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# Effects of fluorine incorporation on the properties of Ge p-MOS capacitors with HfTiON dielectric

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ABSTRACT

In this work, Ge p-MOS capacitors with HfTiON gate dielectric were fabricated by sputtering method. Pre-deposition fluorine plasma treatment and post-deposition fluorine plasma annealing were used to improve the electrical and reliability properties of Ge p-MOS capacitors. Experimental results showed that both methods could improve the interface quality with lower interface-state density, less frequency dispersion, and also enhance the reliability properties with smaller increases of oxide charge and gate leakage after high-field stressing. Compared with pre-deposition fluorine-plasma treatment, post-deposition fluorine plasma annealing achieved higher quality of high-*k*/Ge interface such as lower interface-state density, higher dielectric constant and lower stress-induced gate leakage current. By XPS and AFM analyses, the improvements should be due to the passivation effects of fluorine on oxygen vacancies, dangling bonds and the dielectric surface.



## 1. Introduction

Germanium is a promising channel material for future CMOS devices due to its high intrinsic electron mobility (2×) and hole mobility (4×) as compared to that of conventional channel material Si. Although Ge is in the same group as Si, its native oxide is unstable and water soluble [1,2]. As a result, high-*k* dielectric materials such as $HfO_2$ [3–5], $ZrO_2$ [6,7], and HfTaON [7] were used as the gate dielectric of Ge MOS devices. Different methods were studied to passivate the Ge surface, e.g. $NH_3$ treatment [8], atomic N surface nitridation [9], $SiH_4$ treatment [10], wet-NO pretreatment [11], $AlN_x$ passivation [12–14] and $TaO_xN_y$ interlayer [7]. Also, it was reported that fluorine was a good passivant for $HfO_2$/$SiO_2$ interface due to formation of strong Hf–F and Si–F bonds [15,16], while Xie et al. [17] used F to anneal the $HfO_2$ in Ge MOS transistors for improved electrical properties.

In this work, high-performance Ge MOS capacitors with a higher-*k* dielectric (HfTiON) were fabricated by sputtering method. Fluorine was incorporated to improve the quality of high-*k*/Ge interface by two methods of pre-deposition pretreatment of Ge surface or post-deposition annealing of the dielectric. Electrical properties and reliability characteristics of Ge MOS capacitors were measured in terms of capacitance–voltage, gate leakage current and their changes under high-field stress. Experimental results showed that F incorporation could improve the electrical characteristics of the capacitors, e.g. less frequency-dependent capacitance dispersion and smaller high-field induced oxide-charge increase. Moreover, compared with the fluorine pretreatment, post-deposition fluorine annealing gave better electrical and reliability properties.

## 2. Experiments

Germanium MOS capacitors were fabricated on (1 0 0) n-type substrate with a resistivity of 0.040–0.047 Ω cm. The wafers were cleaned in organic solvent followed by a rinse in 2% HF and de-ionized water for several times [3]. After $N_2$ blow dry, one sample (Pre-F) received a $CHF_3 + O_2$ plasma pretreatment at 5 °C for 300 s before dielectric deposition. The RF power was 20 W, and the flow rate was 10 sccm for $CHF_3$ and 1 sccm for $O_2$. The $O_2$ was used to remove the carbon and hydrogen. The chamber pressure was 105 mTorr. A thin (~9 nm) HfTiN film was subsequently deposited by reactive co-sputtering of Hf and Ti in an Ar plus $N_2$ ambient. Another sample (Post-F) had the same fluorine plasma treatment after the same HfTiN deposition as that for the Pre-F sample. A control sample without any F plasma treatment was also made. Then, all three samples went through a post-deposition annealing (PDA) in $N_2$ (500 ml/min) at 500 °C for 5 min to convert HfTiN into high-*k* HfTiON [11]. Al was evaporated and patterned as gate electrode with an area of $7.85 \times 10^{-5}$ cm$^{-2}$.

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Finally, a forming-gas anneal was performed at 300 °C for 20 min to achieve better electrical contacts.

High-frequency (1-MHz) capacitance–voltage (*C–V*) characteristics were measured at room temperature using HP4284A precision LCR meter. Capacitance equivalent thickness (*CET*), flat-band voltage ($V_{fb}$), and oxide-charge density ($Q_{ox}$) were extracted from the *C–V* curve. Interface-state density near midgap ($D_{it}$) was extracted by the conductance method [18]. The gate leakage current was measured by HP 4156A precision semiconductor parameter analyzer. High-field stress at 10 MV/cm with the capacitors biased in accumulation by HP 4156A was used to examine device reliability in terms of gate-leakage increase and $V_{fb}$ shift. Atomic force microscope (AFM) was used to measure the surface roughness of the gate dielectrics, while its physical thickness was measured by an ellipsometer. All measurements were carried out under a light-tight and electrically-shielded condition.

## 3. Results and discussion

Fig. 1 shows the high-frequency *C–V* curve for the samples. It is clearly shown that the accumulation capacitance of the Post-F sample is slightly larger than the control sample due to suppressed $GeO_x$ growth during the post-deposition annealing by F incorporation. This is because fluorine with higher electro-negativity than oxygen is a good passivant for defects at the high-*k*/Ge interface, thus suppressing the growth of $GeO_x$ [16]. Moreover, the *C–V* curve of the Post-F sample is steeper than that of the control sample, implying less interface states [18]. However, the accumulation capacitance of the Pre-F sample is smaller than the control sample, which is possibly due to the growth of a $GeO_x$ interfacial layer (IL) in the oxygen plasma ambient. Fig. 2 shows the XPS spectrum for Ge 3d. As compared to the control sample, the two main peaks in the Ge 3d spectrum of the Post-F sample shift to higher energy, resulting in higher binding energy for Ge 3d. Particularly, the peak at 32 eV corresponding to Ge oxide shifts to a higher energy of around 1.8 eV, which is possibly due to the higher electro-negativity of fluorine than that of oxygen. On the other hand, the XPS spectrum is almost the same for the Pre-F sample and the control sample. A possible reason is that the fluorine incorporated by the pre-deposition fluorine plasma treatment is very little due to the growth of a $GeO_x$ IL in the oxygen-containing ambient during the pretreatment. This could be supported by no obvious fluorine detected by the surface XPS scanning for the Pre-F sample, while significant fluorine is observed for the Post-F sample, as depicted in Fig. 3. Fig. 4 shows the O 1s XPS spectrum of the samples. In order

