Anomalous positive flatband voltage shifts in metal gate stacks containing rare-earth oxide capping layers

J. A. Caraveo-Frescas, M. N. Hedhili, H. Wang, U. Schwingenschlögl, and H. N. Alshareef

Citation: [Applied Physics Letters](#) **100**, 102111 (2012); doi: 10.1063/1.3692580

View online: <http://dx.doi.org/10.1063/1.3692580>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/100/10?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Effects of fluorine incorporation and forming gas annealing on high- k gated germanium metal-oxide-semiconductor with Ge O₂ surface passivation](#)

[Appl. Phys. Lett.](#) **93**, 073504 (2008); 10.1063/1.2966367

[Improved electrical properties of Ge metal-oxide-semiconductor capacitor with HfTa-based gate dielectric by using Ta O_x N_y interlayer](#)

[Appl. Phys. Lett.](#) **92**, 262902 (2008); 10.1063/1.2954012

[Influences of annealing in reducing and oxidizing ambients on flatband voltage properties of HfO₂ gate stack structures](#)

[J. Appl. Phys.](#) **101**, 084118 (2007); 10.1063/1.2721384

[Electrical properties of germanium/metal-oxide gate stacks with atomic layer deposition grown hafnium-dioxide and plasma-synthesized interface layers](#)

[Appl. Phys. Lett.](#) **90**, 112912 (2007); 10.1063/1.2472197

[Metal gate- Hf O₂ metal-oxide-semiconductor capacitors on n - Ga As substrate with silicon/germanium interfacial passivation layers](#)

[Appl. Phys. Lett.](#) **89**, 222903 (2006); 10.1063/1.2396912

An advertisement for Asylum Research, a technology leader in AFM. The background is dark blue. On the left, there is a black mobile phone and a white desktop computer. In the center, there is a white AFM instrument. Text on the left says 'You don't still use this cell phone' and 'or this computer'. Text in the center says 'Why are you still using an AFM designed in the 80's?'. Text on the right says 'It is time to upgrade your AFM', 'Minimum \$20,000 trade-in discount for purchases before August 31st', and 'Asylum Research is today's technology leader in AFM'. At the bottom right, there is a logo for 'OXFORD INSTRUMENTS' with the tagline 'The Business of Science®' and the email address 'dropmyoldAFM@oxinst.com'.

Anomalous positive flatband voltage shifts in metal gate stacks containing rare-earth oxide capping layers

J. A. Caraveo-Frescas,¹ M. N. Hedhili,² H. Wang,¹ U. Schwingenschlögl,¹ and H. N. Alshareef^{1,a)}

¹Materials Science and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

²Imaging and Characterization Laboratory, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

(Received 1 December 2011; accepted 19 February 2012; published online 9 March 2012)

It is shown that the well-known negative flatband voltage (V_{FB}) shift, induced by rare-earth oxide capping in metal gate stacks, can be completely reversed in the absence of the silicon overlayer. Using TaN metal gates and Gd_2O_3 -doped dielectric, we measure a ~ 350 mV *negative* shift with the Si overlayer present and a ~ 110 mV *positive* shift with the Si overlayer removed. This effect is correlated to a positive change in the average electrostatic potential at the TaN/dielectric interface which originates from an interfacial dipole. The dipole is created by the replacement of interfacial oxygen atoms in the HfO_2 lattice with nitrogen atoms from TaN. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3692580>]

Engineering of the metal gate work function in transistor devices is of particular interest for high dielectric constant (high- k) based complimentary metal-oxide-semiconductor (CMOS) devices. One of the most challenging problems has been to develop temperature stable metal gates that can provide the required effective work function (EWF) and low threshold voltages.^{1,2} The use of oxide interfacial layers (e.g., La_2O_3 , Gd_2O_3 , Al_2O_3 , etc.) between metal gates, such as TiN and TaN, and the Hf-based dielectrics in gate stacks has been used as an effective method to tune the EWF of metal gates. In this letter, we show that the flatband voltage (V_{FB}) shift, known to be induced by lanthanide metal oxide capping layers (e.g., Gd_2O_3), can be completely reversed if the polycrystalline silicon (poly-Si) overlayer is not used. The poly-Si overlayers are typically used to cover metal gates to ease the metal gate/high- k stack device integration. Oxygen diffusion into the metal gate and the subsequent nitrogen accumulation at the metal gate/high- k oxide interface are shown to be the cause of this phenomenon.

