

Examination of flatband and threshold voltage tuning of HfO₂/TiN field effect transistors by dielectric cap layers

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The authors have examined the role of sub nanometer La₂O₃ and LaN cap layers interposed in Si/HfO₂/TiN high-*k* gate dielectric stacks in tuning the flatband and threshold voltages of capacitors and transistors. High performance, band edge *n* metal oxide field effect transistors with channel lengths down to 60 nm may be fabricated without significant compromise in mobility, electrical thickness, and threshold voltage. They have carried out a microstructural evaluation of these stacks and correlated these results with the electrical behavior of the devices.

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As high- κ metal gated metal-oxide-semiconductor field-effect transistors (MOSFETs) are developed as a replacement for SiO(N)/polysilicon (poly-Si) based devices, the challenge has distilled to demonstrating a transistor with three simultaneous attributes: (i) a low electrical thickness of the dielectric, (ii) a high mobility, and (iii) an appropriate threshold voltage that is similar to *n*-doped poly-Si for *n*MOSFETs (~ 0 – 0.2 V) and *p*-doped poly-Si for *p*MOSFETs (~ 0 to -0.2 V). It also remains desirable to achieve these specifications in a “gate first” processing sequence, capable of withstanding a 1000 °C, 5 s dopant activation anneal. Over the past few years, HfO₂ based dielectrics have been established as appropriate replacement oxides^{1–3} and when coupled with TiN electrodes yield attributes (i) and (ii).^{4–6} The resulting threshold voltages, however, are unacceptably high and an additional threshold adjustment technique is needed to produce devices suitable for high performance logic applications.

We have recently solved this problem^{7,8} and shown that by introducing ultrathin La₂O₃ cap layers between the HfO₂ dielectric and the TiN electrode, the threshold voltage can be controllably shifted to a position ideal for *n*MOSFETs. Related work using a hafnium silicate dielectric (instead of HfO₂) (Ref. 9) and a La₂Hf₂O₇ cap¹⁰ has also been reported elsewhere. Most importantly this may be done with minimal impact to either the mobility or the electrical thickness of the device.

200 mm Si(100)/1 nm SiO₂/2.5–3 nm HfO₂ substrates were coated with <2 nm La₂O₃ layers. Deposition details have been described in an earlier publication.¹¹ Titanium nitride layers were deposited on the La₂O₃ and capped by a poly-Si layer. Field oxide isolated metal-oxide-semiconductor capacitors and *n*MOSFETs were subsequently processed. The highest temperature seen by these devices was 1000 °C, for a few seconds. Wafers were subjected to a 450–500 °C forming gas anneal. Structural analysis was carried out using x-ray photoelectron spectroscopy (XPS), electron energy loss spectroscopy (EELS), me-

dium energy ion scattering (MEIS), and secondary-ion-mass spectrometry (SIMS).

The effect of the La₂O₃ cap can be seen in capacitance-voltage (*C*-*V*) plots of *n*-Si/HfO₂/TiN/poly-capacitor structures with and without the presence of an ultrathin La₂O₃ cap inserted between the HfO₂ and the TiN [Fig. 1(a)]. Without a La₂O₃ cap, the flatband voltage is ~ 0.2 V. With the La₂O₃ cap, there is a distinct negative shift of the flatband voltage of ~ -400 mV, translating to an ideal threshold voltage in a *n*MOSFET for complementary metal-oxide-semiconductor applications. Importantly, this shift is preserved even after the wafer has seen the standard 1000 °C anneal. It is not necessary that the cap layer be an oxide in order to induce this voltage shift. The figure shows that a similar negative shift to ~ -0.2 V is observed when the cap layer was ~ 0.8 nm of LaN grown using an atomic nitrogen beam. These experiments clearly implicate La as the source of the voltage shift. Long channel *n*MOSFETs were fabricated using the Si/SiO₂/HfO₂/La₂O₃/TiN/polysilicon gate stack and compared to gate stacks that did not contain the La₂O₃ layer. Transistors yielded threshold voltages of ~ 0.0 V (compared to ~ 0.38 V for the devices without La₂O₃ caps), as expected, concomitant with a low electrical thickness (~ 1.4 nm) and a negligible reduction in high field mobility shown in the mobility versus electric field plot of Fig. 1(b). Performance characteristics are retained down to short channel lengths of ~ 60 nm. Figure 1(c) shows the variation of the threshold voltage (*V_t*) as a function of channel length for three different gate stacks: HfO₂/TiN, HfO₂/La₂O₃/TiN, and a reference silicon oxynitride (SiON)/polysilicon structure. As can be clearly seen, the *V_t* variation (known as “*V_t* rolloff”) is comparable to standard SiON structures and is uncompromised by the presence of the La₂O₃ cap layer.

