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Characterization of advanced gate stacks for Si CMOS by electron energy loss spectroscopy in scanning transmission electron microscopy

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ABSTRACT

Novel metal oxide films and new metal gates are currently being developed for future generations of Si based field-effect transistors as the SiO₂ gate dielectric and polycrystalline Si gate electrode are reaching scaling limits. These new gate stacks are often comprised of sub-nanometer layers. Device properties are increasingly controlled by the complex structure and chemistry of interfaces between the layers. Electron energy loss spectroscopy (EELS) in scanning transmission electron microscopy (STEM) is capable of providing insights into interfacial chemistry and local atomic structure with a spatial resolution unmatched by any other technique. Using gate stacks with Hf-silicate dielectrics as examples, we demonstrate the capabilities of STEM/EELS for analyzing the interfacial chemistry of novel gate stacks. We show that *a-priori* unknown reaction layers of a few Å thickness can be detected and identified even in the presence of substantial interfacial roughness that may obscure such layers in a high-resolution image. We discuss some experimental aspects of STEM/EELS chemical profiling applied to gate stacks and the factors affecting the interpretation. In particular, the effects of interfacial roughness, beam spreading, elemental analysis in a heavily scattering matrix, and the interpretation of the EELS core-loss fine-structures from ultrathin layers are discussed.

Keywords: Electron energy loss spectroscopy, gate dielectrics, Z-contrast imaging, STEM

1. INTRODUCTION

Due to the continuous decrease in feature size, Si devices are approaching a number of fundamental limits. In particular, the gate oxide in modern complementary metal oxide semiconductor devices (CMOS) has reached atomic dimensions. When the thickness of the traditionally used gate dielectric materials, SiO₂ and Si-oxynitride, falls below ~ 0.8 nm, leakage currents are excessive due to direct tunneling. Use of a different gate oxide with higher dielectric constant (k) reduces leakage currents as a greater physical thickness of the gate dielectric can be realized [1]. Concurrently with the replacement of SiO₂ as the gate dielectric, heavily doped polycrystalline (“poly”) Si gate electrodes may have to be replaced with metal gate electrodes [2]. Metal gates are attractive because they eliminate gate depletion, dopant penetration problems, may assist in screening remote phonon scattering [3,4], and are potentially thermally more stable in contact with high- k oxides than Si [5].

As the dielectric layer thickness decreases, the device properties are increasingly controlled by the structure and chemistry of interfaces between the gate oxide and Si or the gate electrode, respectively. Interfacial phases, such as silicides, SiO₂, and silicates, are often observed in real high- k dielectric gate stacks after device processing at high temperatures [5]. SiO₂-rich interfacial layers often form during the deposition of a high- k film in an oxygen-rich atmosphere by oxidation of the Si surface. Sometimes interfacial SiO₂ layers are intentionally grown before high- k deposition [6].

One of the most challenging aspects in the investigation of new gate stacks is the need for a physical characterization technique that is able to determine the composition, atomic and electronic structure of high- k oxides, gates and interfacial layers. Interfacial phases and thin gate dielectrics may have very different physical and electronic properties than bulk materials of

nominally the same composition [7]. This difference may be due to strain, deviation from the ideal composition, a higher concentration of point defects or, in case of the thinnest layers, simply due to differences in second (or higher order) nearest neighbor coordination compared to that of the bulk material [8]. As layers become thinner, interfacial roughness becomes an increasing fraction of the total layer thickness and complicates the interpretation of composition profiles, thickness measurements and electrical properties [9,10]. Methods with spatial resolution approaching the Ångstrom level that can detect small amounts of an element are required. Among the most powerful physical characterization techniques for the study of high- k thin films and their interfaces with Si and the gate electrode are scanning transmission electron microscopy (STEM) based analytical techniques, in particular high-angle annular dark-field imaging (HAADF or Z-contrast), 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.

In STEM, the atomic-resolution HAADF image is formed by scanning a focused electron beam (a few Å in diameter) and collecting the electrons that are elastically scattered to large angles (> 50 mrad) on an annular dark field (ADF) detector. For thin samples, the image contrast in HAADF is roughly proportional to Z^2 (atomic number), and provides the additional benefit of a chemically sensitive image [11,12]. Thus, layers containing lighter atoms (such as interfacial SiO₂) can easily be distinguished from those containing heavier elements, such as Hf. Furthermore, the HAADF image is used to position the small electron probe for EELS or EDS. To date, STEM/EELS can routinely be performed using state-of-the-art field emission transmission microscopes originally designed for conventional TEM [13,14]. Furthermore, the near-edge fine-structure of EELS edges (ELNES) reflects the local unoccupied density of states

at the excited atom [15,16], thus additional information on phases, bonding and electronic structure can be obtained in parallel. Using the combination of STEM and EELS, it is possible to measure the composition and obtain electronic structure information with a spatial resolution approaching atomic dimensions [17-20].