Metal-oxide-semiconductor (MOS) capacitors were built on heavily doped p -type substrates with a dopant concentration of $1.0 \times 10^{18} \text{ cm}^{-3}$. Pre-gate cleaning was performed using diluted hydrofluoric acid (HF) followed by O_3 -last cleaning. The SiO_2 gate dielectric was grown using thermal oxidation, while the $HfSiO$ film (2.0 nm, 60% SiO_2) was grown by atomic layer deposition. The 1.0 nm Gd_2O_3 interfacial layer and 40 nm TaN gate electrode were then deposited at room temperature using a physical vapor deposition system. This resulted in TaN/ Gd_2O_3 / $HfSiO$ / SiO_2 /Si stacks. Selected samples were then covered with either 100 nm sputtered or 100 nm chemical vapor deposited (CVD) poly-Si overlayers. All samples (with or without the 100 nm poly-Si overlayer) were subsequently annealed using rapid thermal annealing (RTA) at 1000 °C in N_2 for 10 s to simulate a junction anneal. Forming gas annealing (FGA)

was then performed on all samples for 30 min at 400 °C in a 96% N_2 and 4% H_2 atmosphere. The capacitance-voltage (C-V) curves, obtained with an Agilent 4294 A inductance-capacitance-resistance (LCR) meter, were fitted using the NCSU model to extract the equivalent oxide thickness (EOT), flatband voltage (V_{FB}), and substrate doping concentration.³ The effective work function of each electrode was extracted from plots of V_{FB} vs. EOT using a series of SiO_2 thicknesses (1.0–4.0 nm) formed by wet-etching of a thermally grown 4.0 nm SiO_2 layer. The chemical composition and diffusion profiles of the films were examined by high-resolution x-ray photoelectron spectroscopy (XPS). XPS spectra were recorded with an Axis Ultra DLD spectrometer (Kratos Analytical, UK), using a monochromatic Al- $K\alpha$ source ($h\nu = 1486.6$ eV) operating at 150 W energy. XPS depth profiling was done using a 500-eV argon ion beam, a sputter area of 2×2 mm and an etch rate of 1.7 nm/min, calibrated on a standard 60-nm-thick Ta_2O_5 film. High resolution XPS spectra of C 1s, N 1s, Ta 4f, Gd 3d, O 1s, and Si 2p core levels were collected at 110 μm aperture, at pass energy of 80 eV and with a step size of 0.1 eV, and quantified using empirically derived relative sensitivity factors provided by Kratos analytical. The spectra were analyzed using the CASA XPS software. Shirley background subtraction and peak fitting with Gaussian-Lorentzian-shaped profiles were performed for all considered photoelectron peaks.

Figure 1 shows the normalized C-V curves for three different devices annealed at 1000 °C. The insets illustrate the structure of three different devices used: (a) reference device without Gd_2O_3 in the gate stack, (b) device with poly-Si overlayer, and (c) device without poly-Si overlayer (devices in Figs. 1(b) and 1(c) had Gd_2O_3 in the stack). From the well-behaved C-V curves, it is possible to observe that a shift in V_{FB} in opposite directions has occurred for the poly-Si capped and uncapped devices (Figs. 1(b) and 1(c)). The EWF for the different devices in Fig. 1 were extracted using V_{FB} -EOT plots (EOT = 2 to 4 nm) and were (a) 4.45, (b) 4.13, and (c) 4.54 eV, respectively, consistent with the observed trends in Fig. 1.

