ZrO₂ Ferroelectric Field-Effect Transistors Enabled by the Switchable Oxygen Vacancy Dipoles

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Abstract
This paper investigates the impacts of post-rapid thermal anneal (RTA) and thickness of ZrO₂ on the polarization \( P \) and electrical characteristics of TaN/ZrO₂/Ge capacitors and FeFETs, respectively. After the RTA ranging from 350 to 500 °C, TaN/ZrO₂/Ge capacitors with 2.5 and 4 nm-thick amorphous ZrO₂ film exhibit the stable \( P \). It is proposed that the ferroelectric behavior originates from the migration of the voltage-driven dipoles formed by the oxygen vacancies and negative charges. FeFETs with 2.5 nm, 4 nm, and 9 nm ZrO₂ demonstrate the decent memory window (MW) with 100 ns program/erase pulses. A 4-nm-thick ZrO₂ FeFET has significantly improved fatigue and retention characteristics compared to devices with 2.5 nm and 9 nm ZrO₂. The retention performance of the ZrO₂ FeFET can be improved with the increase of the RTA temperature. An MW of ~ 0.46 V is extrapolated to be maintained over 10 years for the device with 4 nm ZrO₂.

Keywords: FeFET, ZrO₂, Memory, Germanium, Amorphous

Background
Doped poly-HfO₂ ferroelectric field-effect transistors (FeFETs) have attracted considerable interest in the non-volatile memory (NVM) applications due to their CMOS process compatibility [1]. Although the decent electrical performance has been demonstrated in doped HfO₂-based FeFETs [2], some fundamental limitations still plague their practical applications, including the high thermal budget of 500 °C annealing required to form orthorhombic crystal phases and the undesired leakage current along the grain boundaries with the scaling down of ferroelectric thickness. Ferroelectricity has been widely observed in a variety of different materials, e.g., Sb₂S₃ nanowires [3], GaFeO₃ film [4], LaAlO₃-SrTiO₃ film [5], and amorphous Al₂O₃ containing nanocrystals [6, 7]. Recently, we reported the FeFETs with partially crystallized ZrO₂ gate insulator functioning as NVM and analog synapse [8]. Although the ZrO₂ transistors exhibited decent electrical performance with the thinner thickness compared to the reported doped HfO₂, the underlying mechanism for the ferroelectricity in ZrO₂ film remains unclear. It is critical and important to elucidate the origin of the switchable polarization \( P \) for evaluating the performance limit of ZrO₂ FeFETs.

In this work, TaN/ZrO₂/Ge FeFETs with 2.5 nm, 4 nm, and 9 nm-thick insulators are fabricated. The switchable \( P \) in TaN/ZrO₂/Ge capacitor is proposed to originate from the migration of voltage-driven oxygen vacancies and negative charges. The impacts of ZrO₂ thickness and the post-rapid thermal annealing (RTA) on the \( P \) of TaN/ZrO₂/Ge and the memory window (MW), endurance, and retention characteristics of FeFETs are investigated.

Methods
FeFETs with ZrO₂ gate insulator were fabricated on 4-in. n-Ge(001) substrate using a similar process in [8, 9].
After the pre-gate cleaning in the diluted HF (1:50) solution, Ge wafers were loaded into an atomic layer deposition (ALD) chamber. ZrO$_2$ films with thicknesses of 2.5 nm, 4 nm, and 9 nm were deposited at 250 °C using TDMAZr and H$_2$O as precursors of Zr and O, respectively. A 100-nm-thick TaN gate electrode was deposited by reactive sputtering. After the gate electrode formation, the source/drain (S/D) regions were implanted by BF$_2$ at a dose of $1 \times 10^{15}$ cm$^{-2}$ and an energy of 20 keV. A total of 15 nm nickel (Ni) S/D contacts were formed by a lift-off process. Finally, the RTA at 350, 450, and 500 °C for 30 s was carried out.

Figure 1 a shows the schematic of the fabricated transistor. Figure 1 b–d shows the transmission electron microscope (TEM) images of the TaN/ZrO$_2$/Ge samples with 2.5, 4, and 9 nm-thick ZrO$_2$, respectively. All the samples underwent an RTA at 500 °C for 30 s. The 2.5 nm ZrO$_2$ sample remains an insulator film after the annealing. For the 4 nm sample, although some nanocrystals are observed, ZrO$_2$ maintains to be an amorphous layer. While full crystallization occurs for the 9 nm ZrO$_2$ film. Notably, an interfacial layer (IL) of GeO$_x$ exists between the ZrO$_2$ and Ge channel region, although it is too thin to be observed in the TEM images.

