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Postmetallization annealing effect of TiN-gate Ge metal-oxide-semiconductor capacitor with ultrathin SiO$_2$/GeO$_2$ bilayer passivation

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The postmetallization annealing (PMA) effect was investigated for a TiN-gate Ge metal-oxide-semiconductor capacitor with an ultrathin SiO$_2$/GeO$_2$ bilayer passivation. PMA at 450 °C led to the incorporation of nitrogen atoms into the gate stack. Consequently, the flat band voltage shifted from −0.79 to +0.23 V, resulting in a decrease in the dipole at the SiO$_2$/GeO$_2$ interface and the accompanying creation of a negative charge. The hysteresis decreased from 98 to 27 mV and the interface state density decreased from $6 \times 10^{11}$ to $2.5 \times 10^{11}$ cm$^{-2}$ eV$^{-1}$, as results of the nitrogen termination of defects at the SiO$_2$/GeO$_2$ interface and/or in the GeO$_2$ interlayer. © 2011 American Institute of Physics. [doi:10.1063/1.3601480]

Germanium (Ge) is of great interest as a candidate channel material for future complementary metal-oxide-semiconductor (CMOS) devices owing to its high intrinsic carrier mobility. In realizing Ge-CMOS technology, however, there are many difficulties associated with the different physical and chemical properties of Ge compared with Si. The formation of a good MOS stack is one of the most challenging issues, and many recent studies on this topic have been published.

Recently, we proposed a method for electrical passivation of a Ge surface by an ultrathin SiO$_2$/GeO$_2$ bilayer. By optimizing this bilayer passivation (BLP) and subsequent gate-insulator deposition, an interface state density ($D_{it}$) of $4 \times 10^{11}$ cm$^{-2}$ eV$^{-1}$ was achieved near the midgap despite the very thin thickness (1.6 nm) of the GeO$_2$ layer.

To apply this BLP to a high-permittivity (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 ($V_{TH}$) control. However, the studies on metal gates for fabricating a good Ge-MOS stack are very few.

In this letter, 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. It was found that PMA at 450 °C led to three good effects; significant improvements of hysteresis (HT), flatband voltage ($V_{FB}$), and $D_{it}$. We will discuss the role of nitrogen incorporated in the Ge-MOS stack.

A p-type (100) Ge substrate with a resistivity of 0.34 Ω cm was used. First, sacrificial oxidation was performed at 450 °C for 30 min by dry oxidation (GeO$_2$ thickness: 3 nm), followed by loading a physical vapor deposition (PVD) chamber for BLP. The details of BLP are given elsewhere. After complete volatilization of GeO$_2$ by vacuum annealing, a 1.0-nm-thick SiO$_2$ interlayer (IL) was deposited on the cleaned Ge surface at 350 °C using rf magnetron sputtering from a SiO$_2$ target with the addition of O$_2$.

Note that a GeO$_2$ layer grows during the SiO$_2$ deposition and its thickness is approximately 1.0 nm. Then, a 10-nm-thick SiO$_2$ film without the addition of O$_2$ was deposited at room temperature (RT) using the same PVD system, followed by the postdeposition annealing (PDA) at 550 °C for 30 min in N$_2$. The physical thickness of GeO$_2$ was found to be increased up to 1.6 nm by the PDA.

A 50-nm-thick TiN film was deposited on the SiO$_2$-gate insulator by rf magnetron sputtering using a TiN target in Ar ambient. During the deposition, the gas pressure was kept at 2.0 Pa. The applied rf power was also kept at 60 W, resulting in a deposition rate of approximately 10 nm/min. The resistivity of the TiN film followed by annealing at 350 °C for 10 min in N$_2$ was 140 μΩ cm, which was close to the value for stoichiometric TiN film.

The PMA of the TiN-deposited sample was performed at temperatures in the range of 350–550 °C for 20 min in N$_2$. Then, a 100-nm-thick Al film was deposited by thermal evaporation. The gate patterning with an area of $2.25 \times 10^{-4}$ cm$^2$ was performed by lithography. First, etching for the Al gate electrode was done by H$_3$PO$_4$ solution at 40 °C, and second, etching for the TiN electrode was performed by wet etching (1 part NH$_4$OH, 4 parts H$_2$O$_2$) at 50 °C. Note that this wet etching method enables us to perform selective etching of TiN film on SiO$_2$ and high-$k$ dielectrics such as HfO$_2$ and HfSiON. Finally, contact annealing was carried out at 350 °C for 10 min in N$_2$ for obtaining electrically good adhesion between Al and TiN films.

