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Electron Energy-Loss Spectroscopy of Alternative Gate Dielectric Stacks

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Continued scaling of silicon technology (ÒMooreÕs LawÓ) requires a paradigm shift in the materials used as gate dielectric in complementary metal-oxide-semiconductor (CMOS) devices. In the near future, the SiO_2 thickness is projected to be thinner than 1 nm. In this thickness range tunneling currents through the SiO_2 become unacceptably high. Currently, alternative dielectrics, such as ZrO_2, HfO_2, Y_2O_3 and their alloys with SiO_2 or Al_2O_3, a re being investigated to replace SiO_2. These oxides have greater dielectric constants (k) than SiO_2, and are potentially stable in contact with silicon. High-resolution analytical capabilities afforded by scanning transmission electron microscopy techniques are essential in analyzing the interface and bulk stability of these ultrathin (< 5 nm) layers.

Here, we apply high-resolution electron energy-loss spectroscopy in combination with atomic resolution Z-contrast imaging to investigate the stability of alternative gate dielectric layers at high temperatures, and under reducing and oxidizing conditions. Z-contrast images are used to image the chemical homogeneity of the layers and to position the probe for electron energy-loss spectroscopy (EELS). EELS is used to measure composition and bonding across the gate dielectric with sub-nanometer spatial resolution. We use oxygen K-edges and Si L-edges to investigate interfacial SiO_2 and silicate formation. In addition, the near-edge fine-structure of these edges and comparison with bulk reference spectra are used to fi ngerprint phase formation and nonstoichiometry. Conventional high-resolution transmission electron microscopy is used to investigate crystallization.

Using the combination of these methods we are able to determine the stability of these ultrathin layers with *a-priori* unknown structures. For example, we show that ZrO_2/Si layers annealed under moderately oxidizing conditions (oxygen partial pressure > ~ 10^{-4} torr), form a low-k interfacial SiO_2 layer through oxygen diffusion through the ZrO_2 and silicon consumption at the interface. Layers annealed under moderately reducing conditions (oxygen partial pressure ~ 10^{-5} torr) do not show extensive SiO_2, formation, whereas layers annealed under even lower oxygen partial pressures (~ 10^{-7} torr) form an interfacial silicide, consistent with predictions from thermodynamic estimates. In contrast to ZrO_2 layers, CVD grown Y_2O_3 films show extensive silicate formation upon annealing, through Si diffusion into the dielectric. We show that thin films transform to

an amorphous yttrium silicate upon annealing, whereas thicker films form an interfacial silicate and crystalline Y_2O_3 on the surface. We will discuss possible mechanisms, in particular the role of crystallization and Si diffusion to explain the observed results. We also show that pre-nitridation of the Si surface impedes the Si diffusion.

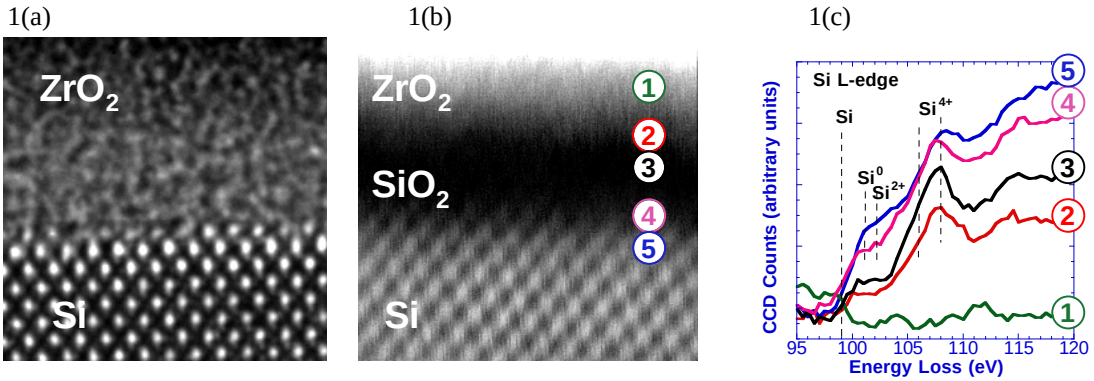

Figure 1: (a) Conventional HRTEM image of an as-deposited ZrO_2 film, (b) Z-contrast image and (c) EELS spectra through the thickness of the gate stack. No Si can be detected in the ZrO_2 layer. Note the atomic number sensitivity of the Z-contrast image that clearly shows the interfacial SiO_2.

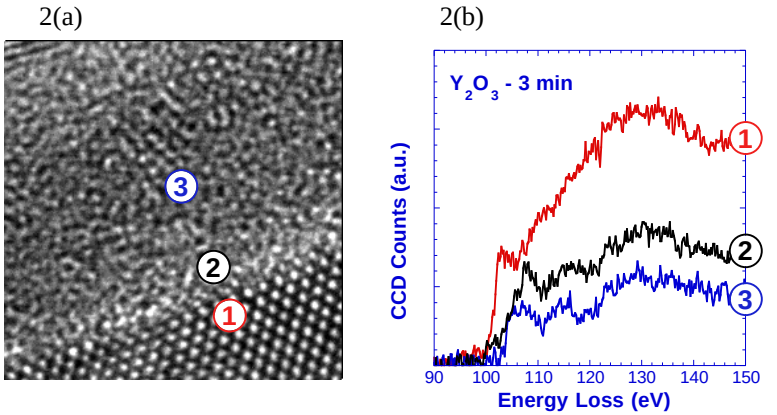

Figure 2: (a) Conventional HRTEM image of an Y_2O_3 film deposited on bare silicon. (b) Fine structure of Si L-edges recorded at different positions in the corresponding Z-contrast image (not shown) shows an interfacial SiO_2 layer and that the film has reacted to a Y-silicate.

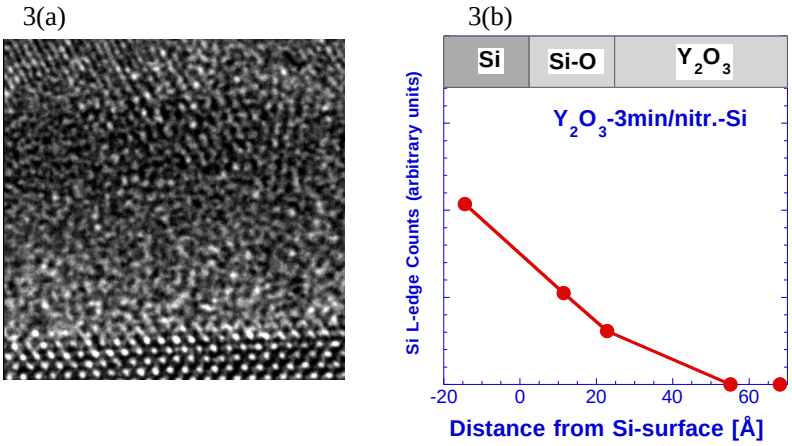

Figure 3: (a) Conventional HRTEM image of an Y_2O_3 film deposited on nitrogen plasma pretreated silicon shows that the upper part of the film crystallizes. (b) Si profile shows that the crystallized film contains no Si.

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