^{a)}Author to whom correspondence should be addressed. Electronic mail: husam.alshareef@kaust.edu.sa.

FIG. 1. (Color online) C-V curves of the studied devices: (a) reference device without Gd_2O_3 capping layer (poly-Si/TaN/HfSiO₂/SiO₂) [$V_{FB} = -0.6446$ V], (b) device with poly-Si overlayer (poly-Si/TaN/Gd₂O₃/HfSiO₂/SiO₂) [$V_{FB} = -0.9952$ V], and (c) device without poly-Si overlayer (TaN/Gd₂O₃/HfSiO₂/SiO₂) [$V_{FB} = -0.5270$ V]. A negative shift [$\Delta V_{FB} = -350.6$ mV] in the flatband voltage is observed for the poly-Si capped device, while a positive shift [$\Delta V_{FB} = 117.6$ mV] is observed for the uncapped one. Extracted EWF values from plots of V_{FB} vs. EOT, for EOTs from 2 to 4 nm and capacitor area of 2×10^{-5} cm² are (a) 4.45, (b) 4.13, and (c) 4.54 eV, support the observed trend.

The 350 mV negative shift in the C-V curve for the sample with poly-Si overlayer (Fig. 1(b)) is expected due to the presence of Gd_2O_3 in the gate stack. This shift in our poly-Si capped devices agrees, in direction and magnitude, with previous reports on the effect of lanthanide oxide insertion into high-k/metal gate stacks on V_{FB} .⁴⁻⁶ However, the shift in V_{FB} for devices without the poly-Si overlayer to the right by nearly 450 mV (relative to the poly-Si capped Gd_2O_3 -containing device) is unexpected. To confirm this unexpected result, we have repeated the experiment three different times, where nearly a hundred devices were measured each time, covering different dielectric compositions and EOTs. In one particularly important experiment, the TaN metal gate was covered with 100 nm sputtered poly-Si overlayer instead of CVD poly-Si overlayer. The device structure was, therefore, sputtered poly-Si/TaN/Gd₂O₃/HfSiO₂/SiO₂/Si, and it was subsequently annealed at 1000 °C with the sputtered poly-Si overlayer in place. The sputtered poly-Si overlayer was then removed by a wet etch process that is highly selective to TaN. The C-V measurement for this sample gave identical results to the sample in Fig. 1(b). This result clearly shows that no matter how the poly-Si overlayer is deposited (sputter or CVD) on the TaN metal gate, the end result is the same: negative V_{FB} shift is only obtained when the TaN is covered by poly-Si prior to the RTA anneal. Otherwise, a positive V_{FB} shift is observed. Clearly, the poly-Si layer plays an important role in the direction of flatband voltage shift in gate stacks containing rare-earth (RE) oxide capping layers.

The negative shift of the V_{FB} in this type of devices, where a lanthanide oxide capping layer is used, has been attributed to the substitution of Hf atoms by the RE element atoms at the HfSiO₂/SiO₂ interface, giving rise to a bond

dipole formation.^{7,8} This model has been corroborated by the recent calculations done by Lin and Robertson.⁹

In a simple MOS structure, the flatband voltage can be expressed as

$$V_{FB} = -EOT \left(\frac{Q_0}{\epsilon_0 \epsilon_{ox}} \right) + \phi_{ms} + \mu_t, \quad (1)$$

where Q_0 is the fixed charge at the SiO₂/Si interface, ϕ_{ms} is the difference between the work functions of the metal and Si substrate, EOT the effective oxide thickness, and μ_t the effective dipole, which in the case of only SiO₂ dielectric is $\mu_t = \Delta_{\text{metal/SiO}_2} + \Delta_{\text{SiO}_2/\text{Si}}$.

