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Advanced Nanoanalysis of a Hf-Based High-*k* Dielectric Stack Prior to Activation

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ABSTRACT

Analytical electron microscopy techniques are used to investigate elemental distributions across a high- k dielectric stack with a metal gate. Electron energy-loss spectroscopy results from a Si(100)/SiO₂/HfO₂/TiN/a-Si gate stack confirm the presence of an oxide interfacial phase at the TiN/a-Si interface prior to activation of the stack.

INTRODUCTION

HfO₂ and HfSiO based systems are among the high-*k* materials currently being investigated for use as the gate dielectric to replace amorphous SiO₂ and Si(O,N) in Si MOSFETs. At the same time, metal gate electrodes are being introduced into the dielectric gate stacks to remove problems associated with poly-Si gate electrodes (1-2). In order to facilitate the integration of these metal gate electrodes, they are typically capped with poly-Si resulting in metal inserted poly stacks (3). Metals with work functions suitable for both *n* and *p* devices, i.e. overlapping with the Si conduction and valence bands are required. For this purpose a range of materials is under consideration with TiN being a candidate for mid-gap requirements. From electrical measurements, it is becoming clear that the thermal budget required to process a device causes significant changes in the behavior of these metal gate systems (4). As a general observation, one can conclude that the work function of most materials shifts towards midgap position upon application of thermal budgets above ~700-900 °C. Thus it is likely that there will be significant interactions between the metal gate and the gate dielectric. Significant interface interactions occurring at the metal/poly interface can also have an adverse effect on device performance. The nature and extent of such interactions will depend on the deposition techniques used as well as the details of the processing and the thermal budget required. We have previously presented results from a fully activated Si/SiO₂/HfO₂/TiN/poly-Si stack (1000 °C for 10 sec) and shown the presence of an amorphous layer at the TiN/poly-Si interface (5-6). The layer was identified as an oxynitride in which Si was bonded to N and O. The source of the O is believed to be

oxidation of the TiN surface during transfer of the wafer between tools during the processing. Here we examine an unactivated stack and confirm that O is indeed present at this interface prior to the 1000 °C activation step.

Electron energy-loss spectroscopy (EELS) when performed in a modern analytical electron microscope offers an excellent method of characterizing the materials and the interactions between the different layers present in high- k dielectric stacks [see, for example, references 5-7]. In many of the systems of current interest, information on all of the elements present can be obtained in a single EELS dataset. Analysis of the energy-loss near-edge structure (ELNES) present on the ionization edges can provide information on the local chemistry, structure and bonding. Since the local bonding and coordination of the atom determines the ELNES, it is possible to separate out the contributions to an edge from atoms in different phases. This can be achieved by modeling the edge shape as a linear combination of the ELNES from appropriate standards. Spectrum imaging uses computer control to position the electron beam and to record one or more spectra at each point, building up an N-dimensional data set where $N \geq 2$ (8). Combined with high angle annular dark field scanning transmission electron microscopy (HAADF STEM) imaging it provides a powerful method of characterizing samples. Here we apply these methods to investigate an unactivated Si/SiO₂/HfO₂/TiN/a-Si stack.

EXPERIMENTAL CONDITIONS

Prior to the gate stack deposition, the Si (100) surface was etched by a HF:H₂O (1:100) solution, to remove the native oxide. Subsequently, the wafer was exposed to an O₃/DI water cleaning sequence, resulting in the growth of ~1.0 nm chemical oxide. This interface has proven to be an ideal starting surface for atomic layer deposition (ALD) growth. HfO₂ was deposited in an ALCVD (TM ASM International, The Netherlands) Pulsar 2000 reactor using an HfCl₄/H₂O process at 300 °C. Target HfO₂ film thickness was 3.5-4.0 nm (80 ALD cycles). The deposited film was given an oxidizing post deposition anneal at 500 °C for 1 minute. At these temperatures, the HfO₂ film crystallizes into poly-crystalline HfO₂. Subsequently, the wafer was covered with 10 nm TiN. A standard degas treatment at 330 °C for 40 sec was applied prior to TiN deposition. The physical vapor deposited (PVD) TiN was grown via a standard DC sputtering process using the following conditions:- Heater temperature: none (onset deposition at room temperature); Process nitrogen flow: 75 sccm; Backside Ar flow: 25 sccm; Pressure: 5 mTorr; DC power: 8000 W; DC power density: 25 W cm⁻². The wafer was capped additionally with 100 nm amorphous Si. In depositing the layers, the surface of a wafer (either the HfO₂ or TiN surface) was exposed to the atmosphere of the clean room as it was moved from process tool to process tool and, in particular, after the HfO₂ anneal and the TiN deposition steps.