This paper is organized as follows. We first present some of our recent studies of interface stability of advanced gate stacks using STEM/EELS (section 2). In the following section, we discuss practical issues affecting the interpretation of EELS of ultrathin layers. In particular, we discuss the effects of interfacial roughness, beam spreading in amorphous or poorly crystallized layers, elemental analysis in a heavily scattering matrix, and the interpretation of the ELNES from ultrathin layers.

2. CHEMICAL PROFILING ACROSS GATE STACK INTERFACES

Experimental

The chemical profiles and ELNES reported here were obtained from gate stacks that incorporate high- k Hf-Si-O films deposited by metal organic vapor deposition (MOCVD). The substrate was HF-last Si, exposed to a 15 s/700 °C NH₃ anneal, which causes a thin ($\sim 8\text{\AA}$) nitrated SiO₂ to form [21,22]. Nitridation is used to achieve a higher capacitance density of the composite dielectric stack by increasing the k -value of the interfacial oxide. The Hf:Si ratio in the high- k layer was nominally 80:20. After high- k deposition a NH₃ anneal at 700 °C for 60 s was performed. The Hf-Si-O films were capped with poly-Si or with TiN/poly-Si electrodes, respectively. All cross-sectional samples were prepared by standard mechanical dimple polishing followed by ion-milling using a Gatan PIPSTM (starting at 4.5 kV, followed by ~ 4 min

at 2.5 kV) with milling angles set to 4°. All samples were plasma cleaned to reduce surface contamination, using a plasma power of 10 W and a 200 mTorr 25% O₂ - 75% Ar gas mixture.

Compositional changes across high- k gate stacks were investigated using a FEI TECNAI F30 instrument equipped with a field-emission gun operating at 300 kV. The point-to-point resolution in conventional high-resolution TEM (HRTEM) was about 0.2 nm (Cs = 1.2 mm). EELS and EDS data were recorded in STEM mode while stepping small focused electron probes of ~ 3 Å and ~ 5 Å diameter, respectively, across the layers comprising the gate stack. EELS spectra were recorded using a post-column imaging filter (Gatan GIF-2001) with a 1k x 1k-YAG CCD camera. The probe forming convergence semi-angle (α) was 10 mrad and the spectrometer collection semi-angle for EELS (β) was 20 mrad (2 mm GIF entrance aperture). HAADF collection semi-angles for imaging were between 50 - 120 mrad using a detector positioned near the spectrometer entrance aperture to allow both image and spectrum collection with a camera length of approximately 40 mm.

Typical novel gate stacks contain both light (O, N, Ti, Si) and heavy elements (Zr, Hf, ...). EELS is more sensitive than EDS for elements with $Z < 10$ if the K-edges are used (O, N) and for elements for which L_{2,3} edges can be analyzed (Si, Ti) [23], whereas EDS was used to detect heavy elements, such as Hf. For chemical profiles, EELS and EDS data were recorded simultaneously. Unless otherwise stated, EELS N K-edges (~ 401 eV), O K-edges (~ 532 eV) and Ti L_{3,2} edges (~ 456 eV) and the Hf L_α-peak in EDS were recorded using 2 s acquisition times. Si L_{2,3} edges could not be collected simultaneously, because the high intensity in this part of spectrum (99 eV) required shorter acquisition times.

After appropriate background subtraction, profiles were generated from spectral counts by integration over suitable energy ranges. Such profiles showed qualitative changes in the concentration of a given element along the profiled line and did not represent true relative elemental concentrations. Quantitative analysis is more involved, requiring knowledge of sample thickness and partial scattering cross-sections, and is the ultimate goal of such analyses. One problem in the simultaneous recording of EELS and EDS was that incident probe intensity and acquisition times are not easily optimized for both EELS and EDS. For the same acquisition time, EELS profiles generally had much better signal to noise ratios because of the inherently higher collection efficiency compared to that of EDS.