Equivalent oxide thicknesses (EOTs) for all fabricated capacitors were approximately 12–13 nm from the capacitance-voltage ($C-V_{TH}$) measurements. Figure 1 shows the $C-V_{TH}$ curves of the MOS capacitors without PMA and with PMA at 450 °C, for which the measurements were performed at RT and a frequency of 1 MHz. The bias was double-scanned from −2 to +1 V and +1 to −2 V. It is interesting that PMA at 450 °C led to a significant shift in $V_{FB}$ and a drastic decrease in HT. The dependences of $V_{FB}$...
and HT on PMA temperature ($T_{PMA}$) are shown in Figs. 2(a) and 2(b), respectively. The HT drastically decreased with an increase in $T_{PMA}$ and achieved a minimum value of 27 mV at 450 °C. It is likely that nitrogen atoms in TiN film diffused into SiO$_2$ and affected the electrical properties of the Ge-MOS 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 3 shows the TOF-SIMS results. The GeN and CsN signals were clearly observed, and the locations 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 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. Since the EOT of the SiO$_2$-gate insulator is much thicker than that of the GeO$_2$ IL, the relation between $V_{FB}$ and EOT is given by $V_{FB}=\Phi_{m,eff}-\Phi_{Ge/Si}-Q_f \times EOT/\varepsilon_{ox}$, where $\Phi_{Ge/Si}$ is the work function of the Ge or Si substrate, and $\varepsilon_{ox}$ is the dielectric constant of SiO$_2$. Thus, $Q_f$ can be calculated from the slope of the $V_{FB}$ versus EOT plot, and $\Phi_{m,eff}$ can be estimated from the $V_{FB}$-intercept value.

The $V_{FB}$-EOT plots for Ge and Si substrates are shown in Fig. 4. The obtained $\Phi_{m,eff}$ and $Q_f$ are summarized in Table I. It can be seen from the $\Phi_{m,eff}$ results for Si that $\Phi_{m,eff}$ changed from 4.55 to 4.68 eV after PMA at 450 °C. It has been reported that the $\Phi_{m,eff}$ of a TiN film on SiO$_2$ prepared from reactive magnetron sputter deposition using Ti target changes from 4.2 to 4.9 eV with an increase in the nitrogen content. Furthermore, the $\Phi_{m,eff}$ of stoichiometric TiN deposited by atomic layer deposition was reported to be around 5.0 eV. Thus, the small increase in $\Phi_{m,eff}$ found in this letter is likely to be attributed to the near-stoichiometry of TiN film.

On the other hand, we can find interesting phenomena from $\Phi_{m,eff}$ results for Ge and Si. The difference ($\Delta V_{dip}$) between $\Phi_{m,eff}$ values for Ge and Si corresponds to $V_{FB}$ shift by electric dipole formation at SiO$_2$/GeO$_2$ interface because the TiN/SiO$_2$ interface should be the same for both cases of Ge and Si. The values of $\Delta V_{dip}$ are listed in Table I. Recently, Kita and Toriumi have proposed an areal density difference model of oxygen atoms at high-$k$/SiO$_2$ interfaces to explain
the physical origin of the dipole formed at high-$k$/SiO$_2$ interface. 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$_{\text{i}}^-$) in SiO$_2$ and positively charged oxygen vacancy (O$_{\text{v}}^+$) in GeO$_2$. As a result, the dipole layer causes a decrease in $\Phi_{\text{m,eff}}$ of TiN. In other words, the $V_{\text{FB}}$ 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 $\Phi_{\text{m,eff}}$ in the range of 3.9–4.4 eV (indicated in Table I) is very attractive from the viewpoint of the $V_{\text{TH}}$ control of Ge-MOS transistors.

Another important factor in understanding the role of nitrogen in SiO$_2$/GeO$_2$ gate stack is $Q_t$. The $Q_t$ in the Si-MOS capacitor with the 450 °C-PMA was $+3 \times 10^{11}$ cm$^{-2}$ and almost the same as that without PMA, as listed in Table I. This suggests that nitrogen atoms cannot terminate the dangling bonds in SiO$_2$ or there is no dangling bond in SiO$_2$. By contrast, the $Q_t$ 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$_{\text{i}}^-$/O$_{\text{v}}^+$)$^0 \rightarrow (O_{\text{i}}^-/O_{\text{v}}^+/N^-)^-$ at the SiO$_2$/GeO$_2$ interface, resulting in negative fixed charges.

