Experimental and theoretical investigation of the effect of SiO₂ content in gate dielectrics on work function shift induced by nanoscale capping layers

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Experimental and theoretical investigation of the effect of SiO₂ content in gate dielectrics on work function shift induced by nanoscale capping layers

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The impact of SiO₂ content in ultrathin gate dielectrics on the magnitude of the effective work function (EWF) shift induced by nanoscale capping layers has been investigated experimentally and theoretically. The magnitude of the effective work function shift for four different capping layers (AlN, Al₂O₃, La₂O₃, and Gd₂O₃) is measured as a function of SiO₂ content in the gate dielectric. A nearly linear increase of this shift with SiO₂ content is observed for all capping layers. The origin of this dependence is explained using density functional theory simulations. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4747805>]

Nanoscale capping layers have been demonstrated to tune the effective work function (EWF) of metal gates in advanced gate stacks with Hf-based gate dielectrics.^{1,2} Many types of capping layers have been investigated including Al-based capping layers^{3–5} and rare earth metal-based capping layers.^{1,6,7} The composition of the capping layer, its thickness, and thermal budget used to fabricate devices incorporating such capping layers have all been thoroughly studied. In addition, several models have already been proposed to explain the capping layer effect on flatband voltage (V_{FB}).^{8–12} However, one area that has not been systematically investigated is the effect of the composition of the dielectric below the capping layer on the magnitude of the flatband voltage shift. In this article, we have investigated four different types of capping layers deposited on dielectrics with varying compositions. We show that the amount of work function tuning by a given capping layer strongly depends on the SiO₂ content in the underlying Hf-based gate dielectric and use density functional theory (DFT) calculations to propose a mechanism to explain this SiO₂ effect.

Metal-oxide-semiconductor (MOS) capacitors were fabricated on a *p*-type Si substrate with a dopant concentration of $1.0 \times 10^{18} \text{ cm}^{-3}$. The substrate was cleaned using diluted hydrofluoric acid followed by O₃-last cleaning. SiO₂ gate dielectric (4 nm thick) was then grown by thermal oxidation of the Si substrate. Different SiO₂ thicknesses were obtained across the wafer (ranging from 1.0 nm to 4.0 nm) by a selective wet-etching process of the thermally grown 4 nm SiO₂ layer. HfO₂ and HfSi_xO_y thin films (2 nm thick) were then deposited by atomic layer deposition on top of the SiO₂ layers. The composition of Hf-silicate film was 60% SiO₂ as measured by Rutherford backscattering spectrometry. Thus, three gate dielectrics with the following SiO₂ content were evaluated: 0% (HfO₂), 60% (HfSi_xO_y), and 100% (SiO₂). These dielectrics were subsequently covered with 1.0 nm of four different capping layers (AlN, Al₂O₃, Gd₂O₃, and La₂O₃), all deposited by physical vapor deposition. TaN metal gate electrodes (10 nm) were then deposited on the capping layers without breaking vacuum in the same physical

vapor system at room temperature. To complete the gate stack, 100 nm polycrystalline silicon (poly-Si) films were deposited on TaN and then implanted by phosphorous. The poly-Si dopant activation was performed at 1000 °C for 10 s in nitrogen. Finally, a layer of Al was deposited on the back-side of the wafer to improve the quality of electrical contact during device measurement. C-V curves were measured with an Agilent 4294 A LCR meter. Fitting of the curves, with quantum mechanical correction, was done with the North Carolina State University (NCSU) model to extract the equivalent oxide thickness (EOT), flatband voltage, and substrate doping concentration.¹³ Plots of V_{FB} vs. EOT were used to extract the EWF of each electrode.

Fig. 1 shows the EWF of devices having the stack TaN/capping layer/gate dielectric/Si. The figure summarizes results from three different gate dielectrics and four capping layers. One device was fabricated without a capping layer to be used as reference (labeled as “No cap” in Fig. 1). The effect of the gate dielectric on the measured EWF of the TaN metal gate for the uncapped device was relatively small (~30 mV). However, for all four capping layers (AlN, Al₂O₃, Gd₂O₃, and La₂O₃), the effective work function of the metal gate showed significant shift (100 s of milliVolts) as the SiO₂ content of the gate dielectric increased (from 0% to 100% SiO₂). Consistent with published reports, the Al-containing and rare earth-containing devices produce opposite work function shifts. Figure 2 shows the absolute value of the magnitude of the EWF shift (as opposed to the value of EWF shown in Fig. 1) with % SiO₂ in the gate dielectric, relative to the uncapped device. Using AlN as an example, the EWF of TaN increased by 350 mV for HfO₂, 610 mV for HfSi_xO_y, and 730 mV for SiO₂ gate dielectric, relative to the uncapped device. Similarly, for the Al₂O₃, the effective work function of TaN increased by 300 mV for HfO₂, 480 mV for HfSi_xO_y, and 680 for SiO₂ gate dielectric. **In comparison**, the EWF of TaN in the case of Gd₂O₃ capping dropped by 80 mV for HfO₂, 310 mV for HfSi_xO_y, and 420 mV for SiO₂ gate dielectric, relative to the uncapped device. Similarly, the EWF of TaN in the case of La₂O₃ capping dropped by 70 mV for HfO₂, 330 mV for HfSi_xO_y, and 440 mV for SiO₂ gate dielectric.

