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Unveiling the Ferroelectric Behavior of HfO_2 Thin Films Using Fast DualEELS Analysis

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Ferroelectric materials are characterized by a spontaneous dipole moment. Much like in ferromagnetic materials, the orientations of ferroelectric domains can be manipulated with suitable material engineering and the polarization states can be used to store digital information. Advantages such as non-volatility in ferroelectric RAM (FeRAM) and typical low power consumption overall in comparison to conventional magnetic storage technology, are key factors for commercial interest in ferroelectric memory. However, these functional advantages are countered by a fundamental disadvantage - ferroelectric behavior typically diminishes gradually with reduced dimensionality. The dipole moment disappears as the size of the crystal is reduced.

Reducing the size of ferroelectric materials has been the ongoing topic of investigation for several years but it is only recently that a suitable material system showing usable ferroelectric behavior at the nanoscale has been identified. Some reports have claimed that hafnium oxide (HfO_2) films exhibit ferroelectric properties, though only if the oxide is grown as a thin film with thickness <10nm. This behavior is quite unexpected, contrasting strongly to the behavior of conventional ferroelectric materials. The ferroelectric behavior of nanostructured HfO_2 coupled with its high silicon compatibility has sparked a lot of interest in the scientific community as potential material for future memories technology [1].

One of the challenges that scientists currently face with the HfO_2 is the limited knowledge of the mechanisms behind the origins of the ferroelectric properties at the nanoscale. At room temperature bulk HfO_2 has a monoclinic structure and shows no ferroelectric properties at all. However, thin films seem to grow in an unexpected way with several different crystal structures that all coexist together across the thin film. To date, a full characterization of HfO_2 thin films in the transmission electron microscope has proven to be very challenging due to the likely presence of multiple phases and the effects of strain and bonding at the interfaces between different regions [1].

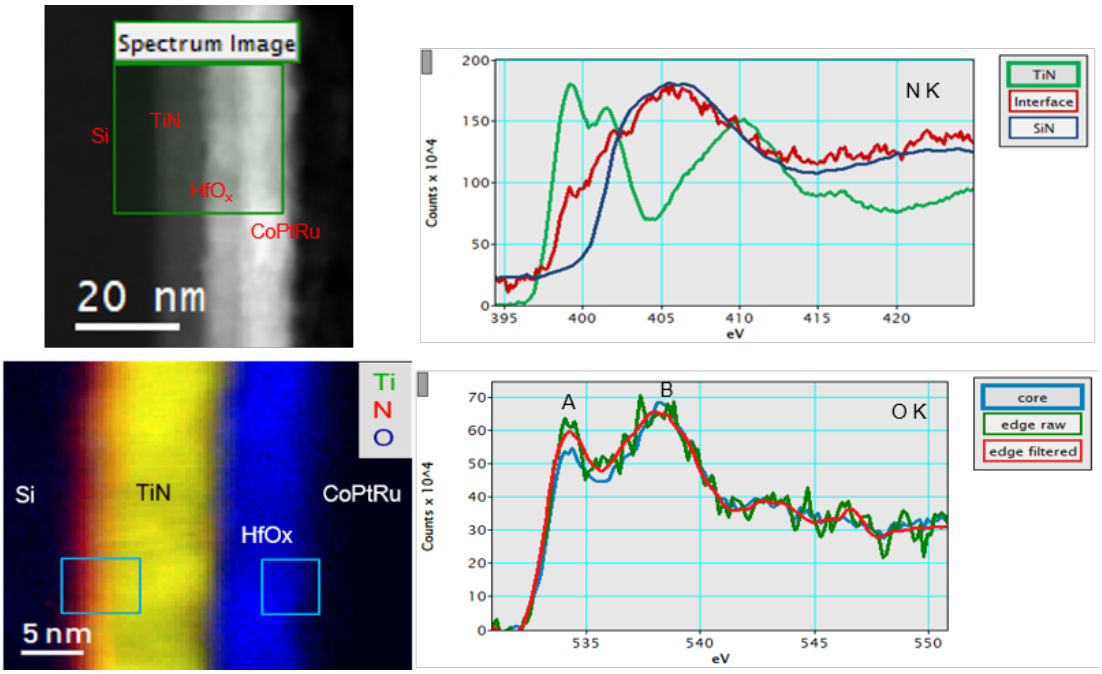
Here we use electron energy loss spectroscopy in the scanning transmission electron microscope (S)TEM to study and identify all the possible different chemical phases or atoms arrangements present across a thin film of HfO_2. The main challenge here is that data collection must be carried out at a high spatial resolution, reasonable energy resolution (<0.75 eV), low noise and low dose as HfO_2 is highly beam sensitive. We have performed EELS data collection using the latest detector technology on a 5 nm HfO_2 film grown on TiN/Si stack. Figures 1a and 1b show the ADF STEM survey image and EELS color maps of Ti, O and N. Oxygen was found to be present only in the HfO_2 layer. Diffusion of N into the silicon layer at the Si/TiN interface was also seen, leading to the conclusion that two distinct phases must form, one containing pure SiN and the other one a mixture of SiN and TiN. This is further supported by changes observed in the N K-edge EELS spectra shown in Figure 2a. ELNES analysis performed on the O K-edge (Figure 2b) shows two distinct phases at the HfO_2 interfacial layers. The two main peaks in the O K-edge

are labeled A and B. Spectra were extracted from the region in the core of the HfO_2 layer and along the interfaces that are labelled as edge in Figure 2b. Spectra were normalized to the peak B maximum for comparison. After normalization, peak A seems much less pronounced in the spectrum extracted from the core region. This behavior was also observed in another dataset where the Pd $M_{4,5}$-edges extracted from similar regions in the HfO_2 layer were compared. ELNES variation in the O K-edge shown in the spectra in Figure 2b indicate the presence of different phases, particularly HfO_2 with different atomic arrangements. These spectra are to be compared with HfO_2 standards of different crystallographic structures to help unveil the various crystal structures present in the unknown specimen presented herein.

This presentation will demonstrate how EELS through a methodical approach using pure HfO_2 crystals grown under specific crystallographic structures can be used to understand the origins of the ferroelectric behavior that is observed in thin HfO_2 layers and how can be manipulated.

References:

[1] ED Grimley et al., Advanced Materials Interfaces **5** (2018), p. 1701258.



Figures 1. a) ADF STEM survey image. The region inside the green box is where the beam was scanned for the EELS SI acquisition; b) EELS elemental maps of Ti L in green, N K in red and O K in blue.

Figures 2. EELS spectra extracted from the selected regions in the blue box in Figure 1b; a) N K EELS spectra extracted from the TiN region in green, interface with Si in red and from a SiN standard sample. Indeed, the region at the interface contains both phases of TiN and SiN; b) O K EELS spectra extracted from the HfO2 layer, the core in blue and the edge or interface in green. The spectrum extracted from the edge was also smoothed to reduce the noise.

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