Effective Passivation of Interface Dipole in TiN-Gate Ge-MOS Capacitor with Ultrathin SiO₂/GeO₂ Bilayer by Nitrogen Incorporation

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1. Introduction

Recently, we proposed a method for electrical passivation of a Ge surface by an ultrathin SiO₂/GeO₂ bilayer, which can be processed through the thermal etching of GeO₂ by vacuum annealing and subsequent SiO₂ deposition. By optimizing bilayer passivation (BLP) and subsequent gate-insulator deposition, an interface state density (Dₛ) of 4 x 10¹¹ cm⁻²V⁻¹ was achieved near the midgap despite the very thin thickness (1.6 nm) of the GeO₂ layer.¹

To apply this BLP to a high-k/Ge gate stack, there are two major topics to be addressed. One is high-k film fabrication matched with BLP. Another is the optimization for the metal gate process such as TiN or TaN, because such nitrides are important as thermostable electrodes and also for threshold voltage (Vₜₚₜ) control.² However, the studies on metal gates for fabricating a good Ge-MOS stack are very few.

In this work, we focused on the TiN metal gate and investigated the effect of postmetallization annealing (PMA) on the electrical properties of a TiN-gate Ge-MOS capacitor.

2. Experimental

Fabrication process flow of Ge-MOS capacitor is shown in Fig. 1. A p-type (100) Ge substrates with a resistivity of 0.25 Ωcm was used. First, sacrificial oxidation was done at 450°C for 30 min by dry oxidation, followed by loading a physical vapor deposition (PVD) chamber for BLP. After volatilization of GeO₂ by vacuum annealing, a 1.0 nm-thick SiO₂ interlayer (IL) was deposited on the Ge surface at 350°C using rf magnetron sputtering from a SiO₂ target with the addition of O₂. Note that a GeO₂ layer grows during the SiO₂ deposition and its thickness is approximately 1.0 nm.¹ Then, a 10 nm-thick SiO₂ film was deposited at room temperature (RT), followed by the PDA. A 50 nm-thick TiN film was deposited on the SiO₂-gate insulator by rf magnetron sputtering. The PMA was performed at temperatures in the range of 350-550°C for 20 min in N₂. Then a 100 nm-thick Al film was deposited by thermal evaporation. Gate electrodes with an area of 2.25 x 10⁻² cm² were patterned. Finally, contact annealing was done at 350°C for 10 min in N₂.

3. Results and Discussion

Figure 2 shows the C-V₀ curves of the MOS capacitors without PMA and with PMA at 450°C. The PMA at 450°C led to a significant shift in flat band voltage (V₉B) and drastic decrease in hysteresis (HT). Dependences of V₉B, HT and Dₛ on PMA temperature (Tₚₐₘₐ) are shown in Fig. 3. Here, Dₛ indicated at an energy position near the midgap, which was measured by DLTS. The V₉B monotonically increased with an increase in Tₚₐₘₐ and showed +0.23 V at 450°C. HT drastically decreased with an increase in Tₚₐₘₐ and achieved a minimum value of 27 mV at 450°C. Dₛ

Fig. 1. Fabrication process flow of Ge-MOS capacitors which were annealed different temperature.

Fig. 2. C-V₀ curves of Ge-MOS capacitors.
decreased down to $2.5 \times 10^{11}$ cm$^2$ eV$^{-1}$. These improvements are likely to be associated with diffusion of nitrogen from TiN film into the SiO$_2$/GeO$_2$ gate stack.

To clarify the presence of nitrogen in the gate stack, time-of-flight secondary ion mass spectroscopy (TOF-SIMS) measurements were performed for a sample with PMA at 450°C, where the TiN film on the sample was completely removed by wet etching. Figure 4 shows the TOF-SIMS results. The GeN signal was clearly observed, and the location completely coincided with that of GeO$_2$ signal, implying that nitrogen exists in the GeO$_2$ IL between SiO$_2$ and Ge.

To clarify the origin of the $V_{FB}$ shift, we investigated the effective work function ($\Phi_{m,eff}$) and the fixed charge density ($Q_f$) by $V_{FB}$ versus equivalent oxide thickness (EOT) plots for Ge and Si substrates. For Si substrates, Al/TiN/SiO$_2$/Si structures were prepared using the same processes as those for Ge. The $V_{FB}$-EOT plots for Ge and Si substrates are shown in Fig. 5, where the thermal treatments were no-PMA and 450°C-PMA. The obtained $\Phi_{m,eff}$ and $Q_f$ are summarized in Table I.

![Fig. 3. Dependences of $V_{FB}$, $HT$ and $D_a$ on $T_{PMA}$.](image1)

We can find interesting phenomena from $\Phi_{m,eff}$ results for Ge and Si. The difference ($\Delta V_{dp}$) between $\Phi_{m,eff}$ values for Ge and Si corresponds to $V_{FB}$ shift by electric dipole formation at SiO$_2$/GeO$_2$ interface. The values of $\Delta V_{dp}$ are also listed in Table I. An areal density difference model of oxygen atoms has been proposed to explain the physical origin of the dipole at high-$k$/SiO$_2$ interface.\(^4\) If we apply this model to the present results, oxygen atoms are transferred from GeO$_2$ to SiO$_2$ at the interface. This movement leads to negatively charged interstitial oxygen (O$_i$) in SiO$_2$ and positively charged oxygen vacancy (O$_v^-$) in GeO$_2$. As a result, the dipole layer causes a decrease in $\Phi_{m,eff}$ of TiN.

In other words, the $V_{FB}$ shifts by interface dipole formation at SiO$_2$/GeO$_2$ were -0.63 and -0.26 V for MOS capacitors without PMA and with PMA at 450°C, respectively. This means that the PMA at 450°C led to a decrease in the amount of the dipole. The modulation of TiN’s $\Phi_{m,eff}$ in the range of 3.9-4.4 eV is very attractive from the view point of the $V_{FB}$ control of Ge-MOSFET.

Another important factor in understanding the role of nitrogen in SiO$_2$/GeO$_2$ gate stack is $Q_f$. The $Q_f$ in the Ge-MOS capacitor changed from $+3.4\times 10^{11}$ to $-4.2\times 10^{11}$ cm$^2$ after the 450°C-PMA, which is likely to be associated with a decrease in dipole. Since the strength of the dipole depends on the amount of the dipole, the nitrogen incorporated in the gate stack may induce the reaction of (O$_i$/O$_v^-$)$^0 \rightarrow (O/\theta{O}_2^{-2})$- at the SiO$_2$/GeO$_2$ interface, resulting in negative fixed charges.

4. Conclusion

We clarified the PMA effect for a TiN-gate Ge-MOS capacitor with BLP. 450°C-PMA led to positive $V_{FB}$ shift, small $HT$ and low $D_a$. The $V_{FB}$ shift was mainly due to a decrease in the amount of dipole at the SiO$_2$/GeO$_2$ interface and the accompanying creation of negative charge centers.

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References