Effectiveness of Aluminum Incorporation in Nickel Silicide and Nickel Germanide Metal Gates for Work Function Reduction

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1. Introduction

Nickel (Ni) fully-silicided (FUSI) gate is a promising metal gate option, and could potentially be adopted for future CMOS technology nodes. The modulation of NiSi gate work function Φ_m (~4.6 eV) from Si midgap is highly desired for achieving low transistor threshold voltage. Ni-alloys have been used during silicidation to modulate the NiSi gate Φ_m , and ternary Ni_{1-x}Pt_xSi has been reported to successfully obtain PMOS Φ_m tunability [1]– [3]. On the other hand, Ni fully-germanided (FUGE) gate has also attracted interest due to its p-type Φ_m corresponding to Si valenceband edge [4]-[5]. In view of this, a suitable NMOS solution would realize dual gate integration employing either Ni-FUSI, or Ni-FUGE gates. In this paper, we investigate the effectiveness of Al incorporation in NiSi and NiGe gates [denoted by Ni(Al)Si and Ni(Al)Ge, respectively] for NMOS Φ_m modulation. Due to the low Φ_m of Al (4.2 – 4.3 eV), a reduction in Φ_m of ~0.2 eV for Ni(Al)Si, and ~0.6 eV for Ni(Al)Ge was achieved. This was attributed largely to Al segregation at the gate/dielectric interface and not the change in intrinsic gate Φ_m .

2. Experiment

First, $\sim 3 - 7$ nm of thermal SiO₂ was formed by a SiO₂ etchback process (for Φ_m extraction). In addition, a ~ 3 nm thick SiO₂ was separately grown for some samples (for equivalent oxide thickness T_{ox} extraction). Next, ~ 50 nm of Si (chemical vapour deposited), or Ge (sputtered) was deposited and patterned. After a HF-dip to remove native oxide, ~ 40 nm of Ni, or Ni_{1-x}Al_x (x = 0.07, 0.22 or 0.42) was deposited by sputtering and co-sputtering, respectively. Rapid thermal annealing (RTA) at 450 or 550°C for 60 s in N₂ was eched by dilute HNO₃ (5%) to complete the gate stacks.

3. Results and Discussions

Fig. 1 shows the C-V curves of Ni(Al)Si gate silicided at 450 and 550°C. We see a more negative flatband voltage $V_{\rm FB}$ shift when Ni(Al)Si gate was silicided at the higher temperature. Secondary ion-mass spectroscopy (SIMS) was employed to determine the Al profile in the Ni(Al)Si gate stacks (Fig. 2). Due to the high sensitivity of Al in SIMS positive ion mode, both Al ion and Al₂ ion cluster profiles were monitored to confirm the difference in Al intensity, if any, between the samples. Higher Al and Al_2 intensity for a 550°C RTA showed that a higher temperature favoured Al diffusion towards the Ni(Al)Si/SiO₂ interface during silicidation. Therefore, a 550°C anneal was employed for subsequent FUSI and FUGE gates. The Al SIMS profile also indicated that the Ni(Al)Si gate consisted of a Al-rich top layer. Fig. 3 shows the transmission electron microscopy (TEM) image of a bilayer FUSI Ni(Al)Si gate (silicided with Ni_{0.78}Al_{0.22}). Electron dispersive X-ray spectroscopy (EDX) verified that Al was not uniformly distributed in the Ni(Al)Si gate: the top $Ni_xAl_ySi_z$ layer had a higher Al atomic concentration. The Ni(Al)Ge gate also had the same bilayer structure and a similar Al distribution (not shown).

The Al content in $Ni_{1-x}Al_x$ was varied to investigate its effect on gate Φ_m . Fig. 4 (a) shows that silicidation using a $Ni_{0.93}Al_{0.07}$ alloy was sufficient to modulate the V_{FB} by ~0.16 V (from NiSi). There was negligible V_{FB} change as the Al ratio increased. Fig. 4(b) indicates that the $V_{\rm FB}$ of Ni(Al)Ge could also be modulated by Al incorporation. The results from Ni(Al)Ge gate germanided with Ni_{0.58}Al_{0.42} was excluded, as the gate was not FUGE. The smaller T_{ox} for both Ni(Al)Si and Ni(Al)Ge gate stacks suggested that a reaction between Al and SiO₂ dielectric occurred during RTA (Fig. 5). $V_{\rm FB}$ vs T_{ox} plots in Fig. 6 (a) and (b) were used for effective gate Φ_m extraction by eliminating the contribution of fixed oxide charges $Q_{\rm f}$. Lower Ni(Al)Si and Ni(Al)Ge gate Φ_m are expected from the $V_{\rm FB}$ values in the plots.

