusion across interfaces that occurs during high temperature annealing (> 1000°C). Although electrical defects sometimes occur at concentrations well below the detection limits of even the most sensitive physical methods, a thorough atomic scale understanding of composition, structure, bonding and electronic properties, resulting from a correlation of materials and electrical experimentation is essential to the successful evolution of nanoscale devices.

Electron microscopy: Among the most powerful physical characterization methods are those based on scanning transmission electron microscopy (STEM). These techniques include high-angle annular dark-field (HAADF) imaging (also known as Z-contrast imaging), energy-dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS). The combination of EDS, EELS and HAADF allows the determination of *a priori* unknown interface chemistry and structure. State-of-the-art field-emission transmission electron microscopes (TEMs) allow for the acquisition of EDS

and EELS spectra concurrent with an atomic resolution HAADF image such that chemical information can be correlated with the gate stack structure.

In STEM measurements, an atomic-resolution HAADF image is formed by scanning a small focused electron beam (1-2 Å in diameter) and collecting the electrons that are scattered to large angles (> 50 mrad) on an annular dark field (ADF) detector (see Figure 1). Inelastically scattered electrons that pass through the hole in the annular detector can be analyzed via EELS. Atomic resolution HAADF images have several advantages over conventional high resolution transmission electron microscopy (HRTEM) images. In particular, the contrast in these images is highly sensitive to the atomic number (Z) of elements present in the area of interest. Thus, layers containing lighter atoms (such as interfacial SiO₂) can easily be distinguished from those containing heavier elements, such as Hf (see Figure 2a). For high-Z elements, the contrast in HAADF images is sensitive enough to detect dopant atoms such as Sb in crystalline silicon[3] or very small quantities of Hf in amorphous SiO₂. [4]

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Electron microscopy	STEM, TEM, SEM
Ion-based methods	MEIS, RBS, SIMS, NRP
Photon-based methods	XRD, XRR, FTIR, EXAFS
Photoelectron spectroscopy	XPS, UPS
Other nontraditional methods	scanning probe microscopy, neutron scattering, positron annihilation spectroscopy, electron spin resonance

Table I. Techniques Yielding Atomic Scale Gate Stack Information

>> Complementing HAADF, EELS is sensitive to light elements, and can also easily detect many of the transition and rare earth metals that may be used in novel gate dielectrics or electrodes. The sensitivity of EELS for light elements is typically around 1-2 atom%, but may vary greatly, depending on the specific sample. In STEM, compositional line profiles are obtained by scanning the small focused electron probe across the layers comprising the gate stack and acquiring a spectrum at each point. For example, the segregation of nitrogen to the interface with silicon is easily detected in STEM/EELS composition profiles (see Figure 2b). While in principle the same incident probe used in HAADF imaging can be used for EELS, the signal-to-noise ratio suffers from small probe sizes, often requiring a compromise between spatial resolution and detection.

Instrumentation for STEM continues to develop with significant improvements in both spatial resolution (sub-Ångstrom with aberration correction) and probe intensities on the horizon.[5] Obtaining meaningful results requires expertise as well as knowledge of the principles of electron scattering. For CMOS gate stack applications, EELS and EDS have mostly been used for qualitative analysis of elemental distributions.[6] Quantitative analysis is possible but requires a knowledge of the electron optical parameters, scattering cross sections and correction for multiple scattering in thicker speci-

mens.[7] Electron beam damage is an important concern in some cases, and sample preparation may also induce artifacts and should be carefully controlled.

Medium energy ion scattering (MEIS) spectroscopy is another very powerful tool used to determine composition and structure. MEIS can be thought of as a high resolution, low energy version of conventional Rutherford backscattering spectroscopy (RBS).[8] Incident ion energies of ~100 keV make it possible to use ion detectors with very high resolving

power (which translates into very high depth resolution) while at the same time maintaining the great strength of RBS: quantitative thin film compositional analysis. By using isotope tracing, such as ^{18}O and ^{16}O , one can study not just the structures of such ultrathin films, but also the diffusion processes responsible for their formation or degradation.