The spacing of sampling points along a line from which spectra were recorded is limited by the probe size if minimal overlap of subsequent points is needed in cases where specimen damage is dependent on the total electron dose, or when time-dependent surface contamination is a problem. Whether electron beam-induced sample damage occurs for given experimental conditions can be determined by recording spectra from the same layer while monitoring the ELNES of a core-loss edge, such as the O K-edge, during the acquisition at different levels of beam exposure [24]. Spectra were recorded along lines oriented diagonally across the gate stack. This method reduced overlap of probe tails and due to beam spreading. The chemical profile normal to the gate stack interfaces was then obtained by converting the diagonal profile using the ratio of the diagonal to horizontal lengths. In chemical profiling, sample drift is often a problem when long acquisition times are used to increase signal-to-noise ratios. If the sample drifted at a constant rate and direction, a spatial correction was made. However, as the spatial resolution required for the analysis of interfaces and thin dielectric layers is very high, a conservative interpretation of spatial resolution was often preferred. Despite these issues,

chemical profiles sensitively reflected changes in the concentration of elements across gate stack layers and provided insights into interfacial stability with very high spatial resolution, which was the goal of the experiments presented here.

An *ab-initio* self-consistent real space multiple scattering calculation of ELNES was performed using a commercial software package (FEFF 8.20) [25]. Simulations of O K-edges of HfSiO_4 were performed for different sizes of clusters centered on the absorbing O atom in order to provide insight into the origin of ELNES features. A supplemental code (ATOMS) was used to generate an atoms list and a list of unique potential index for each atom in the structure.

Results

Figure 1(a) shows a typical HRTEM image of a Hf-Si-O film deposited by MOCVD and capped with a poly-Si gate electrode. Shown in Fig. 1(b) is the HAADF-STEM image of the same stack. The Si substrate (aligned along $\langle 110 \rangle$) is at the left and the poly-Si electrode at the right in the HAADF image. The interfacial SiO_2 at the Si substrate interface is clearly visible as a dark band. Significant interfacial roughness is observed at the interface with the poly-Si. Hf-Si-O films experience a strong driving force to phase separate during high-temperature anneals into HfO_2 -rich and SiO_2 -rich phases [26,27]. Thin Hf-Si-O films phase separate laterally (in the film plane) [28], and the HfO_2 -rich phase crystallizes during high-temperature anneals. This causes the film surfaces to roughen significantly.

Figure 1 (c) shows line intensity profiles across the HAADF image that were used to estimate the thickness of the high- k and interfacial layers. Using the inflection points in the HAADF line profile as a measure of the average position of interfaces with finite roughness, the thickness of the interfacial SiO_2 is about 1.4 nm (Fig. 1 (d)). As discussed in detail by DIEBOLD

et al., this method provides an accurate measure of the layer thickness if the layer is thicker than the distance between the probe tails (i.e., a sufficiently small probe forming aperture must be used) [9] and accurate results are obtained for interfaces that are not too rough. In contrast to HERTM, the strong Z-contrast in HAADF images does not require lattice fringes to be present on both sides of the interface for accurate thickness measurement. The Hf-containing high- k layer appears bright in the HAADF image due to the greater atomic number of Hf compared to Si and is approximately 2.6 nm thick.

Figures 1 (d-e) show chemical profiles across this gate stack obtained by EELS and EDS, obtained from regions of the TEM sample with different thickness. The energy ranges for integrating counts underneath EELS absorption edges after background subtraction were chosen to allow for easiest comparison of several elements in one profile. EDS integration windows were chosen to provide profiles with maximum signal to noise ratios. EELS clearly shows that a second interfacial SiO₂ layer exists at the interface between the high- k oxide and poly-Si, although no dark layer that could be assigned to a second interfacial SiO₂ layer was detected at this interface in the HAADF image shown in Fig. 1 (b). This is likely due to the low brightness of the poly-Si and/or due to interfacial roughness. The poly-Si in this area is not oriented near a low-index zone axis and appears darker compared to the Si substrate, which is oriented along $\langle 110 \rangle$, and in which electrons channel along well aligned columns of atoms. EDS showed that the interfacial layer contained no Hf (within the detection limit of the method), i.e. the layer is chemically distinct (SiO₂) rather than part of the Hf-silicate gate dielectric. The layer was also visible as a bright layer in the HRTEM image shown in Fig. 1(a). SiO₂ layers at the high- k /poly-Si interface have also been observed by other authors [29]. Low- k SiO₂ layers ($k_{\text{SiO}_2} = 3.9$), connected in series with the high- k oxide, severely reduce the achievable