For our stack, μ_t has to account for the different interfaces

$$\mu_t = \Delta_{\text{TaN/Gd}_2\text{O}_3} + \Delta_{\text{Gd}_2\text{O}_3/\text{HfSiO}_2} + \Delta_{\text{HfSiO}_2/\text{SiO}_2} + \Delta_{\text{SiO}_2/\text{Si}}. \quad (2)$$

The dipole formation at these different interfaces has to be related to the net positive shift we observe since Q_0 in our stacks was low (4.5×10^{10} cm⁻²) and cannot account for the dramatic positive V_{FB} shift observed in the absence of the poly-Si overlayer.

Figure 2 shows the XPS depth profiles of samples (a) with poly-Si overlayer and (b) without poly-Si overlayer. Important information is extracted from these profiles. First of all, the elemental species in the gate dielectric layers show no discernable difference between the two samples. This is shown in detail in Figure 3(a) where the Gd profiles are identical independent of the presence of a poly-Si overlayer. This observation suggests that the bond dipoles at the dielectric interfaces (e.g., Gd replacing Hf at the HfSiO₂/SiO₂ interface), are not likely to be profoundly different for the two samples and hence both samples should have exhibited a negative V_{FB} shift, as is typically expected for gate stacks with Gd_2O_3 capping layers.⁷ Another observation is that the oxygen and tantalum diffusion profiles (Figs. 3(b) and 3(c)) show more oxygen diffusion into TaN in the absence of the poly-Si overlayer. It should be noted that RTA was performed in a commercial tool with small traces of residual

FIG. 2. (Color online) XPS depth profiles of the device (a) with and (b) without poly-Si overlayer. Oxygen diffusion into the TaN metal gate can be observed, while the dielectric layer seems to behave the same.

FIG. 3. (Color online) Comparison of (a) Gd, (b) O, (c) Ta, and (d) N depth profiles for the capped and uncapped devices. Oxygen downward diffusion oxidizes the TaN metal gate in the upper part but does not reach the TaN/high-K interface, where more nitrogen has accumulated (d). Gd exhibits the same profile regardless of the presence of the poly-Si overlayer layer (a).

oxygen, explaining the incorporation of oxygen during the N_2 ambient anneals. The degree of oxidation of the TaN metal gate is of strong concern. Oxidation of the TaN can change the work function of the metal gate and contribute to the observed V_{FB} shift.¹⁰ Nevertheless, it is evident the Ta oxidation is taking place at the upper part of the TaN layer and not at the TaN/dielectric interface, suggesting that the TaN work function is not being modified near the TaN/dielectric interface. Furthermore, the filling of vacancies due to O diffusion into the bulk of TaN and any bond dipole this may produce will be screened by TaN metal and is not expected to shift the V_{FB} by much.¹¹ In fact, it has been shown that O replacing N in the bulk of TiN metal gate results in only small increase in the EWF (~ 30 meV).¹¹

The increase of N levels at the TaN/dielectric interface (Fig. 3(d)) in our devices is interesting. It has only occurred in the samples annealed without a poly-Si overlayer. Samples where the TaN metal gate was capped with either CVD or sputtered poly-Si overlayer did not show this effect. We can, therefore, conclude that the *cancellation* of the negative V_{FB} shift observed in Fig. 1(c) is related to N accumulation at the TaN/dielectric interface. What remains now is to explain how the accumulation of this nitrogen cancels the well-known negative V_{FB} shift.

It has been reported that a large and positive shift (~ 200 – 400 mV) could be induced in the equilibrium electrostatic potential due to dipoles at the interface between a TiN metal gate and HfO_2 gate dielectric by replacing oxygen (O) atoms in the HfO_2 lattice with nitrogen (N) atoms near TiN/ HfO_2 interface.¹¹ Using density functional theory (DFT) analysis, this effect was shown to be due to a balance of two opposing dipoles associated with the Ti and Hf atoms at the

