Evaluation of titanium silicon nitride as gate electrodes for complementary metal-oxide semiconductor

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Evaluation of titanium silicon nitride as gate electrodes for complementary metal-oxide semiconductor

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The effect of deposition temperature and film thickness on the work function of TiSiN gate electrodes has been studied. It is shown that the work function of TiSiN can be tuned from 4.28–4.74 eV on SiO₂, 4.40–4.79 eV on HfO₂, and 4.44–4.83 eV on HfSiO₃. For high-k dielectrics, the work function can be tuned by 200 meV on each side of the band gap, making it a suitable electrode for fully depleted silicon-on-insulator devices. Furthermore, TiSiN deposition at high temperature increases the work function to 4.87 eV while Si implantation increases it to 4.93 eV, making TiSiN a good p-type metal candidate. © 2006 American Institute of Physics. [DOI: 10.1063/1.2188380]

Metal gate electrodes have been evaluated as replacements for polycrystalline silicon (poly-Si) gates to continue scaling the equivalent oxide thickness (EOT) of metal-oxide-semiconductor field-effect transistors (MOSFETs). In part, this focus is necessary to address the issue of the undesirable series capacitance associated with poly-Si depletion and to circumvent performance degradation related to boron penetration. Consequently, an appreciable research effort is underway to identify the most appropriate n- and p-type metal electrode materials that exhibit band-edge work functions, threshold voltage (Vₜ) stability, and chemical stability with the underlying dielectric as a function of temperature. Concerns pertaining to materials interactions, impurity diffusivity, minimization of layer stress mismatch effects, and etch characteristics support the notion that an amorphous metal electrode structure is preferred. Many pure metals and metal alloy films have recently been proposed as candidates for dual metal gate applications, including bimetal alloys, binary/ternary metal nitrides, metal silicon nitrides, conductive metal oxides, and metal silicide films. In this letter, we report on the evaluation of chemical vapor deposited (CVD) TiSiN as a gate electrode and identify the dependence of the effective work function on deposition temperature and film thickness.

To investigate the influence of CVD TiSiN electrodes on the electrical properties of MOS devices, capacitors were fabricated on heavily doped p-type substrates. Terraced oxide SiO₂ was used as the sole dielectric layer to provide a comprehensive dielectric thickness series for the efficient and reliable work function extraction from a single wafer for each electrode material being evaluated. The TiSiN films were deposited by CVD with tetrakis(diethylamido) titanium as the Ti precursor. SiH₄ and NH₃ were used as the Si and N sources. A 150 nm poly-Si layer (phosphorus-doped) was then deposited on top of the TiSiN layer followed by annealing at 1000 °C for 5 s. Three nm thick (physical thickness) HfSiOₓ films (30 mol % SiO₂) or 2 nm thick HfO₂ films were deposited by atomic layer deposition on the terraced oxide wafers for comparison with TiSiN/SiO₂. Work functions of the TiSiN electrode were extracted by plotting the flatband voltage (Vfb) versus the EOT of the capacitors. Vfb and EOT values were extracted by fitting the capacitance-voltage (C-V) curves to the conserved vector current program. The film stress was calculated by the wafer bow difference before and after film deposition on the wafers. All the work function data presented in this letter were calculated after the 1000 °C for 5 s thermal budget.

Figure 1 shows the dependence on film thickness of the CVD TiSiN work function. For these gate dielectrics, the work function increases with film thickness and saturates when the thickness reaches about 20 nm. The work function changes from 4.28 to 4.74 eV on SiO₂, 4.40 to 4.79 eV on HfO₂, and 4.44 to 4.83 eV on HfSiO₃, when the thickness increases from 2.5 to 20 nm. The C-V curves for 2.5 and 20 nm TiSiN/HfSiO₃ are shown in the inset in Fig. 1. Both C-V curves look well behaved with no evidence of any distortion. The Vfb difference in the C-V curves is consistent with work function differences for the two samples. The similar thickness dependence of work function was observed for the TiN gate electrode case. In addition, Fig. 2 shows the Vfb vs EOT plots for TiSiN/HfSiO₃ with different TiSiN

FIG. 1. Work function of CVD TiSiN on SiO₂, HfO₂, and HfSiO₃ vs film thickness.
thicknesses. Note that the data show an excellent linear fit and small interface fixed charge for all thicknesses, suggesting an accurate work function extraction methodology. There are several possible mechanisms that must be considered to explain the thickness dependence of the effective work function of TiSiN. These include (1) fixed or mobile charge changes in the high-$k$ film, and (2) composition changes in TiSiN with thickness. The first possibility, charges in the high-$k$ film increase work function as the TiSiN thickness increases, can be excluded. An experiment with different high-$k$ thickness shows that the high-$k$ thickness has little effect on the work function of TiSiN. The density of bulk charge in the high-$k$ film calculated by modeling the relation of effective work function with the thickness of high-$k$ film from this experiment is lower than $1 \times 10^{18}$ cm$^{-3}$.

The second possibility is that the TiSiN film composition changes with TiSiN film thickness, thereby increasing work function. To test this possibility, x-ray photoelectron spectroscopy analysis was done to measure the composition of TiSiN; the results are summarized in Fig. 3. Figure 3 shows that the Ti/Si ratio changed as the TiSiN film thickness was increased even though no major changes in the bonding energies were detected. Specifically, the amount of Ti in the film decreased and the Si content increased with increasing film thickness. Both Auger and secondary-ion-mass spectroscopy (SIMS) show that Ti, Si, and N equally distribute through the film (see Fig. 4). This can be explained by 1000 °C annealing after poly-Si implantation. It is possible that the reduction in Ti metal concentration may have contributed to the work function increase since Ti metal has a relatively low vacuum work function (4.3 eV).

Figure 5 shows the dependence on deposition temperature of the 20 nm TiSiN work function. The work function increases with deposition temperature on both HfO$_2$ and HfSiO$_x$, but it tends to saturate at $\sim$4.9 eV at 400 °C. The higher deposition temperature will generate stronger chemical bonds and higher film density, thereby leading to a higher work function. The Misra group$^{10,11}$ and the Kwong group$^{12,13}$ also reported the effective work function increase of metal Ru, TaSiN, TaN, and HfN by high temperature post metal-deposition anneal. Another approach that was evaluated to increase the TiSiN work function was Si implantation into the TiSiN film. This was done based on the earlier result in Fig. 3 that showed the work function increases with Si content in the TiSiN electrode. Figure 6 shows the result of the implant study, where the work function of TiSiN could be increased to 4.93 eV. The implantation was done by Si$^+$ with energy of 10 keV and a dose of $5 \times 10^{15}$ cm$^{-3}$ on 25 nm TiSiN. The results show that CVD TiSiN with ex-
pressed structure and composition is a good candidate for $p$-type metal on HfSiO$_x$.

In conclusion, the work function of CVD TiSiN can be tuned by changing the film thickness. The results show CVD TiSiN can be a good candidate for silicon-on-insulator devices where a tunable midgap work function is needed. In addition, the work function of CVD TiSiN increases with deposition temperature, but tends to saturate at 400 °C. Si implanted into TiSiN will also increase its work function. All these results show that CVD TiSiN is a good $p$-type metal candidate.

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