Composition dependence of the work function of Ta$_{1-x}$Al$_x$N$_y$ metal gates

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It is shown that the work function of Ta$_{1-x}$Al$_x$N$_y$ depends on the electrode and gate dielectric compositions. Specifically, the work function of Ta$_{1-x}$Al$_x$N$_y$ increased with SiO$_2$ content in the gate dielectric, reaching as high as 5.0 eV on SiO$_2$; the work function was nearly 400 mV smaller on HfO$_2$. In addition, the work function decreased with increasing nitrogen content in the Ta$_{1-x}$Al$_x$N$_y$ metal gate. Increasing Al concentration increased the work function up to about 15% Al, but the work function decreased for higher Al concentrations. Chemical analysis shows that Al–O bonding at the interface correlates with the observed work function values. © 2006 American Institute of Physics. [DOI: 10.1063/1.2174836]

Metal gates with a band-edge work function are critical if complementary metal-oxide-semiconductor (CMOS) scaling is to continue at its historical pace. The need for metal gates is driven by the polysilicon (poly-Si) depletion effect and the fact that poly-Si is incompatible with high-$k$ dielectrics. For conventional CMOS devices, the metal gates must have work functions of 4.0 and 5.1 eV, for $n$-channel and $p$-channel devices, respectively. However, the quest for band-edge metal gates presented a significant challenge and it is therefore important to understand the factors that control the work function. In this study, we report for the first time on Ta$_{1-x}$Al$_x$N$_y$ metal gates with band-edge work function and propose a mechanism to explain the observed work function variations.

Capacitors were built on $p$-type substrates with a dopant concentration of $1.2 \times 10^{18}$ cm$^{-3}$. Pregate cleaning was performed using diluted hydrofluoric acid followed by O$_2$-fast cleaning. The SiO$_2$ dielectric was grown at 1100 °C using a single-wafer system. The HfO$_2$ and HfSiO$_3$ films were grown using an atomic layer deposition at 350 °C. The high-$k$ films were then annealed in NH$_3$ to densify the films. The Ta$_{1-x}$Al$_x$N$_y$ metal gates (10 nm) were then deposited by physical vapor deposition (PVD). The stack was then capped with poly-Si that is implanted by phosphorous and annealed at 1000 °C for 5 s. The stack was etched using a commercial etch system. The backside of the wafer was coated with Al to improve electrical contact. The capacitance-voltage (C-V) curves were fitted using the NCSU model to extract the equivalent oxide thickness (EOT), flat-band voltage ($V_{FB}$), and substrate doping concentration. The work function of each electrode was extracted from plots of $V_{FB}$ versus EOT using the linear extrapolation method. A series of oxide thicknesses were formed on the same wafer to minimize the impact of fixed charges on work function extraction. The composition of the Ta$_{1-x}$Al$_x$N$_y$ films was measured using Rutherford backscattering spectrometry (RBS). The bonding was studied using x-ray photoelectron spectroscopy (XPS). Figure 1 shows the Ta$_{1-x}$Al$_x$N$_y$ work function variations with composition. Note that the work function increased with % SiO$_2$ in the gate dielectric. Using the 10% Al gate as an example, the work function increased from 4.4 to 4.62 and to 4.82 eV as SiO$_2$ content in the gate dielectric increased from 0 to 30% to 100%, respectively. Furthermore, the work function increased with Al content in Ta$_{1-x}$Al$_x$N$_y$ gate. For example, the work function increased from 4.4 to 4.82 eV on SiO$_2$ when the Al content was increased from 0 to ~15%. For any dielectric, the work function begins to decrease for Al concentrations higher than about 15%. Figure 2 also shows that the work function is a strong function of nitrogen content in the Ta$_{1-x}$Al$_x$N$_y$ gate. Two nitrogen flows were used (4 and 30 sccm) and the corresponding nitrogen fraction measured by RBS was 0.35 and 0.68, respectively. The data show that the work function increases at lower nitrogen content, and that a 5.0 eV work function was achieved at 4 sccm. Notice that when the gate electrode had no Al (TaN electrode), the effect of nitrogen flow on the work function was reversed. This result is consistent with previous observations where the work function of PVD TaN and several other PVD nitrides increased with N$_2$ flow in the PVD process. It also suggests that the increase in the work function of Ta$_{1-x}$Al$_x$N$_y$ at lower N$_2$ flow is closely related to the presence of Al in metal gate. Figure 3 shows the C-V curves.

![Figure 1](image-url)  
**FIG. 1.** Effect of gate dielectric and electrode composition on the work function of Ta$_{1-x}$Al$_x$N$_y$ metal gate work function.
of devices with Ta$_{1-x}$Al$_x$N$_y$ metal gates on gate dielectrics with various Al concentrations. The data show well-behaved C-V curves and a clear shift in the $V_{FB}$, consistent with the work function data shown in Fig. 1. Figure 4 shows the $V_{FB}$-EOT plot used to extract the work function of Ta$_{1-x}$Al$_x$N$_y$ deposited on three dielectrics. The fits are excellent and the slope of the three curves is similar, indicating comparable interfacial fixed charges ($\approx 2 \times 10^{11}$ cm$^{-2}$).