interface (the sequence O–Hf–O–Ti–N is being replaced by O–Hf–N–Ti–N).¹¹ Due to the larger polarizability of the Hf atom compared with that of Ti, the dipole associated with the Hf atom is more pronounced creating a positive shift in the average electrostatic potential at the TiN/ HfO_2 interface. The positive shift reported for TiN is in the same direction as the experimental V_{FB} voltage shift measured in our TaN devices without Si overlayer. Thus, one reasonable model to explain the positive V_{FB} shift in our TaN devices, in analogy to TiN, is the replacement of O atoms in the Hf-based dielectric by N atoms from the accumulated nitrogen (Fig. 3(d)). Expecting a similar dipole mechanism at the TaN/ HfO_2 interface is reasonable, since the polarizability of Ta, like Ti, is smaller than that of Hf. To prove that such atomic replacement can produce a positive shift in the equilibrium electrostatic potential at the TaN/ HfO_2 interface, we have carried out a DFT first principle calculations of the TaN/ HfO_2 interface.

The electrostatic potential across the TaN/ HfO_2 interface is simulated employing the supercell approach. The supercell is constructed along the line of previous calculations for the TiN/ HfO_2 interface.¹² A hexagonal interface is built between monoclinic HfO_2 (–111) and $P6_3mc$ TaN(001) surfaces with an area of $128.8 \text{ \AA}^2$. The mismatch of the in-plane lattice parameters amounts to only 0.4% and 2.3%. Besides the ideal interface, a second interface with the oxygen atoms at the interface replaced by nitrogen atoms is calculated. From the technical point of view, the VIENNA AB-INITIO SIMULATION PACKAGE¹³ is used with the Perdew–Burke–Ernzerhof¹⁴ parametrization of the generalized gradient approximation and pseudopotentials generated by the projector augmented wave method.¹⁵ A full relaxation of the

atomic positions is performed before the electrostatic potential is evaluated. The potential is averaged in planes parallel to the interface and smoothed by a macroscopic average of 37 points. Finally, the change in the electrostatic potential between the ideal and the nitrogen-substituted interface (Δ) is calculated as a function of the distance to the interface and is shown in Fig. 4. Clearly, replacing O atoms in HfO_2 with N atoms has produced a positive shift ($\Delta = 240$ meV) in the average electrostatic potential at the TaN/ HfO_2 interface. Like the case of TiN, we surmise that this replacement produces a balance of two opposing dipoles associated with the Ta and Hf atoms at the interface (the sequence O-Hf-O-Ta-N is being replaced by O-Hf-N-Ta-N). Due to the larger polarizability of the Hf atom compared with that of Ta, the dipole associated with the Hf atom is more pronounced creating a positive shift in the average electrostatic potential at the TaN/ HfO_2 interface, which is consistent with our measured devices.

The calculated electrostatic potential shifts are in the same direction and in same order of magnitude as our experimental results, but the exact value is smaller than the V_{FB} shift measured in Fig. 1(c) (240 mV vs 460 mV). In our DFT simulation, we noticed that the magnitude of the calculated electrostatic potential shift increased linearly with the number of oxygen atoms replaced by nitrogen atoms at the interface. The simulation supercell size used in our DFT simulation produced a shift of 240 mV after all oxygen atoms at the interface were replaced with nitrogen. Since replacing more oxygen atoms showed a linear increase in the measured electrostatic potential shift at the TaN/ HfO_2 interface, it is possible that using a larger cell size (more atoms) in the simulation can produce an even larger shift. However, it would require significantly longer computational time and computational power to reach a point where this effect saturates. We believe that the simulations we have carried out thus far are sufficient to provide a sound atomistic explanation for the positive V_{FB} shift measured in our TaN devices (Fig. 1(c)). In addition, the model we propose is in fact in agreement with other models reported for nitride metal gates (e.g., TiN metal gate devices that were subjected to nitridation anneals).¹¹ Finally, since our dielectric is also doped with Gd, we attempted a similar calculation in which Gd atoms were placed on selected Hf atomic sites, but the calculated electrostatic potential shift was completely in the opposite direction from the measured V_{FB} shift. We, therefore, conclude that the measured positive V_{FB} shifts in devices without Si overlayer are primarily driven by replacement of interfacial oxygen atoms that are bonded to Hf in the HfO_2 lattice at the interface.