capacitance densities of alternative gate stacks, and are thus undesired. Careful analysis of the O K-edge fine structure in both interfacial regions proved that both layers exhibited SiO₂-like bonding, consistent with the observation that the Hf signal did not extend significantly into the interfacial SiO₂ layers. Excess oxygen present in the high-*k* oxide may have reacted with the poly-Si to form a second SiO₂ layer at the top interface. The profiles also showed that nitrogen was preferentially located at the lower interface. The nitrogen was due to the surface and high-*k* NH₃ anneals described above. Scans were performed in reverse direction to ensure that the segregation was not electron beam induced, as previously reported in the literature [30]. Very little nitrogen was detected in the high-*k* layer. This may be due to a preferential segregation of nitrogen to the lower interface or due to the difficulty in detecting small concentrations of lighter elements in a heavily scattering matrix, as will be discussed below. The influence of sample thickness (cf. Figs. 1(d) and (e)) on the chemical profiles will also be discussed below (section 3).

A second example of chemical profiling across an advanced gate stack is shown in Fig. 2. This stack consisted of an Hf-Si-O layer covered with a TiN/poly-Si gate electrode stack. Figures 2 (a) and (b) show the conventional HRTEM image and the STEM-HAADF image respectively. Both images confirmed the presence of a thin SiO_x layer at the substrate interface (dark band in the HAADF image). No low-*k* interfacial layer could be detected between the Hf-Si-O and TiN. Chemical profiles obtained with two different spot sizes (3 Å and 5 Å, respectively) are shown in Figs. 2 (c-d). These profiles showed an unexpected oxygen-rich layer at the interface between TiN and poly-Si, as well as nitrogen at the lower interface, as already discussed above. An oxide between the TiN and poly-Si electrodes likely impedes the proper function of the gate electrode stack. The profiles also indicated the presence of Ti and N

in the high- k oxide. This is likely an artifact due to overlap of TiN and Hf-Si-O along the beam direction due to interfacial roughness. Approaches to separate interfacial roughness from real interdiffusion using ELNES will be discussed in section 3.

3. ISSUES IN THE INTERPRETATION OF EELS OF NOVEL GATE STACKS

Layers containing heavy elements

Typical gate oxides are rare-earth or transition metal oxides that contain heavy elements, such as Hf, Zr, or La. In many cases, it is of interest to quantify the oxygen stoichiometry of these layers, or to study the interdiffusion of Si or N. For example, nitrogen profiles are of interest because many candidate gate electrodes contain nitrogen (TiN, TaN, TaSiN, etc.) or because nitridation of the Si interface has been performed prior or after high- k deposition. While EELS is ideally suited to detect lighter elements, problems arise even in a qualitative analysis when heavy elements are present. The profile shown in Figure 1(d), recorded from a relatively thick part of the sample, exhibited a reduction in the O K-edge integrated intensity in the interior of the Hf-Si-O film relative to the intensity in the interfacial SiO₂. This reduction could be interpreted as oxygen deficiency of the high- k oxide, but is more likely a consequence of elastic scattering in the Hf-Si-O, as will be explained below.

The mean free paths for elastic and inelastic scattering for SiO₂ and HfO₂ are shown in Table I. The elastic scattering cross-section increases with Z . The elastic scattering angles are larger than those for inelastic scattering, and heavy atoms that produce a large elastically scattered intensity outside the collection aperture reduce the intensity of the EELS spectrum. Thus, for a given set of experimental conditions, counts in the ionization edges decrease as the

probe is moved into a region with strong elastic scattering. In addition to elastic scattering, phonon scattering also produces large scattering angles [31]. Phonon scattering cross-sections also increase with the atomic number (roughly proportional to $Z^{3/2}$ [15]). Furthermore, for thicker samples, elastic scattering causes the fraction of plural scattered electrons collected in the entrance aperture to be different for different elements [32]. Elastic scattering preferentially reduces the intensity of the lower loss edge. Thus, the relative ratios of the elements may be affected, unless very large collection apertures are used [32]. EGERTON has shown how to correct for the effects of elastic scattering [33,34]. The minimum detectable number of atoms also depends on the reduction of intensity by the inelastic scattering of the other matrix elements that produce a background [35], because an increased background will increase the uncertainty in the measurement.