A cross-sectional transmission electron microscopy (TEM) specimen was prepared from the wafer by standard grinding, polishing, dimpling and ion milling methods. The TEM specimen is examined in an FEI Tecnai F20 TEM/STEM equipped with a field emission gun and a Gatan ENFINA electron spectrometer. Spectrum imaging is performed using Gatan DigiScan and Digital Micrograph software. Typical probe

conditions for the EELS used in this work consisted of a ~ 0.5 nm diameter probe with 69 pA of current and a convergence semi-angle of 13 mrad. The single crystal Si substrate was used to orientate the sample such that the growth direction was perpendicular to the electron beam direction. The spectrometer had a collection semi-angle of 18 mrad. For the core loss spectrum imaging results presented here, the energy range ~ 80 eV to ~ 740 eV was recorded at a dispersion of 0.5 eV/ch and a typical dwell time of 3 sec per pixel.

RESULTS AND DISCUSSION

Figure 1 shows two high resolution TEM images of the unactivated Si/SiO₂/HfO₂/TiN/a-Si stack. The SiO₂ and a-Si layers are amorphous while the HfO₂ and TiN layers are crystalline. The HfO₂/TiN interface in the upper image appears quite flat whereas in the lower image it is difficult to distinguish as a result of its non-flat nature. Interestingly, the TiN/a-Si interface is also less even in this region of the wafer. These images were taken from the same TEM cross-section sample and illustrate the level of variation which may be observed within a given wafer. Figure 2 contains a lower magnification bright field image, also from the same TEM specimen, which illustrates the local unevenness of the TiN/a-Si interface more clearly. The columnar nature of the TiN layer (9) can also be seen in figures 1 and 2: continuous grains are observed extending from the bottom to the top of the TiN layer.

A HAADF STEM image of this stack is shown in figure 3a. As the HAADF image is sensitive to the average atomic number, Z , the HfO_2 layer appears as a bright line, with the TiN on the right less bright and the Si substrate on the left darker. An EELS spectrum image covering the energy range including Si $L_{2,3}$ -edges ($\sim 99\text{eV}$), Hf $N_{4,5}$ -edges ($\sim 214\text{ eV}$), N K-edge ($\sim 400\text{ eV}$), Ti $L_{2,3}$ -edges ($\sim 455\text{ eV}$) and O K-edge ($\sim 532\text{ eV}$) was acquired from the area illustrated on figure 3a by the horizontal white line. Background removal under each edge was performed by fitting a function AE^{-r} to the background preceding the edge, extrapolating it under the edge and then subtracting it. Elemental distribution profiles were created from the spectrum image by integrating the counts in these background subtracted edges. The resulting profiles are shown in figure 3b. As in the case of the activated stack reported earlier (5-6), there is a peak in the O profile at the TiN/a-Si interface; examination of the raw data confirmed that this peak corresponds to the presence of a real O edge. In the case of the activated stack, this peak in the O signal was accompanied by a clear separation of the N and Ti signals with the N signal extending further into the poly-Si than the Ti signal. Here, while there is a separation of the N and Ti signals at the same position as the peak in the O profile, it is less pronounced than in the case of the activated sample. Other regions of the same sample analyzed showed either a similar level of separation of signals or, more frequently, no discernible separation at all although an O peak was always observed at this interface. While the separation is less pronounced, it is real since the intensities at a given pixel are obtained from the same spectrum and the sensitivity of the technique to N is less than that to Ti. At this stage it is not clear if the difference between the unactivated and activated stacks is larger than the variations within a given stack, but it is plausible that the high temperature of the activation step alters the chemistry of the interface.