High resolution TEM images in Fig. 7 (a) and (b) show good dielectric integrity for both Ni(Al)Si and Ni(Al)Ge gate stacks (using Ni_{0.78}Al_{0.22}). The segregation of Al in Ni(Al)Ge could be clearly observed [Fig. 7 (b)]. Therefore, gate Φ_m modulation was attributed to segregation of metallic Al at the gate/dielectric interface [3]. X-ray diffraction (XRD) on corresponding blanket films confirmed that no ternary silicide or germanide was formed (Fig. 8). This further supports the fact that the Φ_m reduction was largely due to Al segregation, and not a change in intrinsic gate Φ_m (i.e. ternary silicide or germanide formation). However, this caused a decrease in T_{ox} for both Ni(Al)Si and Ni(Al)Ge gates, as highlighted in Fig. 5. It was reported that implanted Al atoms segregated towards the SiO₂ interface during Ni-silicidation to form a stable layer of Al₂O₃ (~0.5 nm) [6]. Therefore, it is believed that Al scavenges O from SiO2 during silicidation/germanidation to form a thin Al₂O₃ interfacial layer. Hence, the compensation of negative $Q_{\rm f}$ from Al₂O₃ possibly caused the reduction in positive $Q_{\rm f}$ for Ni(Al)Ge and Ni(Al)Ge gate stacks (Fig. 9). Fig. 10 summarizes the effective gate Φ_m values obtained through Al incorporation in NiSi and NiGe. The saturation in Ni(Al)Si Φ_m tunability at ~4.4 eV could be due to a combination of Fermi-level pinning by interfacial Al₂O₃ [7], as well as the non-uniform distribution of Al in the gates. The small ~0.1 eV shift in Ni(Al)Ge Φ_m (germanided with Ni_{0.93}Al_{0.07}) was attributed to the high NiGe Φ_m (~5.0 eV), coupled with less Al segregation in sputtered Ge during germanidation. However, with increased Al ratio in Ni-Al alloy, a significant ~0.6 eV shift in Ni(Al)Ge Φ_m was obtained.

4. Conclusions

Work function Φ_m reduction through Al incorporation in NiSi and NiGe was achieved. A higher annealing temperature enhances Al segregation toward the gate/dielectric interface, which directly modulates the gate Φ_m . The non-uniform distribution of Al in the gate, and formation of interfacial Al₂O₃ are mainly responsible for saturation in both Ni(Al)Si and Ni(Al)Ge gate Φ_m at ~4.4 eV. This current Φ_m value is suitable for transistors with advanced structures like multiple-gate field-effect transistors.

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Fig. 1: The C-V curves show a more negative $V_{\rm FB}$ shift for the Ni(Al)Si gate silicided at 550°C than 450°C.



Ni(Al)Si SiO, Si-sub Relative Intensity (a.u.) 10 Al 10 Silicidation 10 Temperature Solid symbols: 450°C Open symbols: 550°C 10[°] 200 400 0 600 Sputtering Time (s)

Fig. 2: SIMS profile indicates more Al present at the Ni(Al)Si/SiO₂ interface after a 550° C silicidation. A higher Al concentration was also observed at the top of the gate.



Fig. 4: *C*-*V* curves for (a) Ni(Al)Si and Ni(Al)Ge gates formed using different Ni_{1-x}Al_x alloys. A saturation in Ni(Al)Si V_{FB} was observed with varying Al ratio. Ni(Al)Ge gate was also able to achieve approximately the same V_{FB} through Al incorporation (using Ni_{0.78}Al_{0.22} alloy).



Fig. 6: V_{FB} vs T_{ox} plots for Φ_m extraction of (a) Ni-FUSI and (b) Ni-FUGE gates in this work. Lower Ni(Al)Si and Ni(Al)Ge gate Φ_m are expected from the V_{FB} values in the plots.



Fig. 8: NiSi and NiGe XRD peaks from Ni(Al)Si and Ni(Al)Ge films indicate the absence of ternary silicide or germanide formation.



Fig. 9: The decrease in Q_f when Al was incorporated in NiSi and NiGe gates was due to the growth of an interfacial Al₂O₃ layer.



Fig. 3: TEM image of a bilayer FUSI Ni(Al)Si gate stack. EDX verified that the Al profile was not uniformly distributed in the Ni(Al)Si gate.



Fig. 5: A decrease in T_{ax} was observed for both Ni(Al)Si and Ni(Al)Ge gates from NiSi and NiGe gates, respectively, suggesting that Al had reacted with the SiO₂ dielectric.



Fig. 7: High resolution TEM images of (a) Ni(Al)Si and (b) Ni(Al)Ge gates showing good dielectric integrity. Al segregation after germanidation could be clearly detected from (b).



Fig. 10: Al incorporation was able to reduce the Φ_m of NiSi and NiGe by ~0.2 eV and ~0.6 eV, respectively.