The efforts to replace polycrystalline silicon transistor gate electrodes with metal gates continue unabated. However, the development of metal gates with effective work functions near the Si bandedges has been difficult on Hf-based gate dielectrics due to Fermi level pinning and/or interfacial dipole formation.\cite{1,2} Significant activity is therefore taking place to engineer the metal gates/dielectric stacks to achieve the desired band edge work functions (4.05 eV for n-channel and 5.15 eV for p-channel devices). One approach that has been extensively studied includes using interfacial layers such as Al2O3 and La2O3, inserted between the metal gate and the Hf-based high-κ material.\cite{3,4} Additional approaches include using low thermal budget flows,\cite{5} nitrogen coating at the interface,\cite{6} and metal capping layer for interface oxide control.\cite{7} In this article, we correlate La depth profile, measured with depth resolution as low as 0.2 nm by high resolution Rutherford backscattering spectrometry (HR-RBS), to measure device characteristics in La2O3-containing gate stacks. Lightly doped p-type Si wafers were used for the study. Prior to deposition of the gate stacks, the substrates were thoroughly wet cleaned. The gate stack (La2O3/HfO2) was formed by first depositing 2.0 nm HfO2 films using atomic layer deposition at 250°C. The HfO2 films were then annealed at 750°C in NH3 for 60 s. La2O3 (1–2 nm) was then deposited ex situ at room temperature by a sputter deposition system equipped with a shield. No SiO2 layer was intentionally grown in these stacks and any reference to the SiO2 layer here refers to SiO2 that normally result from surface cleaning or thermal anneals. The presence of nearly 1.0 nm SiO2 could be seen using transmission electron microscopy (not shown). Some blanket samples were subsequently annealed at 1000°C, 10 sec to simulate standard junction anneals. Carrier mobility was measured on transistors with identical La2O3 thickness as the blanket wafers by using a previously described transistor flow. HR-RBS analysis was performed using a KOBE’s proprietary HR-RBS software. A 450 keV beam of He\textsuperscript{+} ions was generated with 25 nA current and a beam size of 1 mm x 1 mm.\cite{8} A relatively high detection angle (110°) was selected in order to separate La from Hf without compromising depth resolution.

Figure 1 shows the experimental spectra collected from all samples. Each sample was measured with optimized channeling through the Si substrate to maximize depth resolution. More significant changes can be seen in the La signal compared to Hf or oxygen, suggesting that La is the main diffusing species. For example, the 2.0 nm La2O3 sample (labeled c in Fig. 1) shows a widening of the La peak after annealing (labeled d), but not the Hf or Si peaks. The inset of Fig. 1 shows the experimental and simulated Rutherford backscattering (RBS) spectra for a 1.0 nm La2O3/HfO2/Si sample.

Note that the simulated spectra fit the experimental data very well, which permits the extraction of depth information with high accuracy. The kink in the Si signal at about 200 channel number is due to channeling through the Si substrate, which was maximized by carefully manipulating the geometry of the setup to improve the depth resolution. Using these spectra, the depth profile for each one of the elements was generated using KOBE’s proprietary HR-RBS software. The results of this analysis are shown in Fig. 2 for the 1.0 nm La2O3/HfO2 sample annealed at 1000°C, 10 s. Figure 2 shows that the elemental depth information can be obtained with excellent resolution (resolution is estimated at 0.2 nm at the surface of the stack and degrading to 0.6 nm at a depth of 4 nm for La and Hf). The La atoms that seem to have diffused slightly passed the midpoint of the HfO2 film. Furthermore, the La profile appears to be uniform in depth, showing an average atomic concentration of roughly 10%. The La signal disappears nearly 0.7 nm away from the Si substrate. In comparison, the 2.0 nm La2O3/HfO2 sample, annealed at 1000°C, 10 s is shown in Fig. 3. The data in Fig. 3 show that the La atoms have diffused completely throughout the HfO2 film, nearly reaching the Si substrate interface. This sample also shows that the La distribution in the HfO2 film is rather uniform, with an average of 10 atom % concentration. Figure 4 shows the effective mobility curves of n-channel devices of gate stacks containing 0.0, 1.0, and 2.0 nm La2O3 annealed at 1000°C, 10 s. These mobilities are an average of at least five curves on each wafer. It is clear from Fig. 4 that a lower carrier mobility is obtained with increased La2O3 thickness, where the La atoms diffuse closer to the Si substrate. For the 1.0 and 2.0 nm La2O3 stacks, La diffused to about 0.7 nm and essentially 0 nm from the Si substrate surface, respectively; this resulted in 9 and 20% drop, respectively, in mobility compared to samples having no La2O3. Similar to published reports, we also observe a transistor threshold voltage shift with La2O3 thickness, but this effect seems to quickly saturate (inset of Fig. 4). An interesting observation is that the n-channel transistor mobility varies more strongly with the distance of the tail-end of the La signal from the Si substrate than the threshold voltage. While the threshold voltage shifted by up to 500 mV in total, most of this shift occurred by the time the La2O3 thickness is increased to 1.0 nm. The shift in the threshold voltage then slows down varying by only ~40 mV as the La2O3 thickness was increased from 1 to 2 nm. In contrast, the mobility degradation nearly doubles (9 vs 20%) as the La2O3 thickness increases from 1 to 2 nm.