Note that, perturbations in the background from underlying edges can cause difficulties with background removal resulting in unphysical signals being obtained in the profiles. For example, the 'Si L_{2,3} signal' can be negative in the presence of Hf or Ti. Therefore care must be taken in interpreting the data. In the case of the Si edges, the weaker Si L₁-edge is also present in the data at 149 eV (see the inset in figure 4a) and can be used to provide further information on the presence of Si in the sample. While the background removal procedure for this edge is less affected by the presence of Ti and Hf, it is very sensitive to the ELNES on the Si L_{2,3}-edges and therefore, with the simple background removal procedure used here, it cannot be used for quantification purposes. Nevertheless, it is useful for the detection of the presence of Si. The Si L₁ profile in figure 3b qualitatively depicts the presence, but not the quantity, of Si more accurately than the Si L_{2,3} profile. Further, it reveals the involvement of the Si in the oxide phase present at the TiN/a-Si interface.

Further information on the chemistry of the stack may be obtained by examining the ELNES in detail. For example, the change in ELNES observed on the Si L_{2,3}-edges is illustrated in figure 4a. The ELNES from the Si substrate and the a-Si region are very similar. However, distinct changes in the ELNES and also the energy of the edge onset are observed in the case of the edges from the SiO₂ layer and the TiN/a-Si interface regions. The edge from the SiO₂ layer is characteristic of SiO₂ or SiO_x. A good fit to the edge from the TiN/a-Si interface region can be obtained by multiple linear least squares (MLLS) fitting using a combination of Si edges from the a-Si and SiO_x regions along with an edge from an amorphous SiN_y reference film. This indicates that, as in the case of the activated sample, Si is present at this interface in the form of an oxynitride.

Applying the MLLS fit to the whole of the background subtracted spectrum image results in the distribution of the different Si environments across the stack. In order to avoid the MLLS fits from going negative, dummy spectra from HfO₂ and TiN were also used in the fitting procedure (5). The Si edges used in the fitting procedure were normalized to the same maximum height prior to fitting. Differences observed in the ELNES on the N K and O K-edges are currently under investigation.

CONCLUSIONS

The results presented above show that there is an oxide layer present at the TiN/a-Si interface in a Si/SiO₂/HfO₂/TiN/a-Si stack prior to activation. Analysis of the Si L-edges indicates that this oxide is likely to be an oxynitride as was observed in the case of an activated stack reported previously. However, the separation of N and Ti signals which was observed in the activated stack, appears to be less pronounced here. Further detailed analyses of the ELNES on the other edges are currently underway in order to investigate whether Ti is involved in this interfacial phase and also into the nature of the HfO₂/TiN interface. Such investigations help to develop an understanding of the interfacial reactions which occur during deposition and processing steps. As we have observed before, formation of a dielectric layer between the TiN metal electrode and the poly-Si connecting electrode reduces the junction capacitance and hence device performance. Thus control of this interface is important if the desired performance is to be achieved. Hence, it is imperative that these interfaces are investigated with techniques such as the

ones used here in order to improve understanding of the work function behavior of metal gate electrode/dielectric stacks to be used in future CMOS technologies.

The usefulness of EELS spectrum imaging to investigations of interface reactions has been demonstrated. Further, such techniques can be applied to a wide variety of other functional materials where boundaries and interfaces play an important role and are applicable to interface analyses in many material systems.

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FIGURES

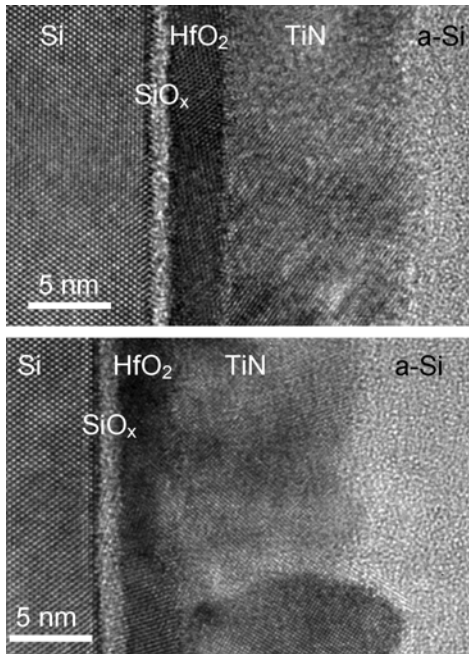


Figure 1. High resolution TEM images of the unactivated Si/SiO₂/HfO₂/TiN/a-Si stack.