The question we attempt to answer is why the observed EWF shift increases with SiO₂ content in the gate stack. We

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FIG. 1. Extracted EWF of the devices used in this study for three different gate dielectrics: HfO₂, HfSi₂O₄, and SiO₂. Four different capping layers of 1 nm have been used: AlN, Al₂O₃, Gd₂O₃, and La₂O₃. Uncapped devices, marked as No Cap, have been used as reference. For the capped devices, there is clear shift of the EWF as the % SiO₂ in the gate dielectric increases. Al-based capping layers cause a positive shift on the EWF, while the rare earth-based capping layers shift in the opposite direction.

use a combination of experimental and theoretical arguments to answer this question. It has been reported that both Al and rare earth metals show significant diffusion in Hf-based gate stacks.^{1,5,9} Upon diffusion, the aluminum and rare earth metals were found to react with the gate dielectric and interfacial SiO₂ layers. Some studies suggested the formation of silicates such as LaSiO_x at the interface near the substrate,¹⁴ while others indicated the formation of a HfLaSiO gate dielectric as a result of these reactions.¹⁵ Figure 3 shows the interfacial fixed charge density extracted from the plots of

FIG. 2. Magnitude of the shift on the EWF for the capped devices as a function of % SiO₂ present in the gate dielectric. 0% SiO₂ corresponds to devices built with HfO₂ gate dielectric, while the 60% SiO₂ corresponds to the HfSi₂O₄ dielectric. The magnitude of the shift in the Al-based capping layers is higher than the rare earth based ones.

FIG. 3. Interfacial fixed charge density extracted from the plots of V_{FB} versus EOT for all the devices in this study. The interaction between the capping layer and the underlying gate stack increases with % SiO₂ in the gate dielectric, resulting in more charges at the interface. Fixed charge density is higher for Al-containing capping layers compared to the lanthanide capping layers. This may be due to the lower melting point and smaller size of any elemental Al, allowing more extensive diffusion and subsequent interfacial reactions.

V_{FB} versus EOT for all the devices in this study. For every capping layer, the fixed charge density increases with SiO₂ content in the gate dielectric, reaching its maximum for 100% SiO₂. These data suggest that interaction between the capping layer and the underlying gate stack increases with % SiO₂ in the gate dielectric, resulting in more fixed charges at the interface. Interestingly, the fixed charge density is higher for Al-containing capping layers compared to the lanthanide capping layers. This may be due to the lower melting point and smaller size of elemental Al, causing more extensive diffusion and subsequent interfacial reactions. Nonetheless, the measured fixed charge concentrations are not enough to produce the observed shift in EWF, but they indicate that more Al is reaching the interface, causing a higher shift in the EWF when compared to the lanthanide capping layers. For example, it can be easily shown using a simple calculation ($Q = CV$) that the magnitude of fixed charge in our devices (10^{10} – 10^{12} cm⁻²) can only account for 10s of millivolts in voltage shift in the C-V curves, but the measured voltage shifts in our devices are in the hundreds of millivolts. So, fixed charges alone cannot account for the observed voltage shifts.

Given these experimental observations, we explain the dependence of EWF shift on % SiO₂ in the gate dielectric. Recent calculations by Lin and Robertson have correctly predicted the magnitude and the sign of the EWF shift using HfO₂ dielectric.¹⁰ For any of the atoms studied here (Al, La, or Gd), it is expected that reactions within the bulk of the dielectric cannot produce a dipole. This is because dipoles cannot exist in the bulk of a dielectric, but only at the interface between two different materials. Thus, only atoms that diffuse to the interface between Hf-containing gate dielectric and interfacial SiO₂ layer can produce a dipole. We surmise,

based on our fixed charge data shown in Fig. 3, that when the % SiO₂ in the gate dielectric increases, a larger number of capping layer atoms (Al, La, or Gd) are able to reach the interface and form interfacial bonds, leading to dipole formation. To prove this hypothesis, we calculate the magnitude of the voltage shift for different levels of Al, or La introduced at the dielectric/SiO₂ interface by DFT.