Figure 5 shows $D_{\text{it}}$ distributions for Ge-MOS capacitors with and without PMA. The $D_{\text{it}}$ was measured by deep-level transient spectroscopy (DLTS), where an injection pulse for the hole capture was set at an accumulated bias ($V_{\text{AP}}$) of $-2$ V, and a quiescent reverse bias ($V_{\text{R}}$) corresponding to a band bending of $\phi_B$ ($\phi_N$; the energy between Fermi-level and intrinsic Fermi-level) was set for hole emission, as shown in Fig. 5. Although the $D_{\text{it}}$ values near the valence band edge were almost the same for all capacitors, the $D_{\text{it}}$ near the midgap decreased with an increase in $T_{\text{PMA}}$ up to 450 °C. The $D_{\text{it}}$ values near the midgap are plotted in Fig. 2(c). The PMA at 450 °C led to the lowest $D_{\text{it}}$ of $2.5 \times 10^{11}$ cm$^{-2}$ eV$^{-1}$, indicating that 450 °C-PMA is also effective for decreasing $D_{\text{it}}$. The decreasing tendency of $D_{\text{it}}$ with $T_{\text{PMA}}$ is very similar to that of HT. Since HT is associated with defect-related slow traps at the SiO$_2$/GeO$_2$ interface and/or in the GeO$_2$ IL, a decrease in HT should be caused by nitrogen terminations of the slow traps responsible for the trapping phenomenon. Similarly, it is likely that the $D_{\text{it}}$ values near the midgap reflect not only fast traps due to GeO$_2$/Ge interfacial defects but also slow traps at the SiO$_2$/GeO$_2$ interface and/or in a GeO$_2$ IL. If so, when the $V_{\text{AP}}$ is small, the electric field for the hole injection into a GeO$_2$ IL becomes weak, and the $D_{\text{it}}$ should be decreased.

To clarify the contribution of the slow traps, we performed DLTS measurements for a MOS capacitor with 450 °C-PMA with a $V_{\text{AP}}$ of $-0.5$ V. The obtained result is shown by a broken line in Fig. 5. It is clear that $D_{\text{it}}$ decreased down to $1.2 \times 10^{11}$ cm$^{-2}$ eV$^{-1}$ near the midgap, which agrees well with the reported $D_{\text{it}}$ value of GeO$_2$/Ge. Therefore, we suppose that the good PMA effect on $D_{\text{it}}$ for a capacitor with very thin GeO$_2$ IL results from the dangling bond termination by nitrogen at the SiO$_2$/GeO$_2$ interface and/or in GeO$_2$ IL. The detailed dependence of $D_{\text{it}}$ distribution on $V_{\text{AP}}$ will be reported as another paper.

In summary, we clarified the PMA effect for a TiN-gate Ge-MOS capacitor with BLP. PMA at 450 °C led to a positive $V_{\text{FB}}$ shift, small HT, and low $D_{\text{it}}$. The $V_{\text{FB}}$ 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. The decreases in HT and $D_{\text{it}}$ were attributable to the termination of defects at the SiO$_2$/GeO$_2$ interface and/or in GeO$_2$ IL.

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**TABLE 1.** $\Phi_{\text{m,eff}}$ and $Q_t$ obtained from $V_{\text{FB}}$-EOT plots.

<table>
<thead>
<tr>
<th>PMA</th>
<th>$\Phi_{\text{m,eff}}$ (eV)</th>
<th>$\Delta V_{\text{tip}}$ (eV)</th>
<th>$Q_t$ ($10^{11}$ cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/o</td>
<td>4.55</td>
<td>3.92</td>
<td>(+)3.1</td>
</tr>
<tr>
<td>450 °C</td>
<td>4.68</td>
<td>4.42</td>
<td>(+)2.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(−)4.2</td>
</tr>
</tbody>
</table>

**FIG. 5.** (Color online) $D_{\text{it}}$ distributions for TiN-gate Ge-MOS capacitors with various PMA treatments. The DLTS measurements were performed at an emission rate of 545 s$^{-1}$, a pulse width of 20 $\mu$s, and a $V_{\text{AP}}$ of $-2$ V. The $D_{\text{it}}$ distribution shown by the broken line was measured at a $V_{\text{AP}}$ of $-0.5$ V.