An independent measure of the electrostatic voltage shift in the stack due to the presence of the La₂O₃ can also be gained by XPS. By measuring the binding energy of the Si 2*p* core level and comparing it with the known distance from the Si 2*p* to valence band maximum (99.0 eV), we can directly infer the Fermi-level position.¹² Figure 2 shows the XPS measurements of the Si 2*p* binding energy from a TiN/HfO₂ (2.5 nm)/Si sample, where, following a 950 °C densification anneal, the TiN was grown *in situ* at 500 °C.

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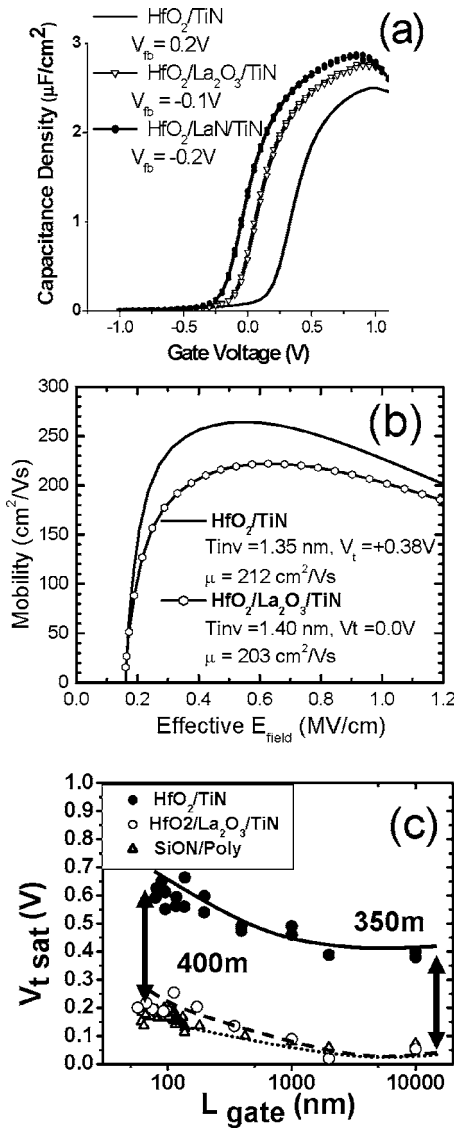


FIG. 1. (a) Comparison of capacitance-voltage characteristics for $\text{Si}/\text{SiO}_2/\text{HfO}_2/\text{TiN}/\text{poly-Si}$, $\text{Si}/\text{SiO}_2/\text{HfO}_2/\text{La}_2\text{O}_3/\text{TiN}/\text{poly-Si}$, and $\text{Si}/\text{SiO}_2/\text{HfO}_2/\text{LaN}/\text{TiN}/\text{poly-Si}$ stacks. Note the negative flatband voltage shifts observed with the La based cap layers. (b) Mobility vs perpendicular electric field plot for HfO_2/TiN based $n\text{MOSFETs}$ with and without the La_2O_3 cap layer (c) Threshold voltage as a function of channel length for stacks with and without La_2O_3 layers, compared to a standard silicon oxynitride-poly-Si stack based $n\text{MOSFET}$.