The DFT simulations were performed according to the work of Lin and Robertson.¹⁰ The HfO₂/SiO₂ interface structure is built with lateral size of $7.30 \times 7.30 \text{ \AA}^2$. Along the *z* direction, the lattice constant in HfO₂ layers is 5.12 Å; and in SiO₂ layers, it is 7.30 Å. For neutral charge condition, the O atoms at the interface are removed only from Hf-O bonds, not from Si-O bonds. This is exactly the same as the c-322 interface in Sharia's notation.¹⁶ The relaxed structures for 0%, 50%, and 100% La substituted interfaces are partly shown in Fig. 4. There are 6 Si layers and 9 Hf layers in the whole interface structure without substitution. Each Si layer has two Si atoms and each Hf layer has four Hf atoms. In the modified structures, the Al and La atoms replace either half of the Hf atoms at the interface, for 50% substitution, or all the Hf atoms at the interface, for 100% substitution. For every two substituted atoms, an O atom is removed from the oxygen layer between Hf and the substituted atoms (Al or La). The VIENNA AB-INITIO SIMULATION PACKAGE¹⁷ is employed for the calculations, where the generalized gradient approximation of the exchange correlation potential in the Perdew-Burke-Ernzerhof¹⁸ form and the projector-augmented wave method¹⁹ are used. We employ a $4 \times 4 \times 1$ k-point mesh centered at the Gamma point. The cut-off energy is set to 400 eV. In addition, the atomic positions are fully relaxed by force minimization. The sign of the valence band offset (VBO) is considered to be positive if the top of the O 2p valence band in HfO₂ is higher than in SiO₂. The O 2p partial

density of states (PDOS) is averaged over all the atoms within one oxygen layer to determine the value of the VBO.

As an example, the O 2p PDOSs for 0%, 50%, and 100% La substituted interfaces are depicted in Fig. 4. The VBO of the pure HfO₂/SiO₂ interface is 0.6 eV and represents the magnitude of the dipole that is present in Hf-based gate stacks without capping layer. Figure 4(c) shows that for the 100% La substituted case, we obtain a VBO of 1.1 eV (and of −1.0 eV for 100% Al substitution, which is not shown). These results are in line with Robertson's findings.¹⁰ In comparison, Figure 4(b) shows that for 50% La substitution, we obtain a VBO of 0.5 eV (−0.5 eV for 50% Al). We conclude that the magnitude of the VBO increases with the concentration of capping layer atoms at the interface, which is consistent with experimental observation. As capping layer atoms arrive at the interface, they change the bonding arrangement. We expect more Al, Gd, and La atoms at the interface with increasing % SiO₂ in the gate dielectric. Hence in our DFT simulations, we gradually increase the interfacial concentration of La or Al and observed a corresponding increase in the VBO compared to the reference structure, showing the same trend observed in our experiments. The original dipole [Hf-O-Si], formed at the HfO₂/SiO₂ interface, is therefore being replaced by the [(La/Gd/Al)-O-Si] dipole as the % SiO₂ in the gate dielectric increases. The reason for the opposite shifts obtained by the Al and rare-earth capping layers has to do with the relative magnitude of electronegativity of these elements compared to Hf.¹⁰

In conclusion, we show experimentally and theoretically that the magnitude of the EWF shift induced in capped Hf-based gate stacks depends strongly on the SiO₂ content in the gate dielectric. With increasing SiO₂ content, downward diffusion of the capping elements (Al,Gd,La) is enhanced and more dipoles form at the HfSi_xO_y/SiO₂ interface, resulting in

FIG. 4. O 2p PDOS for (a) 0%, (b) 50%, and (c) 100% La substitution at the HfO₂/SiO₂ interface. The valence band offset (VBO) is measured from the top of valence band of O 2p states in HfO₂ with respect to the O 2p states in SiO₂ (indicated by the vertical solid lines in the PDOS graphs). The VBO of pure HfO₂/SiO₂ interface, which indicates the magnitude of the dipole that is present in the uncapped stack, is 0.6 eV. 50% La doping shows a VBO of 0.5 eV, while 100% La doping shows VBO of 1.1 eV. The magnitude of the VBO increases with the concentration of dopants, matching experimental observation. The corresponding relaxed structure is shown on top of the PDOS graphs. Similar behavior was obtained using Al-based capping layers.

larger EWF shift. DFT simulations indicate that the dipoles change from Hf-O-Si to (Al/Gd/La)-O-Si as elements from the capping layers (Al, Gd, La) diffuse toward the dielectric/SiO₂ interface.

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