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Nanochemistry and Structure of Zr and Hf Based High Dielectric Constant Films

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The atomic scale chemistry and structure of zirconium and hafnium based thin films on silicon are of great interest since they are prominent candidates to replace SiO_2 gate oxides in CMOS and other devices. Ideally, these films would be either single crystalline or amorphous, to avoid the current leakage paths associated with grain boundaries, and all layers of the films should be stoicheometric with atomically sharp chemical and structural interfaces, so that the equivalent oxide thickness (EOT) is a linear combination of the dielectric constants of the constituent layers weighted by the layer thicknesses. Our results show that this simple behavior does not occur. Films we examined were deposited by ALCVD on Si with a chemical oxide interlayer, at 400C substrate temperature. Both as-deposited and annealed films were examined. Electrical measurements on the ZrO_2 films showed that their dielectric constants differed from expected bulk values, implying that interdiffusion occurred, even in as-deposited films[1]. Our results indicate similar behavior occurs for HfO_2 based films. Typical high-K oxide layer thicknesses were 4 nm with ~ 1 nm interlayers (IL). HREM, ADF and small probe spectroscopies were used to examine the layer structure and chemistries.

The structure of the Hf based as-deposited and annealed layers is shown in figure 1. Zr based layers are very similar. In general the as-deposited oxide high-K layers were amorphous, with the occasional observation of nanocrystals. The metal oxide /IL/{100} Si substrate interfaces were mostly flat, with occasional steps or roughness. Small probe EELS showed that by comparison to spectra from the nearby Si substrate, the low loss peak from the interlayers had shifted a few eV higher in energy and broadened, corresponding to substoicheometric SiO_x, $x<2$. This is not surprising since they were not formed by high temperature thermal oxidation [2,3]. After annealing in oxygen at 600 or 700C, the high-K oxide layers were nanocrystalline and the thickness of these layers did not change appreciably. However, the interlayer thicknesses nearly doubled and the oxygen content increased, indicating oxygen had diffused though the metal oxide and formed more interlayer at its interface with the substrate Si.

The EELS low loss regions of ZrO_2, HfO_2, zircon ($ZrSiO_4$), and hafnon ($HfSiO_4$) provided useful information about the compositions of the metal oxide layers. Strong core loss peaks for these metals occur at relatively high energies, and are less accessible at the low beam currents necessary for high spatial resolution. Each of these oxides [4] and silicates has a double-peak low loss structure, with the first peak occurring at ~15 eV loss, and the second at ~ 26 eV loss. The first of these two peaks is strongest for both oxides, whereas the second is the strongest for the silicates. Thus the resolution of the two peaks and their relative intensity indicated whether Si had diffused into the metal oxide layers during deposition or annealing. Fig. 2 shows spectra from the layers in as-deposited Zr-based film. Here, the low loss double peak is not resolved, but the peak breadth is as expected. Figs. 3, 4 and 5 show the low loss region for annealed Zr-based and Hf-based thin film stacks as well as Hf-based reference spectra, respectively. The resolved low loss structure has the intensity asymmetry of the silicate throughout the Zr-rich layer, whereas in the Hf-based stack the intensity asymmetry is characteristic of hafnon near the interlayer interface and characteristic of HfO_2 in the middle of the Hf-rich layer. All these results show that Si diffusion from the interlayer occurred, providing the explanation for the observed electrical results.

[1] S. K. Dey et al., J. Appl. Phys. *in press*(2003).
[2] M. J. Kim and R. W. Carpenter, J. Mater. Res. 5 (1990) 347.
[3] M. Catalano et al., J. Mater. Res. 8 ((1993) 2893.
[4] C. C. Ahn, et al., EELS Atlas, ASU HREM Facility and Gatan, Inc.(1983).

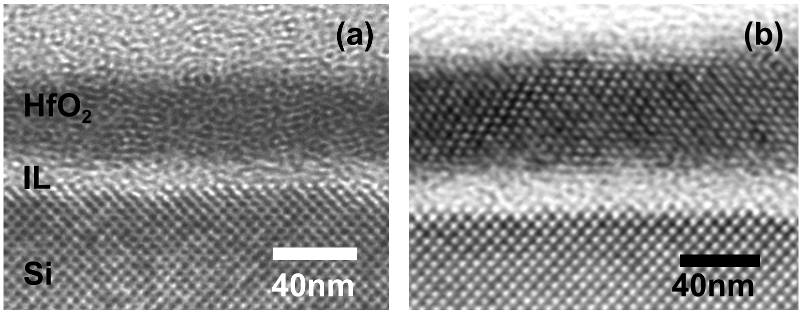

FIG. 1. As-deposited (a) and annealed (b) Hf-based layers.

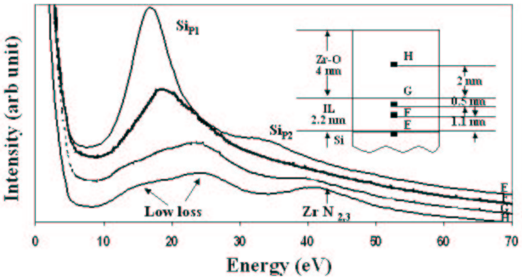

FIG. 2. EELS spectra from as-deposited Zr-based thin film stack

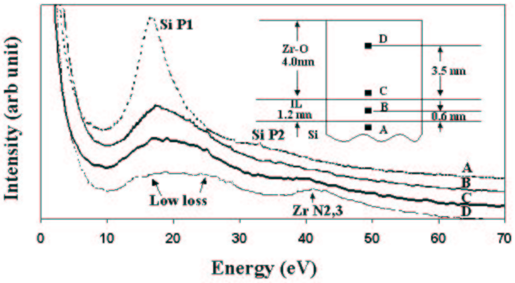

FIG. 3. EELS spectra from annealed Zr-based thin film stack

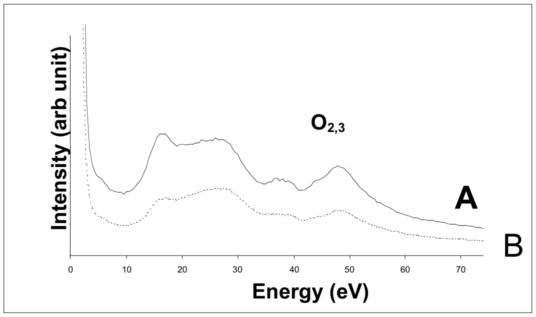

FIG. 4. EELS spectra obtained (A) within the Hf-rich layer and (B) near the IL/HfO_2 interface.

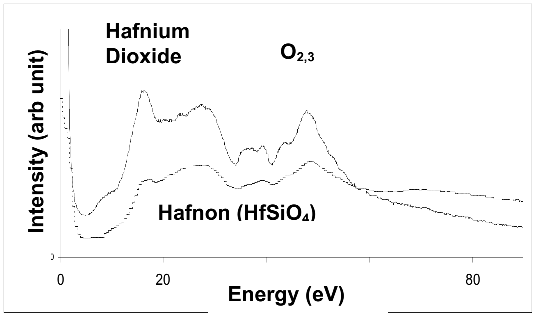

FIG. 5. Hf-based EELS reference spectra.