The $\text{Si } 2p$ binding energies for n and p wafers correspond to Fermi levels of the system that are ~ 0.7 and 0.8 eV above the Si valence band edge, respectively. On the other hand, when a La_2O_3 capping layer was included, the $\text{Si } 2p$ binding energy increased, placing the Fermi level of the metallized sample at the conduction band edge. There are two important points to note about this result. First, we see the same 300–400 meV shift induced by the presence of the La_2O_3 capping layer, in agreement with the electrical data. Second, because the sample were fabricated with a minimum of processing steps, we can be assured that the threshold voltage shifts are a real effect rather than an unanticipated artifact induced by some postprocessing step.

Given that the stack consists of nanometer thick films, significant interdiffusion of the layers is expected and studied by MEIS. For this experiment 2.5 nm HfO_2 layers were capped with 3 nm of La_2O_3 and annealed for 5–10 s at 800,

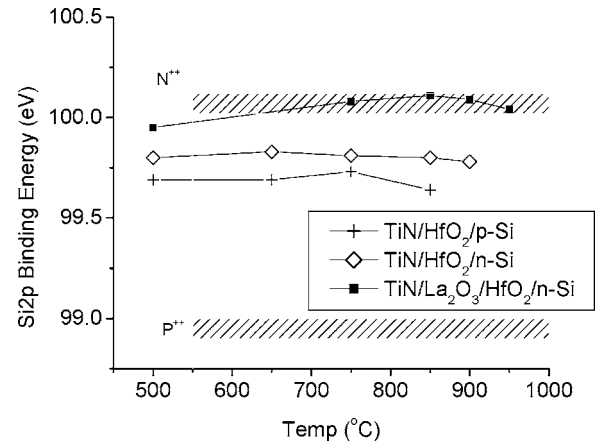


FIG. 2. X-ray photoelectron spectroscopy measurements of the $\text{Si } 2p$ binding energy for TiN/HfO_2 stacks with and without an intervening La_2O_3 cap layer. A binding energy of 101.1 eV (99.0 eV) would indicate that the Fermi level is at the conduction (valence) band edge. A 300–400 meV shift towards the conduction band is seen with the inclusion of a La_2O_3 capping layer. Measurements were done with $\text{Mg } K\alpha$.

900, and 950 $^\circ\text{C}$ *in situ* in an ultrahigh-vacuum chamber. The “as-deposited” profile is shown in Fig. 3, fitted to a simulated curve for the La and the Hf profiles,¹³ along with the profile evolution as a function of annealing temperature. With increasing annealing temperature, the peak corresponding to the Hf and the shoulder corresponding to the La (near the surface) become less distinct as the features broaden—clearly indicating that intermixing of the layers takes place even ~ 800 $^\circ\text{C}$. Electron microscopy based EELS measurements carried out on device structures corroborate the mixing and show the penetration of La both into the HfO_2 and into the TiN electrode to a depth of ~ 5 nm (Fig. 4). The EELS results further show that the La mixing has been inhomogeneous across the thickness of the dielectric stack, resulting in an asymmetric profile. The observed intermixing raises the obvious concern of the subsequent diffusion of the La into the silicon substrate. However, back side SIMS measurements in $\text{HfO}_2/\text{La}_2\text{O}_3$ samples that were grown on a silicon-on-insulator wafer indicated no noticeable La or Hf penetration into the underlying silicon substrate. This likely plays a role in the high observed channel mobilities in the La_2O_3 cap containing $n\text{FETs}$.

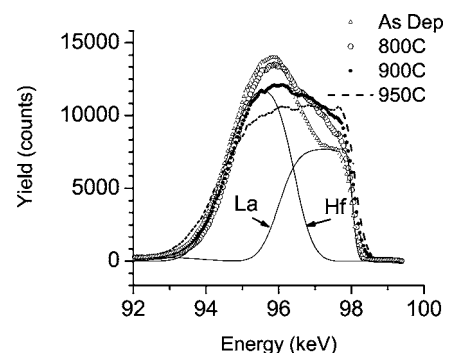


FIG. 3. MEIS measurements from a 2.5 nm $\text{HfO}_2/3$ nm La_2O_3 stack on Si showing the Hf and La distributions in the as-grown sample and samples annealed at 800, 900, and 950 $^\circ\text{C}$. The larger cross section of Hf compared to La gives rise to a greater intensity in the HfO_2 . After annealing, a uniform intensity is seen due to intermixing. Using simulation, the “as-grown” trace is separated into the depth dependent signal from Hf and La solid lines.