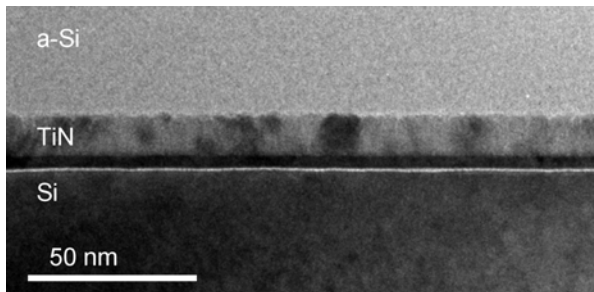


Figure 2. Bright field TEM image of the unactivated Si/SiO₂/HfO₂/TiN/a-Si stack.

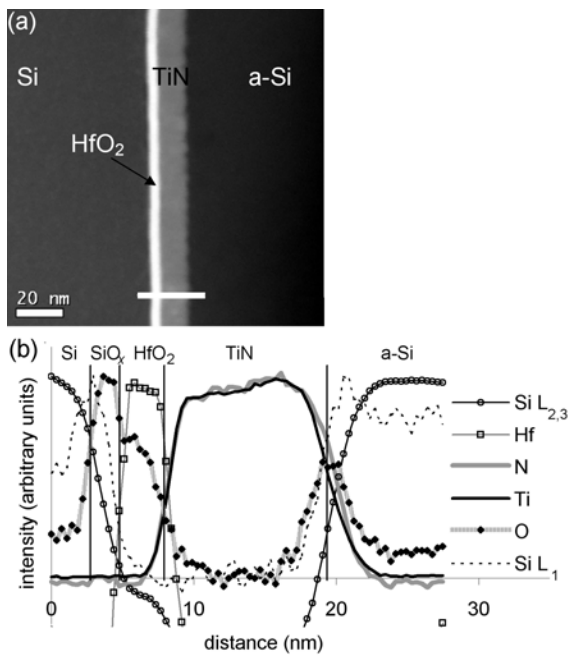


Figure 3. (a) HAADF STEM image of an unactivated Si/SiO₂/HfO₂/TiN/a-Si stack. (b) Si, Hf, N, Ti and O elemental profiles obtained from EELS spectrum image acquired along the white line indicated on (a). Note that these have been scaled to the same maximum height and do not relate directly to concentrations.

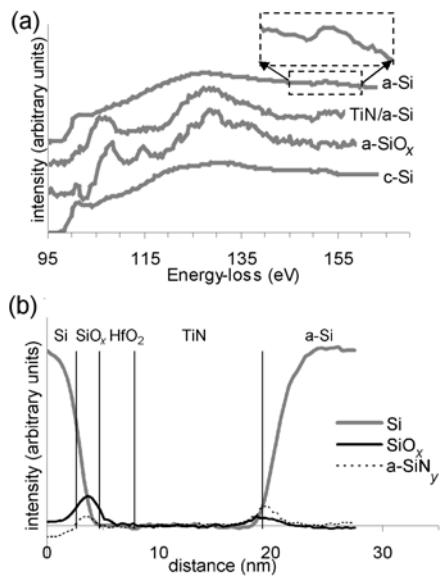


Figure 4. (a) ELNES on the Si $L_{2,3}$ -edges observed in different regions of the unactivated Si/SiO₂/HfO₂/TiN/a-Si stack. The inset contains an enlarged region of the a-Si spectrum to show the Si L_1 edge at 149 eV. (b) Results of MLLS fitting to Si $L_{2,3}$ -edges in the whole spectrum image using reference edges from a-Si, SiO_x and SiN_y.