As an example of the kind of information the technique can yield, Figure 3 shows MEIS data for an HfO_2 film containing nitrogen on Si(100). The ion

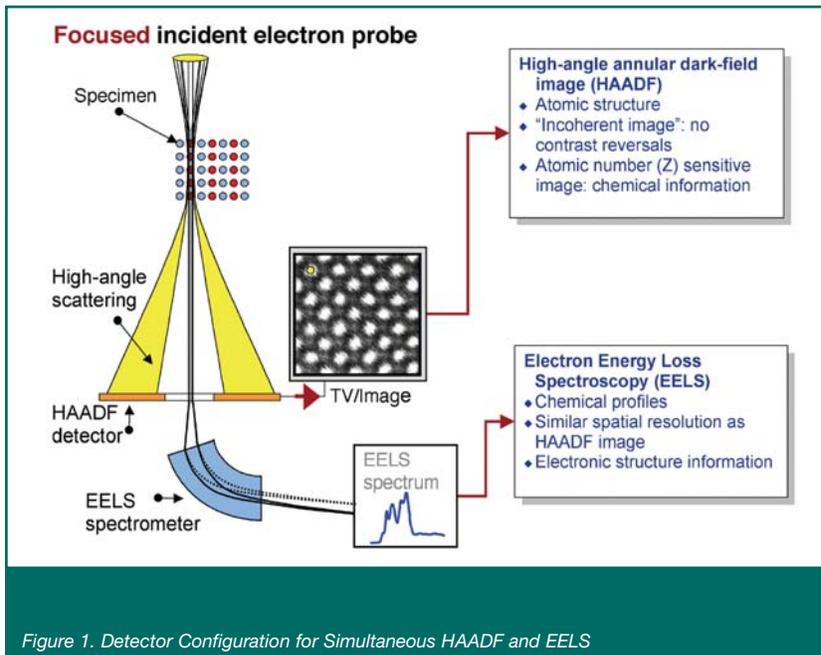


Figure 1. Detector Configuration for Simultaneous HAADF and EELS

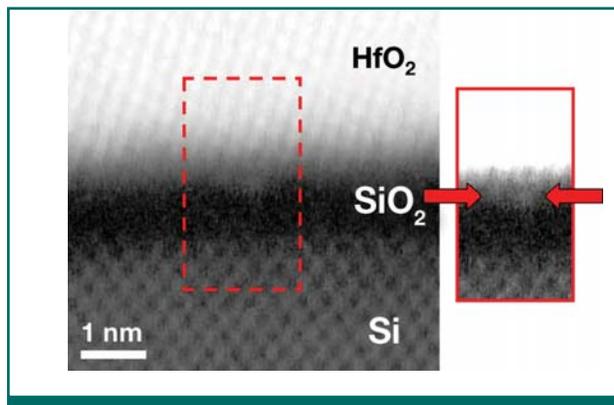


Figure 2a. Cross-section high-angle annular dark-field (HAADF) image of an Si/HfO₂ gate stack. Due to the strong atomic number contrast, the HfO₂ film appears bright, while the interfacial SiO₂ layer is dark. Lattice fringes are visible in the crystallized HfO₂ film. The SiO₂/HfO₂ interface shows roughness, with occasional clusters of Hf(O) protruding a significant distance into the interfacial SiO₂, as can be seen in the center of the image. The image on the right corresponds to the center section with brightness/contrast adjusted for better visibility of the protruding Hf(O) clusters (block arrows). Image courtesy of Melody Agustin (UCSB).

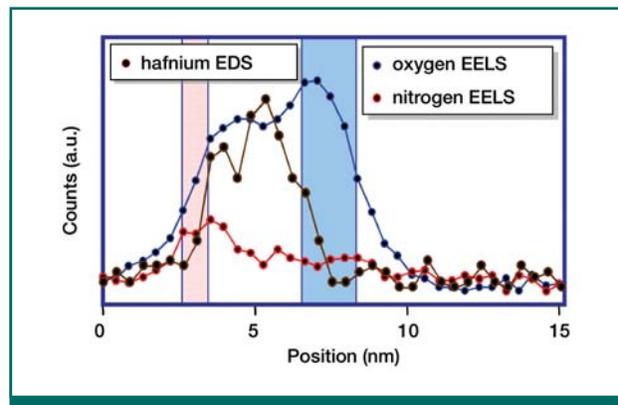


Figure 2b. EELS and EDS chemical profiles recorded across a high-k gate stack with an Hf-Si-O gate dielectric and a poly-Si electrode. The Si substrate is to the left and the interfacial SiO₂ layer is shaded pink. EELS shows that a second, unintentional interfacial SiO₂ layer exists at the interface between the high-k oxide and poly-Si electrode (shaded in blue). The profiles also show that nitrogen (introduced by NH₃ anneals) was preferentially located at the lower interface. Figure courtesy of Dr. Brendan Foran (ATDF).

