Combinatorial study of Ni–Ti–Pt ternary metal gate electrodes on HfO$_2$ for the advanced gate stack

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(Received 14 April 2006; accepted 11 August 2006; published online 4 October 2006)

The authors have fabricated combinatorial Ni–Ti–Pt ternary metal gate thin film libraries on HfO$_2$ using magnetron co-sputtering to investigate flatband voltage shift ($\Delta V_{\text{fb}}$), work function ($\Phi_m$), and leakage current density ($J_L$) variations. A more negative $\Delta V_{\text{fb}}$ is observed close to the Ti-rich corner than at the Ni- and Pt-rich corners, implying smaller $\Phi_m$ near the Ti-rich corners and higher $\Phi_m$ near the Ni- and Pt-rich corners. In addition, measured $J_L$ values can be explained consistently with the observed $\Phi_m$ variations. Combinatorial methodologies prove to be useful in surveying the large compositional space of ternary alloy metal gate electrode systems. © 2006 American Institute of Physics. [DOI: 10.1063/1.2357011]

Due to aggressive demands to increase device performance, the traditional gate stack, SiO$_2$ gate dielectric, and polycrystalline Si gate electrode need to be replaced due to high leakage current density ($J_L$), polycrystalline Si depletion, and dopant diffusion effects. The International Technology Roadmap for Semiconductors dictates that a 0.8 nm equivalent oxide thickness (EOT) gate dielectric is required for the 50 nm technology node in 2009. In the past five years, high-k gate dielectrics have been studied extensively, and many potential materials such as HfO$_2$, ZrO$_2$, and their silicates and oxynitrides have shown promise as replacements for SiO$_2$. However, identification of the metal gate electrode to replace polycrystalline Si is not as advanced. Metal gates offer an advantage over polycrystalline Si due to their intrinsically higher conductivity. However, metal gate stack integration involves complex issues such as the work function ($\Phi_m$), flatband voltage shift ($\Delta V_{\text{fb}}$), oxide charge ($Q_{\text{ox}}$), and thermal stability of the gate stack with regard to crystallization, interdiffusion, and interfacial reactions. Elemental metal gates, even with appropriate $\Phi_m$, may suffer adhesion and thermal stability problems. Alloy metal gates might be a better solution, since one can tailor the desirable properties. However, exploring metal gate electrode alloys is not trivial, since fabrication based on a one-composition-at-a-time approach is too time consuming to investigate even one of the many possible ternary alloy systems. Combinatorial methodology offers a viable approach, since it incorporates high throughput and rapid characterization in parallel, and a large number of samples may be characterized. The goal of this research is to demonstrate the efficiency of combinatorial techniques to enable rapid exploration of the electrical and physical properties of the Ni–Ti–Pt ternary metal gate electrode system on HfO$_2$, through the deposition of a combinatorial ternary alloy “library.” The strategy for choosing these three elements is their wide range of $\Phi_m$ in the bulk (Ni: 4.9 eV, Pt: 5.3 eV, and Ti: 4.1 eV). Thus, in the ternary metal system, one can expect n-channel metal-oxide-silicon (NMOS) metals (4.05±0.2 eV, aligned with the Si conduction band edge) and p-channel metal-oxide-silicon (PMOS) metals (5.17±0.2 eV, aligned with the Si valence band edge). We systematically investigated $\Delta V_{\text{fb}}$, $\Phi_m$, and $J_L$, which offer a basis for understanding the gate stack properties, through capacitance-voltage (C-V) and current-voltage (I-V) analyses of Ni–Ti–Pt/HfO$_2$ capacitors.