In summary, we have shown that positive V_{FB} shifts can be realized in gate stacks with rare earth oxides (Gd_2O_3) capping by removing the poly-Si overlayer prior to device

FIG. 4. (Color online) Change of the average electrostatic potential between the ideal and nitrogen-substituted TaN/ HfO_2 interfaces. It is clear that such substitution of nitrogen on O sites in the HfO_2 lattice can produce a positive shift in the electrostatic potential, consistent with our experimental observation for TaN devices without Si overlayer.

annealing. This V_{FB} shift was correlated to positive change in the average electrostatic potential at the TaN/ HfO_2 interface, which completely cancels out the V_{FB} shift normally observed in gate stacks containing Gd_2O_3 capping layers. The atomistic origin of this shift is the replacement of interfacial oxygen atoms in the HfO_2 lattice with nitrogen atoms, which creates a dipole that favors a positive V_{FB} shift.

- ¹J. K. Schaeffer, L. R. C. Fonseca, S. B. Samavedam, Y. Liang, P. J. Tobin, and B. E. White, *Appl. Phys. Lett.* **85**(10), 1826 (2004).
- ²H. C. Wen, P. Majhi, K. Choi, C. S. Park, H. N. Alshareef, H. R. Harris, H. Luan, H. Niimi, H. B. Park, G. Bersuker *et al.*, *Microelectron. Eng.* **85**(1), 2 (2008).
- ³J. R. Hauser, *NCSU Software, Version 5.0*, Department of Electrical and Computer Engineering, NC State University, Raleigh, NC, 2000.
- ⁴K. Kakushima, K. Okamoto, M. Adachi, K. Tachi, P. Ahmet, K. Tsutsui, N. Sugii, T. Hattori, and H. Iwai, *Solid-State Electron.* **52**(9), 1280 (2008).
- ⁵Y. Yamamoto, K. Kita, K. Kyuno, and A. Toriumi, *Jpn. J. Appl. Phys.* **46**, 7251 (2007).
- ⁶P. D. Kirsch, P. Sivasubramani, J. Huang, C. D. Young, M. A. Quevedo-Lopez, H. C. Wen, H. Alshareef, K. Choi, C. S. Park, K. Freeman *et al.*, *Appl. Phys. Lett.* **92**(9), 092901 (2008).
- ⁷H. N. Alshareef, J. A. Caraveo-Frescas, and D. K. Cha, *Appl. Phys. Lett.* **97**(20), 202108 (2010).
- ⁸J. Robertson, *Eur. Phys. J.: Appl. Phys.* **28**(03), 265 (2004).
- ⁹L. Lin and J. Robertson, *Microelectron. Eng.* **86**(7–9), 1743 (2009).
- ¹⁰E. Cartier, M. Hopstaken, and M. Copel, *Appl. Phys. Lett.* **95**(4), 042901 (2009).
- ¹¹C. L. Hinkle, R. V. Galatage, R. A. Chapman, E. M. Vogel, H. N. Alshareef, C. Freeman, E. Wimmer, H. Niimi, A. Li-Fatou, J. B. Shaw *et al.*, *Appl. Phys. Lett.* **96**(10), 103502 (2010).
- ¹²E. Wimmer, R. Najafabadi, G. A. Young, Jr., J. D. Ballard, T. M. Angeliu, J. Vollmer, J. J. Chambers, H. Niimi, J. B. Shaw, C. Freeman *et al.*, *J. Phys.: Condens. Matter* **22**, 384215 (2010).
- ¹³G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- ¹⁴J. P. Perdew, M. Ernzerhof, and K. Burke, *J. Chem. Phys.* **105**, 9982 (1996).
- ¹⁵P. E. Blochel, *Phys. Rev. B* **50**, 17953 (1994).