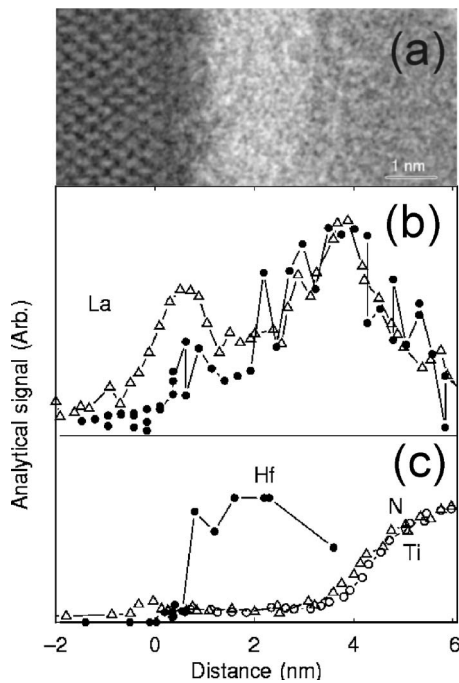


FIG. 4. EELS data across a TiN/La₂O₃/HfO₂/Si stack. Data are shown for measurements made using a 0.5 nm probe at 200 keV in a JEOL 2010F electron microscope (triangles), and a 0.08 nm probe at 120 keV in an IBM scanning transmission electron microscope (circles). The inset at the top shows an annular dark field image of the Si/HfO₂/La₂O₃/TiN gate stack structure with Si on the left and the TiN gate on the right.

What causes these threshold voltage shifts? Positively charged oxygen vacancy defects in HfO₂ (Ref. 14) have been recently invoked to explain the negative flatband (or threshold) voltage shifts in HfO₂ based *p*FETs.^{15,16} We expect the reaction (using standard Kroger-Vink notation): $\text{La}_2\text{O}_3 = 2\text{La}'_{\text{Hf}} + 3\text{O}^{\times}_{\text{O}} + \text{V}^{\bullet}_{\text{O}}$. Here, La substitution of Hf results in a negatively charged defect (La'_{Hf}) and the formation of positively charged oxygen vacancy defects to ensure charge neutrality. In similar vein, all group IIIB or IIA elements are expected to increase the concentration of oxygen vacancies. A La:HfO₂ film will remain neutrally charged, however, and this alone cannot explain the results. On the other hand, if we assume that the oxygen vacancies are mobile, then a nonuniform distribution of the La'_{Hf} and the $\text{V}^{\bullet}_{\text{O}}$ defects across the dielectric, such that the positive and negative charge centroids within the film do not coincide, will result in a net dipole that could explain the observed flatband voltage shifts. The above argument should hold true for an aliovalent impurity with a valence less than 4 that substitutes at a Hf site. This, however, does not appear to be the case since Al₂O₃ caps induce a slightly positive, instead of negative, voltage shift. Interestingly, however, when either La₂O₃ (Ref. 17) or MgO alone are used as single dielectric layers rather than as cap layers, one observes a large negative shift in the flatband voltage from the expected value, compared to Al₂O₃,¹⁷ where the flatband voltage shift is small. There is obviously

no aliovalent substitution involved argument to be made in these cases. An alternate explanation is that the presence of charged defects or dipoles within the La₂O₃ or MgO layer result in these observed shifts with similar effects caused by the formation of lanthanum or magnesium silicates at the bottom, silicon-dielectric interface (note the La profile in Fig. 4). This is likely related to the strongly electropositive nature of the cations, and dipoles due to asymmetry induced by differences in the ionicity of the bonds formed at the ends of the dielectric layer due to the interfaces with the silicon and the metal.

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