Chemical analysis was carried out to study the interface between the gate dielectric and the Ta$_{1-x}$Al$_x$N$_y$ gate. Figure 5 shows XPS results for a 3.0 nm Ta$_{1-x}$Al$_x$N$_y$/SiO$_2$/Si stack prepared specifically for XPS measurement. The stack was annealed at 1000 °C. 5 s in N$_2$ ambient after pumping down to a base pressure of $< 10^{-8}$ Torr and then backfilling with high-purity nitrogen. The spectra in Fig. 5 show clear chemical shifts in the Al 2p peak toward higher binding energy and in Si 2p peak toward lower binding energy after anneal. The shift in the Al 2p binding energy is consistent with Al-O bond formation (Al oxidation). In contrast, the shift in the Si 2p binding energy is consistent with Si suboxide formation (SiO$_2$ reduction). The oxidation of Al and reduction of SiO$_2$ after annealing at 1000 °C is actually not surprising. Published thermodynamic data predict that high-temperature annealing of Al can readily reduce SiO$_2$ even when Al is bonded to nitrogen (Al–N), as is the case in Ta$_{1-x}$Al$_x$N$_y$. The free energies of formation for Al$_2$O$_3$, SiO$_2$, and AlN are $\approx 1582$, $\approx 853$, and $\approx 287$ kJ/mol, respectively. In contrast to SiO$_2$, a similar XPS shift was not observed in the case of Ta$_{1-x}$Al$_x$N$_y$ on Hf-based dielectrics, suggesting that Al-O bond formation did not occur in significant quantities as in the case of SiO$_2$. This may be explained by two factors. One is the fact that HfO$_2$ is thermodynamically more stable than SiO$_2$ as reflected in their free energy of formation ($\approx 1088$ versus $\approx 853$ kJ/mol) and is therefore less susceptible to being reduced by Al in the metal gate. The other is that the Hf-based films here contained nearly 6 at. % nitrogen from the NH$_3$ nitridation process, which is largely concentrated near their top surface. The nitridation near the film surface likely reduced the concentration of oxygen atoms available for Al-O bond formation.

The above results correlate the effective work function changes with Al-O bond formation. There is more than one possible way for the Al-O bond to change the effective work function of a metal gate. One possibility is that the Al-O bonds form a dipole at the metal gate-dielectric interface, producing an internal electric field, which introduces shifts in the band diagram, leading to a change in the effective work function of the metal gate. Alternatively, the chemical reactions at the interface (oxidation of Al and reduction of SiO$_2$) create defects that possess gap states that pin the Fermi level. Chemical reactions at the interface have been reported to change the band offset for other material systems. Furthermore, the possibility that Al-related bulk charges in the gate dielectric may have contributed to these changes in Ta$_{1-x}$Al$_x$N$_y$ work function cannot be completely discounted. However, the presence of such charges cannot, alone, explain the large work function difference between SiO$_2$ and the Hf-containing dielectrics.

The drop in work function with higher N$_2$ flow during the Ta$_{1-x}$Al$_x$N$_y$ deposition (Fig. 2) can be similarly explained. Figure 2 shows the effect of nitrogen flow on the work function was reversed when the gate electrode had no Al (TaN electrode). This result was reproduced several times and suggests that the increase in work function of
Ta$_{1-x}$Al$_x$N$_y$ at lower N$_2$ flows is closely related to the presence of Al in this metal gate. One possibility is that the Al–O bond formation described earlier may be hindered in the presence of excessive nitrogen. Figure 6 shows XPS analysis performed on two Ta$_{1-x}$Al$_x$N$_y$/SiO$_2$ samples of identical thickness, but with two different N$_2$ flows: 4 and 30 sccm. The XPS spectra show that the film deposited at higher N$_2$ flow has a N 1$s$ photoelectron binding energy that is nearly 0.6 eV higher than the 4 sccm sample. The proximity of the Al–N, Ta–N, and Si–N bonding energies makes it difficult to separate these bonds. However, in combination with the Al 2$p$, Ta 4$f$, and Si 2$p$ binding energies, we note two effects. First, the Al 2$p$ spectra at low N$_2$ flow showed a peak corresponding to elemental aluminum, suggesting relatively poor nitridation of Al. This may have made it easier to form Al–O bonds and hence increase the work function. In contrast, at higher N$_2$ flow, the peaks of the photoelectrons of Al–N, TaN, and Si–N bonds show a shift consistent with the formation of more stoichiometric nitrides. We postulate that the increase in Al–N, Ta–N, and Si–N bonding helps minimize Al–O bond formation at the Ta$_{1-x}$Al$_x$N$_y$/SiO$_2$ interface at high N$_2$ flow, and therefore the work function is lower. Finally, the increase and subsequent drop in work function with Al content in the gate (Fig. 1) can be explained as follows. The higher Al content in the metal gate may result in high enough Al concentration at the metal/dielectric interface, such that the Al–O character of the interface starts to diminish, thus lowering the work function toward that of Al, which is 4.2 eV for Al metal.

A Ta$_{1-x}$Al$_x$N$_y$ gate electrode is reported for the first time with a work function as high as 5.0 eV. The work function is found to depend strongly on the electrode as well as gate dielectric composition. Al–O bond formation at the metal gate/dielectric interface is proposed as the key reason for the observed work function variations.

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