A comparison of the profiles shown in Figs. 1(d) and (e), obtained from the same gate stack but at different sample thicknesses, showed the influence of sample thickness on the O K-edge counts in Hf-Si-O. The sample thickness was estimated from t/λ_i (where λ_i is the total mean free path for all inelastic scattering, calculated in Table I), which was obtained from the low-loss (0 - 50 eV) part of spectrum (t/λ_i is given by $\ln(I_0/I_t)$, where I_0 is the intensity under the zero-loss peak and I_t the intensity of the low loss spectrum) [15]. Fig. 1(d) was obtained from a thinner part of the sample, and showed much smaller relative reduction in the O K-edge intensity when the probe is moved into the Hf-Si-O layer. These findings confirm that the contribution of elastic scattering poses a difficulty in obtaining correct relative changes in concentrations of elements in chemical profiles across gate stacks and that thin samples must be used to obtain accurate results.

Separating the effects of interface roughness from interdiffusion or reaction

For ultrathin gate stack layers, interfacial roughness may be a significant portion of the total layer thickness. In particular, silicate films that have a strong tendency to phase separate during high-temperature annealing [26,28], which causes very rough surfaces. For example, the Hf-Si-O film shown in Fig. 1(a) exhibits roughness of about half the total film thickness. For TEM sample thickness comparable to the length scale of interfacial roughness, layers with different composition will overlap significantly along the electron beam direction and interdiffusion or reaction may be difficult to distinguish from roughness. A convenient way to distinguish between roughness and chemical intermixing of layers is to obtain complementary bonding information from ELNES. For example, Ti was detected within the Hf-Si-O layer (and Hf within the TiN) in the chemical profiles shown in Fig. 2. If the observed Ti were due to chemical interdiffusion into the high- k layer, the fine-structure of the Ti $L_{2,3}$ -edge should resemble that of a transition metal oxide, with crystal-field splitting of both the L_2 and L_3 edges [36]. Instead, as shown in Fig. 3, the Ti $L_{2,3}$ -edge ELNES recorded from within the Hf-Si-O layer resembles that of TiN [37], showing no splitting. Thus, chemical profiles showed Ti in the Hf-Si-O because of overlap along the beam direction due to interfacial roughness. Some change in the relative intensity of the L_2/L_3 edges was observed. Interpretation of these changes is beyond the scope of the present work. As discussed below, the probe sizes employed in this experiment were small enough so that no Ti should have been detected for smooth layers of the given thickness.

Spatial resolution

In the absence of beam broadening, which will be further discussed below, the spatial resolution in EELS is determined by the cross-section of the inelastic scattering process. The delocalization of the inelastic scattering has been treated by several authors [20,38-40] and determines the ultimate spatial resolution in EELS of crystalline materials. While significant delocalization has been predicted [38], more recent experimental results claim that in crystalline, zone-axis crystals, the probe size, rather than delocalization, limit the spatial resolution of the EELS core-loss scattering [39]. However, in low-loss EELS, for example of plasmons or the Hf O-edge (30 eV), delocalization causes the spatial resolution to be comparable to the thickness of typical gate stack layers [38]. Furthermore, in these very thin layers interface plasmons may significantly contribute to the signal, making the interpretation of low loss EELS difficult [15,38,41].

In crystalline, zone-axis materials, channeling effects may cause the small (1-2 Å in diameter), focused electron probe to travel down the atomic column without significant broadening and EELS with near atomic resolution may be possible [42]. In this case, the probe size used for EELS analysis of crystalline, zone-axis samples can be estimated by performing a deconvolution from the experimental incoherent HAADF image [14,43]. In HAADF imaging with a detector with sufficiently large inner angle, the contribution from highly localized 1s Bloch states to the image is maximized [12]. However, recent theoretical simulations show that even in channeling conditions, a significant amount of intensity in the EELS spectrum may arise from neighboring columns [44-46]. Clearly, further work is needed to establish the experimental conditions under which true atomic resolution EELS is possible, in particular in EELS of interfaces and defects.

Amorphous or poorly crystallized layers often comprise gate stacks. In this case, channeling effects may not limit probe spreading by random elastic scattering. In addition, if a convergent beam is used, geometric considerations result in a beam spreading of $2t \tan \alpha$, where t is the foil thickness and α the convergence semiangle (Fig. 4). Beam spreading may then limit the attainable spatial resolution in EELS (and EDS) chemical profiles. The thicker the sample, the wider the probe becomes. The beam broadening due to elastic scattering can be estimated from an analytical expression given by REIMER (ref. [47], eqn. (5.99)):

$$x_0 = 1.05 \times 10^5 \frac{\rho \alpha^2}{A} \frac{Z}{E} \frac{1 + E/E_0}{1 + E/2E_0} t^{3/2} \quad (1)$$

