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Effective Passivation of Interface Dipole in TiN-Gate Ge-MOS Capacitor with Ultrathin SiO_2/GeO_2 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 SiO_2/GeO_2 bilayer, which can be processed through the thermal etching of GeO_2 by vacuum annealing and subsequent SiO_2 deposition. By optimizing bilayer passivation (BLP) and subsequent gate-insulator deposition, an interface state density (D_{it}) of 4×10^{11} cm^{-2}eV^{-1} was achieved near the midgap despite the very thin thickness (1.6 nm) of the GeO_2 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 (V_{TH}) control.[2,3] 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) camber for BLP. After volatilization of GeO_2 by vacuum annealing, a 1.0 nm-thick SiO_2 interlayer (IL) was deposited on the 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.[1] Then, a 10 nm-thick SiO_2 film was deposited at room temperature (RT), followed by the PDA. A 50 nm-thick TiN film was deposited on the SiO_2-gate insulator by rf magnetron sputtering. The PMA 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. Gate electrodes with an area of 2.25×10^{-4} cm^2 were patterned. Finally, contact annealing was done at 350°C for 10 min in N_2.

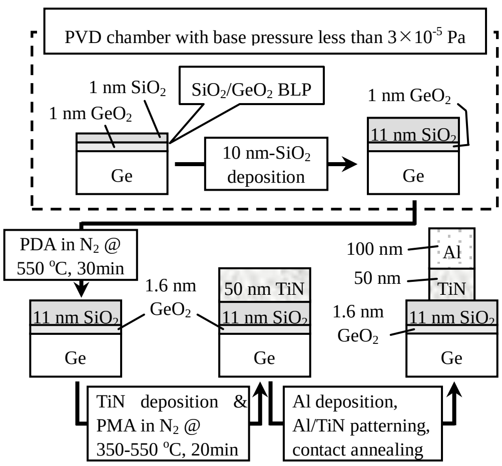

Fig. 1. Fabrication process flow of Ge-MOS capacitors which were annealed different temperature.

3. Results and Discussion

Figure 2 shows the C-V_G 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 (V_{FB}) and drastic decrease in hysteresis (*HT*). Dependences of V_{FB}, *HT* and D_{it} on PMA temperature (T_{PMA}) are shown in Fig. 3. Here, D_{it} indicated at an energy position near the midgap, which was measured by DLTS. The V_{FB} monotonically increased with an increase in T_{PMA} and showed +0.23 V at 450°C. *HT* drastically decreased with an increase in T_{PMA} and achieved a minimum value of 27 mV at 450°C. D_{it}

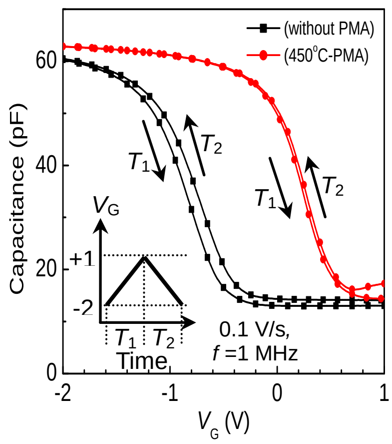

Fig. 2. C-V_G curves of Ge-MOS capacitors.

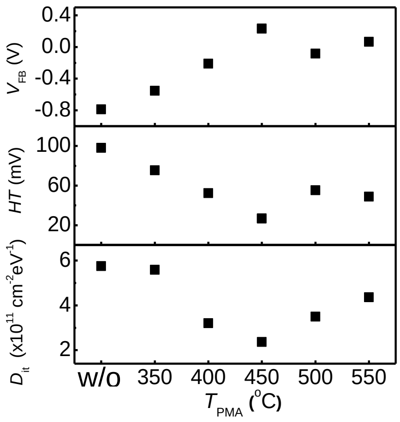

Fig. 3. Dependences of V_{FB}, HT and D_{it} on T_{PMA}.

decreased down to 2.5×10^{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.

We can find interesting phenomena from $\Phi_{m,eff}$ results for Ge and Si. The difference (ΔV_{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. The values of ΔV_{dip} 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

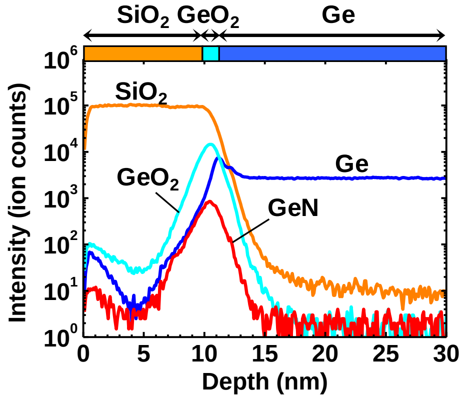

Fig. 4. TOF-SIMS results. Cs and Bi^{3++} ions were used for etching and analysis respectively.

Table I. $\Phi_{m,eff}$ and Q_f obtained from V_{FB}-*EOT* plots.

PMA	$\Phi_{m,eff}$ (eV)		ΔV_{dip} (eV)	Q_f (10^{11} cm^{-2})	
	Si	Ge		Si	Ge
w/o	4.55	3.92	-0.63	(+) 3.1	(+) 3.4
450 °C	4.68	4.42	-0.26	(+) 2.6	(-) 4.2

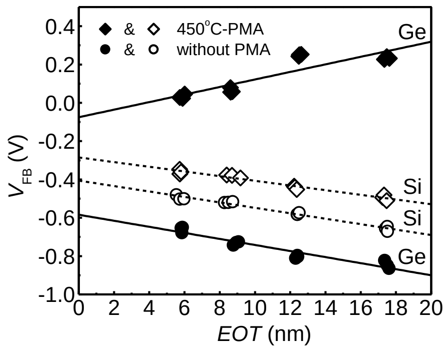

Fig. 5. V_{FB} versus *EOT* plots for Ge and Si substrates.

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_{TH} 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 $+3.4\times10^{11}$ to -4.2×10^{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 $(O_I^-/O_V^+)^0 \rightarrow (O^-/O_V^+\text{-}N^-)^-$ 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_{it}. 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.

Acknowledgements

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