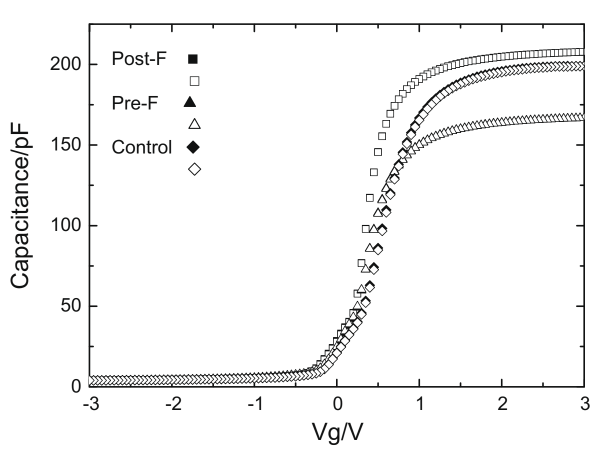


**Fig. 1.** High-frequency (1-MHz) *C–V* curve of the Ge MOS capacitors swept in two directions (solid for depletion to accumulation; open for accumulation to depletion). Area of capacitor = $7.85 \times 10^{-5}$ $cm^{-2}$.

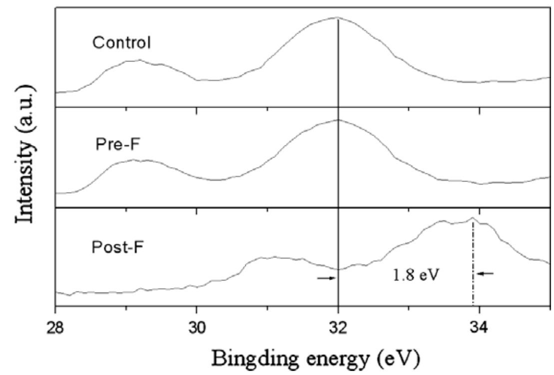


**Fig. 2.** Ge 3d XPS spectrum for the Ge MOS capacitors.

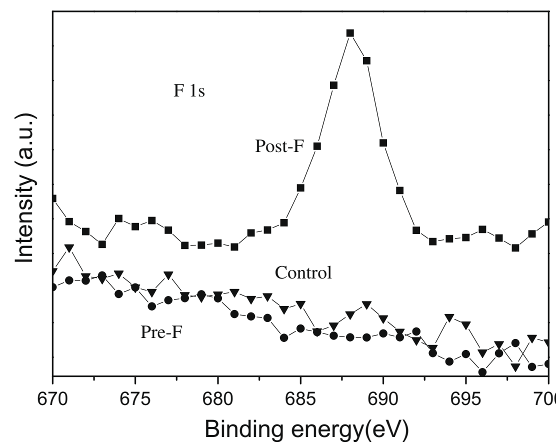


**Fig. 3.** F 1s XPS spectrum for the Ge MOS capacitors.

to get better insight on the bonding structure, the XPS spectrum is decomposed by using Gaussian fitting. It is observed that the predominant peak of the control and Pre-F samples is at 530.6 eV and 531.8 eV, respectively. The peak at 530.6 eV is attributed to the O–Hf or O–Ti bonding, while the peak at 531.8 eV corresponds to the O–Ge bonding. It is very hard to distinguish between O–Hf and O–Ti due to their very similar binding energies (530.4 eV for O–Hf and 530.2 eV for O–Ti). However, the O 1s XPS peaks of the Post-F sample are different from those of the other two samples, especially with three peaks (530.6 eV, 532.2 eV and 533.5 eV). The larger binding-energy shift should be due to the fluorine incorporation, which forms $HfTiO_xN_yF_z$ [19].

The values of gate-dielectric capacitance ($C_{ox}$), capacitance equivalent dielectric thickness (*CET*), flat-band voltage ($V_{fb}$) and oxide-charge density ($Q_{ox}$) extracted from the *C–V* curve in Fig. 1 and the physical thickness of gate dielectrics ($t_{die}$) are listed in Table 1. *CET* is calculated by the two-frequency correction method [20]. The dielectric constant can be calculated by $k_{die} = \varepsilon_{SiO_2} \times t_{die}/CET$, with $\varepsilon_{SiO_2}$ the relative permittivity of $SiO_2$; $t_{die}$ the physical thickness of the dielectric measured by ellipsometry with a mean square error (MSE) within 3–5%. The control sample has the largest negative oxide charges, which possibly result from the broken Hf–O bonds localized at the O atom [16]. After F incorporated in the dielectric, the positive $V_{fb}$ is decreased, indicating reduction of negative charges. This is because fluorine incorporated could bond to the Hf dangling bonds, thus reducing the negative charges. As compared with the Pre-F sample, the Post-F sample has smaller $V_{fb}$, showing better O-vacancy passivation and interface-state reduction. Also, compared with the control sample, the $Q_{ox}$ of the Post-F sample is positive, which should be ascribed to the considerably reduced negative charges after