These results indicate that the origin of the mobility and threshold voltage changes with La2O3 cannot be entirely the same. The mobility degradation seems to correlate well with the physical location of the La tail-end in the gate stack, but not the threshold voltage. It is known that the effective mobility of a device (\(\mu_{\text{eff}}\)) is given by Matthiessen’s rule, where mobilities are limited by various scattering mechanisms.
The average composition of La in the film is around 10 atom %.

Figure 1. (Color online) Experimental RBS spectra for four different samples with various La$_2$O$_3$ thickness or anneal condition. It can be seen that most of the changes in the spectra are due to La interdiffusion. (a) No La$_2$O$_3$, (b) 1.0 nm La$_2$O$_3$ plus 1000°C, 10 s anneal, (c) 2.0 nm La$_2$O$_3$ but unannealed, and (d) 2.0 nm La$_2$O$_3$ plus 1000°C, 10 s anneal. The inset shows that good fits of the experimental data were obtained.

Figure 2. (Color online) Depth profile of a 1.0 nm La$_2$O$_3$/HfO$_2$ sample after annealing at 1000°C, 10 s. The profile indicates that in the case of 2.0 nm La$_2$O$_3$, La reaches the Si substrate interface. The average composition of La with depth in the film is about 10 atom %.

Figure 3. (Color online) Depth profile of a 2.0 nm La$_2$O$_3$/HfO$_2$ sample after annealing at 1000°C, 10 s. The profile indicates that in the case of 2.0 nm La$_2$O$_3$, La reaches the Si substrate interface. The average composition of La with depth in the film is about 10 atom %.

Figure 4. (Color online) Carrier mobility for transistors comprising three different gate stacks: (a) no La$_2$O$_3$, (b) 1.0 nm La$_2$O$_3$, and (c) 2.0 nm La$_2$O$_3$ on HfO$_2$/Si. The mobility degrades with increasing La$_2$O$_3$ thickness in correlation with RBS data showing deeper penetration of La after annealing. The inset shows that the transistor threshold voltage simultaneously shifts with increasing La$_2$O$_3$ thickness.
Figure 5. (Color online) XPS results showing that the Hf4f and La3d regions in the case of the 2 nm La2O3 sample shift to higher energy after annealing (solid line is before and dotted line is after annealing). This shift was much smaller in the Si2p peaks, suggesting that reactions are mainly taking place between Hf and La oxides.

are $10^{10}$–$10^{12}$ charges/cm$^2$, depending on the La2O3 thickness, we calculate only a 36 mV shift in $V_{FB}$ in a stack with $Q_L > 1 \times 10^{12}$ charges/cm$^2$. However, the observed $V_{FB}$ shift is far larger and is $\sim 500$ mV. Therefore, we conclude that most of the threshold voltage shift here is likely to be dipole related.

The X-ray photoemission spectroscopy (XPS) results for our samples are shown in Fig. 5, where the La3d and Hf4f doublets for 2 nm La2O3/HfO2 stack are shown before and after annealing at 1000°C. It can be seen that both peaks shift to higher energy upon annealing by nearly 0.3 and 0.8 eV for Hf4f and La3d, respectively. The Hf4f peak intensity increased while the La3d intensity drops after annealing. This indicates that La diffuses downward, making it easier to detect Hf4f. In comparison, the Si2p peaks (not shown) in these La2O3/HfO2 gate stacks showed a much smaller shift. Similar trends were seen for the 1.0 nm La2O3 sample. This clearly indicates that main reactions taking place in these stacks are predominantly a result of the changing bonding environment of the La2O3 and HfO2, which is consistent with the HR-RBS results. The fact that the Si2p peak (from Si in the interfacial SiO2 layer) in these samples did not shift much upon annealing may indicate that no significant reaction has taken place between La and any interfacial SiO2 layer in these samples.

In conclusion, we have used HR-RBS to determine the depth profile of La in La2O3/HfO2 gate stacks with excellent depth resolution. The La atoms are the main diffusing species and the physical proximity of the La atoms to the dielectric/Si substrate interface correlates well with the carrier mobility degradation. The mobility degradation is surmised to occur as a result of columnar scattering caused by La diffusion to the interface. The threshold voltage shift is most likely caused by the dipole formation, although a small fixed charge contribution cannot be ruled out.

References