backscattering energy is a direct measure of the atomic mass of the atom responsible for scattering the incident proton. The scattering yield from Hf therefore appears at a high backscattering energy, while the nitrogen signal appears at the lowest energy. For both Si and O, two backscattering peaks are observed, which implies that the Si and O atoms exist in two separated regions of the multilayer film. The first Si peak appears at the energy characteristic of surface scattering, indicating surface oxidation. The second, broader peak is evidence for an oxygen-containing region near the interface. The ion beam in these experiments is aligned along a high symmetry direction in the sample, so atoms in the amorphous region of the sample are observed, while those in the substrate are not (except for the first layer). By analyzing the shape of the various peaks one can obtain a quantitative depth profile, qualitatively summarized in the inset of Figure 3. In this film, N is used to help block diffusion across the various interfaces and limit crystallization of the HfO_2 . MEIS and electron microscopy methods complement each other. The truly local information in electron microscopy is an important strength, while overall elemental quantification in a film is often easier in MEIS.

Other highly specialized tools are also being focused on gate stack film systems

to determine if (and which) atomic level physical properties are correlated with the limits of electrical performance. For example, scanning probe microscopy is used not only to quantify roughness at the Ångström level, but also to map out leakage, capacitance and local work function of dielectrics. It has become increasingly critical to measure a set of samples by more than one high resolution spectroscopic technique in an effort to increase analytical confidence. Combining X-ray reflectivity (XRR) and neutron reflectivity (NR) yields accurate characterization of buried interfaces when simulation of one physical model achieves a good fit with the profiles produced by incident radiation with such different scatter length densities. The variable kinetic energy photoelectron spectroscopy available at synchrotron sources enables depth profiling of chemical state changes not available through analytical lab services, and another synchrotron-based method, extended X-ray absorption fine structure (EXAFS), can be used to determine neighboring species, coordination number and phase behavior in thin films. These techniques are directly sensitive to the chemical environment. SIMS is also used to determine composition, especially when high sensitivity is needed such as in dopant profiling or impurity diffusion.[9,10] More exotic methods, such as

small angle neutron scattering (SANS), can be applied in order to extract statistically representative microstructural information of heterogeneous materials (i.e., pore morphologies and void volume fraction size distributions) to complement data obtained from diffraction methods, X-ray microtomography, and the visual information gained from electron microscopy. Electron spin resonance (ESR) is a sensitive technique for quantifying electrically active charge centers such as Si dangling bonds at the Si/dielectric interface. Specific sites, called P_b and E' centers, can be observed by ESR and are ascribed to dangling bonds of the substrate and Si atoms not fully fourfold coordinated with O atoms, respectively. These and other advanced spectroscopic techniques such as positron annihilation spectroscopy are increasing the fundamental understanding of phenomena, properties and behavior, yielding new insight into chemical phase, dynamics, electronic defects, structure (such as voids) and behavior important to materials that will contribute to improving multilayer gate stack systems.

Integrated growth and analysis systems: As CMOS gate stacks require engineering at the atomic scale for control of composition, structure and properties, the highest resolution microscopic and spectroscopic methods are required for characterization. Bringing samples up to ambient conditions often results in the incorporation of impurities such as water, oxygen and hydrocarbons. To avoid this, a new class of tools is appearing that enable in situ growth, processing and analysis, with vacuum transfer between stations. Many parts of these systems are designed to function in ultrahigh vacuum (UHV). An example of such a tool is shown in Figure 4.

This system is capable of thin film deposition using chemical and physical vapor deposition (CVD and PVD) methods including electron beam evaporation, molecular beam deposition, sputter deposition and thermal evaporation methods. Additionally, in situ characterization techniques include XPS and UPS, RHEED, quartz crystal microbalances, Auger electron spectroscopy, atomic force and scanning tunneling microscopy/spectroscopy. The system utilizes 100 mm diameter wafers for university-based cleanroom process >>