Ni–Ti–Pt ternary libraries (composition spreads) were fabricated using an ultrahigh vacuum (base pressure of ~10$^{-9}$ torr) magnetron co-sputtering system. Three sputtering guns were placed in a parallel, triangular configuration that allowed a natural compositional mix due to overlap of the three component metals [Fig. 1(a)]. The applied power for sputtering the Ni, Ti, and Pt targets was adjusted to optimize deposition rate. Each gun was housed in a 2 in. long chimney to minimize cross contamination. The libraries were deposited on Si wafers (p-type, resistivity of ~0.02 Ω-cm) predeposited with 6 nm of atomic layer deposited (ALD) HfO$_2$. A Si shadow mask with hundreds of nominal (250 × 250 μm$^2$) openings was placed directly on top of the wafer to result in in situ metal-oxide-silicon capacitors (MOSCAPS). The thickness of the library films was ~50 nm; a thin layer of Pt (~5 nm) was uniformly deposited after the library deposition to minimize oxidation of the Ti-rich alloys. A forming gas annealing (90% N$_2$ and 10% H$_2$) was carried out at 500 °C for 30 min to lower the interface state density. Wavelength dispersive spectroscopy (WDS) and scanning x-ray microdiffraction were used to characterize the nominal compositions and structures of the library. An LCR meter with a parallel $RC$ circuit mode and a precision semiconductor parameter analyzer were used to measure $C$ and $J_L$, respectively. The modulation signal level was set at 50 mV for the $C$ measurement, and $C$-$V$ behavior
was measured at 1 kHz to avoid series resistance. The Si substrate was biased for both measurements to reduce the noise ratio. The C-V and J-V properties of hundreds of MOSCAPS were measured using an automatic probe. Statistically reliable $J_L$ values were obtained by averaging ten consecutive measurements at an applied dc substrate bias of 1 V. A standard program was used to fit the measured C-V curves, to extract EOT and $\Delta V_{fb}$.

Figure 1(b) shows the composition map of the Ni–Ti–Pt library, characterized by WDS. A wide composition range, with over 90% ±1% atomic ratio of Ni and Ti and 75% ±1% atomic ratio of Pt, was achieved. The lower percentage of Pt resulted from an unintentionally low Pt deposition rate. The MOSCAP EOT values are plotted in Fig. 1(c). Some data points are missing, corresponding to bad devices that could not be fitted automatically. The mode of the EOT values is about 1.9 nm. The extracted equivalent oxide thickness (EOT) across the Ni–Ti–Pt library. The mode of the EOT values is about 1.9 nm.

Figure 2(a) shows the composition map of the Ni–Ti–Pt ternary alloys, characterized by Scanning x-ray microdiffraction was used to study the structure of the Ni–Ti–Pt ternary alloys. Face centered cubic (FCC) polycrystalline structures were observed near the Pt-rich and Ni-rich corners, as expected, but no peaks were observed near the Ti-rich corner, indicating that a nanocrystalline structure is most likely present. Many intermetallic phases observed in the bulk Ni–Ti–Pt phase diagrams were not observed in our library film. This might suggest that few of the expected intermetallic compounds form in the thin film or their nanocrystalline structures cannot be observed by x-ray diffraction.

$\Phi_m$ of various metals can be approximated from the $\Delta V_{fb}$ data, extracted from C-V curves, using the following relationship:

$$\Delta V_{fb} = (\Phi_m - \Phi_s) - (Q/C_\text{ox}),$$  

where $\Phi_m$ and $\Phi_s$ are the work functions of metal and Si, respectively, $Q$ is the charge in HfO$_2$, and $C_\text{ox}$ is the capacitance. Figure 2(a) shows the $\Delta V_{fb}$ map extracted from MOSCAPS across the Ni–Ti–Pt library. A systematic and smooth variation is observed across the library. The smooth variation of $\Delta V_{fb}$ suggests that many of the phases present in the bulk Ni–Ti–Pt alloy phase diagram are suppressed in the thin film. The $\Delta V_{fb}$ values close to the Ni- and Pt-rich corners are less negative ($\sim$0.3 V) than at the Ti-rich corner ($\sim$0.8 V). From Eq. (1) therefore, $\Phi_m$ near the Ni- and Pt-rich corners should be larger than at the Ti-rich corner. Assuming $Q/C_\text{ox}$ is roughly constant as a function of metal gate composition, the variation in $\Delta V_{fb}$ is directly related to the change of $\Phi_m$. Figure 2(b) shows the map of $\Phi_m$ variation across the library, derived from Fig. 2(a), using data generated by the CVC program. The trend is consistent with our expectation. The extracted values close to the three corners are comparable with literature values (round symbols) for Ni and Ti, but only with the low end of the literature values for Pt. Thus, nowhere in the library do we observe an alloy with $\Phi_m$ suitable for PMOS. This might be interpreted in two ways: (1) only 75% Pt was achieved, which results in more negative $\Delta V_{fb}$ (smaller $\Phi_m$) compared to 100% Pt or (2) some midgap states were created at the metal/HfO$_2$ interfaces, resulting in interface dipoles and Fermi-level pinning. Currently, we are making library films with a new combinatorial technique, which will allow us to explore the complete ternary up to 100% of each corner element to further elucidate this issue.

In a metal/insulator/semiconductor structure, metals with higher $\Phi_m$ intrinsically possess higher barrier height ($\phi_0$) based on the equation
\[ \phi_0 = \Phi_m - \chi_i, \]

where \( \chi_i \) is the insulator electron affinity, a constant. From the data of Fig. 2(b), Ni- and Pt-rich alloys, possessing higher \( \Phi_m \), should accordingly have higher \( \phi_0 \), and Ti-rich alloys, possessing smaller \( \Phi_m \), smaller \( \phi_0 \). The relationship between \( J_L \) and \( \phi_0 \) is shown in the following equation:

\[ J_L \propto E^2 \exp \left( -\frac{8\pi m \sqrt{2m (q\phi_0)^{3/2}}}{3qhE} \right), \]

where \( E \) is the electric field across the oxide, \( q \) is the charge of an electron, \( h \) is Planck's constant, and \( m^* \) is the effective mass of an electron in the oxide. One can see that higher \( \phi_0 \) results in smaller \( J_L \). Therefore, Ni- and Pt-rich alloys will result in smaller \( J_L \), and Ti-rich alloys, higher \( J_L \). Figure 3 shows a \( J_L \) map of the Ni–Ti–Pt library. We observe that the devices near the Ni- and Pt-rich corners have smaller \( J_L \) (log \( J_L \) ~ −7.4 A/cm²), gradually increasing towards the Ti-rich corner (log \( J_L \) ~ −5.8 A/cm²). This is consistent with our expectations, and the measured \( J_L \) values are comparable with literature values. Thus, the results of Figs. 2 and 3 are consistent, and \( \Phi_m \) and \( J_L \) vary predictably with compositions in the Ni–Ti–Pt library.

In conclusion, Ni–Ti–Pt ternary metal gate libraries were deposited on HfO₂ dielectrics, and studied systematically by WDS, x-ray microdiffraction, and \( C-V \) and \( I-V \) analyses. WDS results show that over 90% ±1% of Ni and Ti and 75% ±1% of Pt were attained in the library. The fitted \( C-V \) characteristics reveal that the mode of the EOT value is about 1.9 nm, larger than expected, due to interfacial oxide. A more negative \( \Delta V_{th} \) is observed close to the Ti-rich corner than close to the Ni- and Pt-rich corners, implying smaller \( \Phi_m \) near the Ti-rich corners and higher \( \Phi_m \) near Ni- and Pt-rich corners. Measured \( J_L \) values vary predictably and are consistent with the extracted \( \Phi_m \) variations.

The authors would like to thank Chris Long for assistance with the x-ray diffraction analysis. This research was partly supported by Japan Society for the promotion of Science, Core to Core program. This work was performed in part at the NIST Center for Nanoscale Science and Technology’s Nanofab facility in Gaithensburg, MD.