Results and Discussion

Figure 2 shows the $P$ vs. voltage ($V$) curves for the TaN/ZrO$_2$/Ge capacitors with different ZrO$_2$ thicknesses and different annealing temperatures. The solid lines with different colors represent the minor loops with various sweeping voltage range ($V_{\text{range}}$). The measurement frequency is 1 kHz. The 2.5 nm and 4 nm ZrO$_2$ devices can exhibit stable ferroelectricity after an RTA at 350 °C. Figure 3 plots the remnant $P$ ($P_r$) as a function of the sweeping $V$ range curves for the capacitors annealed at various temperatures.

Figure 3 shows the comparison of $P_{\text{max}}$ as a function of $V_{\text{range}}$ for the TaN/ZrO$_2$/Ge capacitors with the different ZrO$_2$ thicknesses and the various RTA temperatures. For the 4 nm ZrO$_2$ devices, as the annealing temperature increases from 350 to 450 °C, a larger $V_{\text{range}}$ is required to obtain a fixed $P_{\text{max}}$. This is attributed to the fact that the higher annealing temperature produces the thicker interfacial layers (ILs) between at Ge/ZrO$_2$ and ZrO$_2$/TaN interfaces, leading to a larger unified capacitance equivalent thickness (CET). For the 2.5 nm ZrO$_2$ capacitors, the sample with 500 °C annealing has a lower $V_{\text{range}}$ than does the 350 °C annealing sample with the same $P_{\text{max}}$. Although the ILs get thicker with the increased RTA temperature, some ZrO$_2$ was consumed by the oxygen scavenging and interdiffusion at the interface. For the very thin ZrO$_2$ device, the latter is dominant. Compared to the 2.5 nm ZrO$_2$ capacitor, a much larger $V_{\text{range}}$ is required to achieve a similar $P_{\text{max}}$. However, the 9 nm ZrO$_2$ capacitor does not exhibit the higher $V_{\text{range}}$ in comparison with the 4 nm device. This is due to the crystal ZrO$_2$ that has a much higher $\kappa$ value than does the amorphous film, which significantly reduces the CET of the 9 nm device.

Figure 4a shows the extracted evolution of the positive and negative $P_r$, denoted by $P_{r+}$ and $P_{r-}$, respectively, for the 4 nm-thick ZrO$_2$ capacitors with RTA at different temperatures over $10^6$ sweeping cycles measured at 1 kHz. The samples underwent an RTA at 500 °C for 30 s.
kHz. Devices annealed at 350 °C and 450 °C exhibit the obvious wake-up effect. No wake up or imprint is observed for the 4 nm ZrO$_2$ ferroelectric capacitor underwent annealing at 500 °C. Figure 4b compares the $P_r$ as a function of sweeping cycles for the devices with the different ZrO$_2$ thicknesses. The 4 nm ZrO$_2$ ferroelectric capacitor achieves improved stability of $P_r$ endurance compared to the 2.5 nm and 9 nm devices during the $10^6$ endurance test.

The switching $P$ is observed in amorphous ZrO$_2$ capacitance, and it is inferred that the mechanism must be different from that of the reported doped poly-HfO$_2$ ferroelectric films. We propose that the underlying mechanism for ferroelectric behavior is related to the oxygen vacancy dipoles. It is well known that, as TaN metal deposited, the Ta oxygen scavenger layers will increase the oxygen vacancy concentration inside ZrO$_2$ [10]. Oxygen vacancies also appear at the ZrO$_2$/Ge interface. Figure 5 shows the schematics of the switchable $P$ in TaN/ZrO$_2$/Ge originating from the migration of oxygen vacancies and negative charges to form the positive and negative dipoles. It is speculated that the negative charges in ZrO$_2$ are related to the Zr vacancy [11], which is similar to those in Al$_2$O$_3$ film [12]. The migration of the voltage-driven oxygen vacancies has been widely demonstrated in resistive random-access memory devices [13, 14]. Notably, this is the first demonstration of three-terminal non-volatile transistors dominated by the voltage-driven oxygen vacancies.