where x_0 is the broadening in cm, ρ the density in g/cm³, A the atomic weight, Z the atomic number, E the incident beam energy in eV, E_0 the rest energy and t the foil thickness in cm. The average atomic number was determined using eqn. (5.5.) in ref. [15]. For sample thicknesses in the order of 50 nm, the beam broadening due to elastic scattering in heavy, amorphous layers such as HfO₂ is predicted to be ~ 0.4 nm for 300 keV electrons. Beam spreading due to the convergent beam results in beam broadening of 0.6 and 1 nm for 30 nm and 50 nm thick specimens, respectively. In any but the thinnest samples (< 50 nm), the spatial resolution in EELS will be determined by the geometry of the detector if the layer is amorphous, contains heavy atoms, such as HfO₂, and for typical convergence angles. The electrons collected by the entrance aperture come from a diameter of about $2r \approx \alpha t$, where α is the collection semi-angle [15]. This diameter is below 1 nm for typical apertures and sample thicknesses (see ref. [15], page 347). Thus, in the analysis of amorphous heavy atom containing layers and for TEM samples that are not sufficiently thin, EELS has a better spatial resolution than EDS. The resolution in EDS is further negatively affected by secondary electrons.

In practice, spatial resolution is often dictated by the requirement of a sufficient signal to noise ratio. Small probes require long acquisition times, which are usually limited by sample drift, beam damage and contamination. While modern instruments are capable of performing extremely stable scans, it is critical that the microscope environment is optimized [48]. Larger probes with higher intensity improve signal-to-noise-ratios for a given acquisition time, albeit at the expense of spatial resolution. Larger probe forming apertures (the condenser aperture of a conventional TEM) increase the beam current but also the current in probe tails and cause delocalization of the HAADF image and of the analytical information [9]. The trade-off between signal to noise ratio and spatial resolution is clearly observed in the results shown in Figs. 2 (c-d). The Hf-Si-O layer in this stack was partially crystallized and the TiN layer was fully crystallized (see Fig. 2(a)); thus beam spreading is likely to be less severe than for an amorphous layer discussed above. The profile obtained with the smaller probe ($3\text{\AA}$) that has a lower intensity ($\sim 0.14\text{ nA}$) has a much better spatial resolution but a higher noise level in the data (Fig. 2(c)). The Hf-Si-O layer and the bottom interfacial SiO_2 layer are spatially separated, but because of the noise, it is difficult to determine whether a N-rich layer is present at the Si-interface. In contrast, the profile obtained with the larger probe ($\sim 5\text{\AA}$) and increased brightness (0.7 pA) causes the Hf-EDS signal to be much more spread out into the adjacent layers, but clearly indicates the presence of N at the Si-interface. The fact that the spatial resolution significantly improved with the $3\text{ \AA}$ probe showed that the lateral spreading of the probe was significantly less than for the amorphous layers discussed above. This indicates some channeling effects although grains were not oriented along a major zone axis. With the advent of Cs corrected probes with increased intensity, spatial resolution can be further improved [49].

ELNES from ultra-thin layers

As shown above, the ELNES was used to identify interfacial phases and to distinguish roughness from chemical intermixing. For core-loss ELNES, the required energy resolution, usually determined by the electron source, depends on edges of interest. For example, an energy resolution of 1 eV (readily attainable in most Schottky-field emitter TEM/STEMs) is sufficient to resolve all ELNES features of O K-edges of transition metal oxides [50]. However, the detection of differences in ELNES from different layers may require much greater energy resolution. In addition to a good energy resolution, a high brightness in a small probe is required. The probe has to be small enough so that regions with dissimilar chemistry or electronic structure will not be sampled simultaneously and beam broadening may limit spatial resolution for amorphous layers. In principle, statistical analysis or MLS fitting could be applied [29,51]. However, MLS fitting requires *a-priori* knowledge of all possible contributing ELNES features, which may not be known, and suitable reference spectra, which may be difficult to obtain independently.

For high-*k* gate stacks employing transition metal (Hf, Zr) oxides and their alloys with silica or alumina, ELNES of O K-edges has been used to show that unintentionally grown thin layers in gate stacks at the Si interface resemble SiO₂ rather than a “silicate”, i.e. SiO₂ mixed with the transition metal [41,52] (in contrast, rare-earth and related high-*k* oxides often rapidly react with underlying SiO₂ layers to form an amorphous silicate [53,54]). The O K-edge and Si-L edge ELNES fine-structure has been used to show that thermally grown SiO₂ layers do not have bulk electronic structure within several Å of the Si interface [7,55]. ELNES of oxygen K-edges of high-*k* oxides has also been shown to be sensitive to changes in the point defect chemistry as well as reflect crystallization [29,41,56].