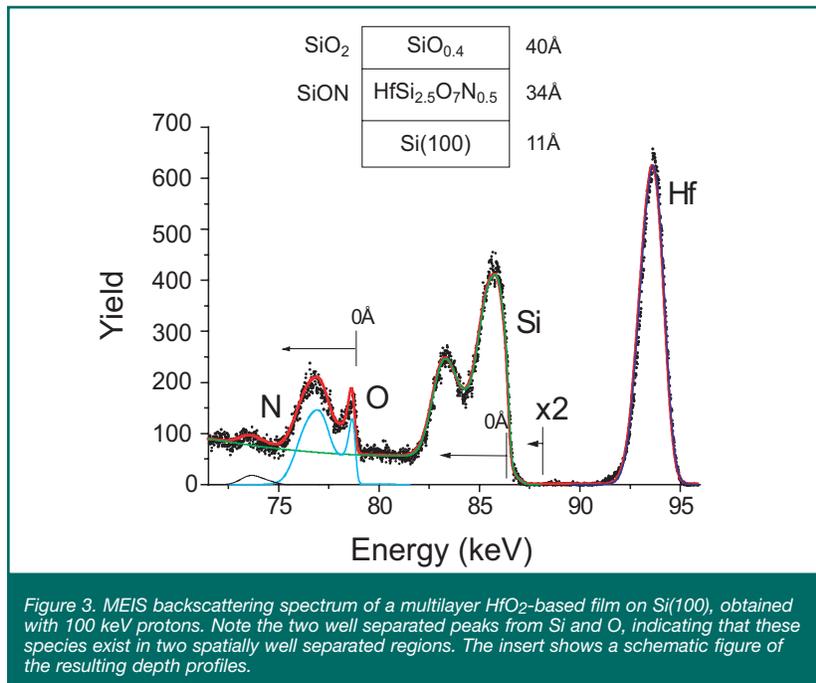


Figure 3. MEIS backscattering spectrum of a multilayer HfO_2 -based film on $\text{Si}(100)$, obtained with 100 keV protons. Note the two well separated peaks from Si and O, indicating that these species exist in two spatially well separated regions. The insert shows a schematic figure of the resulting depth profiles.

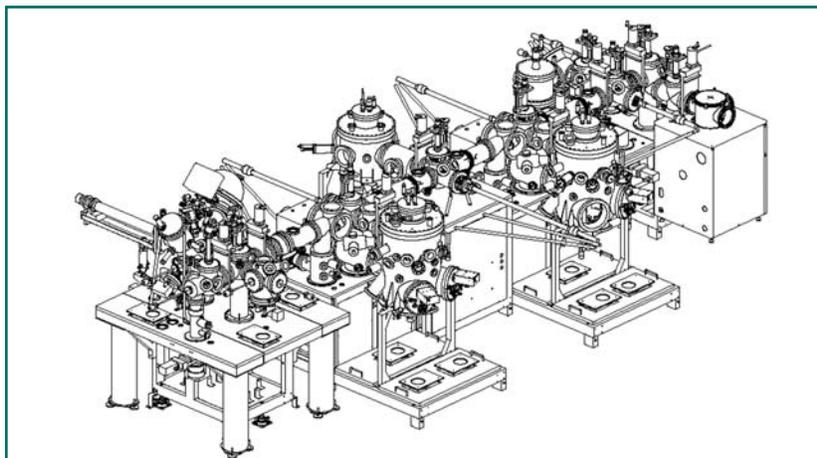


Figure 4. Ultrahigh vacuum cluster tool at the University of Texas at Dallas. From left to right, the multichamber modules are: annealing, metal evaporation, sputter deposition, molecular beam deposition and analytical. The system was fabricated by Omicron Nanotechnology GmbH.

>> research, and modified sample holder plates for smaller samples. Wafers are transported throughout the system in a UHV transfer tube. The UHV capability enables the control and study of film surfaces for reasonable periods of time (several hours) avoiding contamination due to atmospheric exposure. Each deposition module has heating (up to 1200°C) capability for the study of film uniformity and growth kinetics. Although it is today neither feasible nor practical to use a full UHV environment for in-FAB gate stack processing, some R&D teams argue that atomic scale control over contamination may soon lead the tool industry in that direction.

Summary

New atomic resolution techniques are being developed for gate stack characterization of next-generation CMOS devices. STEM, MEIS and other advanced tools as well as synchrotron radiation and neutron scattering instrumentation will continue to contribute significantly to the knowledge base of materials and interfaces, in particular, with respect to phase mixing and segregation in ultrathin high-K dielectric films, and sub-nanometer layer formation during growth or post-growth processing between the semiconducting, high-K and metal electrode layers. The gas phase environment must be tightly controlled during gate stack growth: exposure to ambient gases, such as H₂O, O₂ and hydrocarbons, easily adsorb and react with some of the key elements in a gate stack. Various species can diffuse through layers,

and impurities, defects, atomic scale roughness and film stress may result in device performance degradation.

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