An important difficulty in using ELNES to identify interfacial layers, for example to distinguish between an interfacial silicate and a SiO_2 , is that very thin (few Å) layers often do not have bulk electronic structure. Thus, interpretation of experimental spectra using reference ELNES from bulk materials (“fingerprinting”) is prohibited. For example, NEATON *et al.* have shown that a bulk-like SiO_2 ELNES is only established if the absorbing O atom has a sufficient number of O next-nearest neighbors (achieved within about 5 Å) [8]. Similar conclusions can be drawn for crystalline HfSiO_4 from the multiple scattering simulations [25] of O K-edge ELNES using different cluster sizes, shown in Fig. 5. The calculations show that at least a 30 atom cluster (~ 8 Å in diameter) is needed before bulk-like signatures in the fine-structure are established. Thus HfSiO_4 films thinner than 8 Å, as may be present as an interfacial phase, should not exhibit characteristic features of bulk ELNES and may be difficult to identify (note that the calculations were performed for crystalline HfSiO_4 , a phase that is not observed under typical CMOS device annealing conditions [26]). In addition, their different electronic structure may indicate that the properties (such as dielectric constant) of ultrathin layers may not simply scale with thickness, and their contribution to the composite properties of gate stacks will be complex. With the recent, rapid advances in the theory and accuracy of ELNES calculations, very powerful tools for analyzing the local atomic environment in very thin layers are now available [25,57].

TEM sample quality

As discussed above, very thin samples are required for high spatial resolution analysis of amorphous or poorly crystallized layers. However, TEM samples prepared by ion-milling typically show amorphous surface layers produced by ion-beam damage. These layers degrade the spatial resolution by beam broadening, reduce the resolution in ELNES (by contributing

non-bulk-like features) and change elemental ratios if surface compositions are different from the interior [58]. The contribution of these amorphous layers increasing with decreasing TEM sample thickness. Even in the absence of surface damage, thin samples have a greater contribution from surface signals (for example surface plasmons [15]) and data obtained from ultrathin samples may not be characteristic for the bulk sample. However, if the influence of elastic scattering is to be prevented, samples should thin. A benefit of operating the TEM/STEM at higher acceleration voltages is then an increase in λ_e , permitting greater TEM sample thicknesses that have less contribution from surface layers.

Hydroxyl absorption upon exposure to air, which is particularly severe in case of rare-earth and related oxides, has been associated with interfacial reactivity of uncapped stacks [54,59]. It has also been observed that in Y- and La-based films, OH uptake leads to additional interfacial SiO₂ in the thin part of the TEM sample that is not present in the bulk [60,61]. For the less reactive Hf-Si-O investigated here, interfacial SiO₂ layers did not vary in thickness between the thinner and thicker parts of the TEM sample (see Figs. 1 (d-e)). Thus the SiO₂ layer thicknesses represented bulk values and were consistent with results from independent electrical measurements. Uncapped gate oxides or unannealed samples (post-deposition annealing leads to densification) often showed an increased reactivity. In addition to OH absorption, uncapped films may more easily oxidize or react with epoxy during TEM sample preparation. Care must also be taken during plasma cleaning to not oxidize the Si.

SUMMARY

In summary, EELS in combination with HAADF imaging is capable of routine analysis of ultrathin layers that comprise current gate stacks for Si CMOS with *a-priori* unknown structure and composition with very high spatial resolution. We have shown that reaction layers

of a few Å thickness can be detected and their composition be identified even in the presence of substantial interfacial roughness that may obscure such layers in the image. The studies demonstrated that atomic resolution imaging and spectroscopy techniques are essential in detecting unintentional layers that must be considered in the interpretation of the dielectric properties of alternative gate stacks. Furthermore, thin, low- k interfacial layers may not have bulk electronic properties, and may contribute to the properties of the gate stack in complex ways.

Factors affecting the results of qualitative composition profiles were analyzed and methods to interpret the results were proposed. For amorphous gate oxide films containing heavily scattering atoms and given typical convergence angles (~ 10 mrad), very thin samples (< 20 nm) are required for sub-5Å spatial resolution. Interpretation of ELNES from real layers with unknown stoichiometries requires robust, routinely available simulation techniques that work for imperfect materials, as well as improved (sub-1 eV) energy resolution in experiments. The most recent generation of microscopes equipped with monochromators [50] have excellent energy resolution, but do not yet have required the Ångstrom-level spatial resolution to analyze typical novel gate stacks. Thus, future developments of microscopes that combine Cs corrected and monochromated electron probes are extremely attractive as layers in microelectronic devices approach sub-nanometer dimensions.

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TABLES

Table I:

Estimated elastic (λ_e) and total inelastic (λ_i) mean free paths for SiO₂ and HfO₂ for 300 keV electrons in nm, using eqns. (3.8) and (5.2)-(5.4) in ref. [15]. The elastic mean free path is calculated from the elastic cross-section, σ_e , by $\lambda_e = (\sigma_e n_a)^{-1}$, where n_a is the number of atoms per unit volume [15]. Average atomic number (Z) values were obtained from eqn. (5.5) in ref. [15]. The collection semi-angle is given in square brackets. Experimental values for the λ_i are from reference [62].

Material	λ_e (nm)	λ_i (nm)	λ_i (experimental, in nm)
SiO ₂	660	140 [20 mrad]	247 [10 mrad]
HfO ₂	87	95 [20 mrad]	-

FIGURE CAPTIONS

Figure 1

(a) Conventional HRTEM image of a typical development-level Hf-Si-O gate stack capped with a poly-Si electrode. (b) HAADF-STEM image showing the Si-substrate lattice (along $\langle 110 \rangle$) at left followed by a dark band of an interfacial SiO_2 and the bright, Hf-rich high- k oxide layer. The poly-Si is at the right side of the image and appears darkest. No image contrast that could be assigned to a second interfacial SiO_2 layer could be detected between the high- k oxide and poly-Si. (c) image intensity profile (solid line) across the HAADF imaged (averaged over 2 nm in the vertical direction). The dotted line is the same intensity profile but rescaled to show periodic lattice fringes due to the Si lattice, and the location of the Si/ SiO_2 interface. The thicknesses of the layers (see text) were determined using the inflection points in the intensity profiles. The cross-hatched areas indicate the interfacial SiO_2 (left) and the high- k oxide (right), respectively. (d-e) EELS and EDS chemical profiles recorded across the high- k gate stack shown in (a-b). The profiles shown in (d) were obtained from a region on the TEM sample with thickness $t = 1.5\lambda_i$. The profiles shown in (e) were from a thinner region, $t = 0.7\lambda_i$, where λ_i is the inelastic mean free path of a 300 keV electron in Si, which is about 180 nm [62]. The shaded areas are a guide for the eye to indicate the approximate location of interfacial regions with different composition. Note that the x -axis scales are different in (c) and (d-e).

Figure 2

(a) Conventional HRTEM image of a MOCVD Hf-Si-O film capped with a TiN/poly-Si gate electrode stack. (b) HAADF image of the same stack. The bright layer is the Hf-Si-O. An interfacial oxide was observed between the Si substrate (left most in image) and the high- k layer. The interface between Hf-Si-O and TiN shows significant roughness. (c)-(d) EELS and EDS chemical profiles with two different spot sizes, corresponding to about 3 Å (c) and 5 Å (d), respectively. Nitrogen is detected at the substrate interface and a oxygen-rich layer is present between the TiN and the poly-Si. Apparent spreading of Ti and N into the high- k layer is due to interfacial roughness (see text).

Figure 3

ELNES of Ti $L_{2,3}$ -edges recorded from different locations of the stack shown in Fig. 2, and comparison with a reference spectrum from rutile TiO_2 . Note that due to the extreme roughness of the Hf-Si-O (see text), some Ti is detected at the bottom interface in several locations, such as the one shown here.

Figure 4

Schematic (after ref. [9]) showing that the probe in a zone axis crystal is confined to the atomic columns of the probe size is less than the atomic spacing, reducing the lateral broadening of the peak (left). In an amorphous layer (right) the beam is broadened by elastic scattering and by the convergence of the beam (Δ). The entrance aperture of the spectrometer rejects electrons scattered to angles larger than Δ .

Figure 5

(a) Calculated (FEFF8) O K-edge fine structures for different cluster sizes of crystalline HfSiO_4 [63]. Cluster sizes were specified by the radii used in the calculation. The bulk-like fine-structure with the characteristic double peak at the edge onset is only established for cluster larger than 30 atoms. The atomic arrangement in the 30 atom cluster is shown in (b). Large spheres are Hf, medium spheres Si and small spheres (two sizes) are O.

Figure 1 (a-c)

Figure 1 (d-e)

Figure 2 (a-b)

Figure 2 (c-d)

Figure 3

Figure 4

Figure 5