The $P$-$V$ hysteresis enables the ZrO$_2$ FeFETs to obtain a large and stable MW for the embedded NVM (eNVM) applications. Figure 6 shows the measured $I_{DS}$-$V_{GS}$ curves of 2.5, 4, and 9 nm ZrO$_2$ FeFETs for the two polarization states with 1 μs program/erase (P/E) conditions. The transistors were annealed at 500 °C. Program (erase) operation is achieved by applying positive (negative) voltage pulses to the gate of the ZrO$_2$ FeFETs, to raise (lower) its threshold voltage ($V_{TH}$). $V_{TH}$ is defined as $V_{GS}$ at 100 nA·W/L, and MW is defined as the maximum change in $V_{TH}$. All the FeFETs with various ZrO$_2$ thicknesses have the MW above 1 V with 1 μs

Fig. 2 Measured $P$ vs. $V$ characteristics of the TaN/ZrO$_2$/Ge capacitors with different ZrO$_2$ thicknesses and various annealing temperatures.
P/E pulses. To achieve a similar MW, a higher erase voltage is needed for the 9 nm ZrO\(_2\) FeFET compared to the other two transistors. It is seen that a larger magnitude erase \(V_{GS}\) is required to obtain the roughly equal shift of \(I-V\) relative to the initial curve compared to the program \(V_{GS}\). It is speculated that the oxygen vacancies contributing to the \(P\) mainly come from the reaction between TaN and ZrO\(_2\), like the initial state of the device in Fig. 5a. As a positive \(V_{GS}\) (program) is applied, the oxygen vacancies diffuse and accumulate in the layer near the ZrO\(_2\)/Ge interface (Fig. 5b), where the distribution of the oxygen vacancy dipoles is quite different from the initial state. So it is easy to shift the \(I-V\) curve to a

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**Fig. 3** Comparison of \(P_{\text{max}}\) as a function of \(V_{\text{range}}\) for the TaN/ZrO\(_2\)/Ge capacitors with different ZrO\(_2\) thicknesses and various annealing temperatures.

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**Fig. 4**

- **a** \(P_{\text{r}}\) vs. the number of ms-pulse sweeping cycles for 4 nm ZrO\(_2\) capacitors with different RTA temperatures.
- **b** \(P_{\text{r}}\) vs. number of ms-pulse sweeping cycles for the ZrO\(_2\) capacitors after annealing at 500 °C.
higher $|V_{TH}|$ with a positive $V_{GS}$. However, as a negative $V_{GS}$ (erase) is applied, the back diffusion of oxygen vacancies brings the gate stack back to its original state (Fig. 5c). So the magnitude of the negative erase $V_{GS}$ has to be increased to achieve the equivalent shift of $I$-$V$ to the positive program $V_{GS}$.

As the P/E pulse width is reduced to 100 ns, the ZrO$_2$ FeFETs still demonstrate the decent MW, as shown in Fig. 7a. Especially, the transistor with 2.5 nm ZrO$_2$ annealed at 350 °C achieves an MW of 0.28 V. Figure 7b plots MW vs. cycle number for the FeFETs with various ZrO$_2$ thicknesses with 100 ns P/E pulse condition. The 4 nm ZrO$_2$ device achieves a significantly improved endurance performance compared to the 2.5 nm and 9 nm ZrO$_2$ FeFETs, which exhibit the obvious wake-up effect and fatigue within $10^6$ cycles.

Finally, the retention testing of the ZrO$_2$ FeFETs is characterized and shown in Figs. 8 and 9. Figure 8a shows the evolution of $I_{DS}$-$V_{GS}$ curves for the two polarization states of the 4 nm ZrO$_2$ FeFETs underwent RTA at 350, 450, and 500 °C. The charge trapping leads to the reduction of the devices with the time. As shown in Fig. 8b, the retention
performance of the devices can be improved with the increase of the RTA temperature. An MW of ~ 0.46 V is extrapolated to be maintained over 10 years. Figure 9 compares the retention characteristics of the FeFETs with different ZrO$_2$ thicknesses. The 4 nm ZrO$_2$ device has an improved retention performance compared to the transistors with 2.5 and 9 nm thick ZrO$_2$.

**Conclusions**

In summary, amorphous ZrO$_2$ ferroelectric capacitors are experimentally demonstrated, and the ferroelectricity is speculated to be due to the migration of the voltage-driven dipoles formed by the oxygen vacancies and negative charges. FeFETs with 2.5 nm, 4 nm, and 9 nm ZrO$_2$ have the MW above 1 V with 1 $\mu$s P/E pulses. The
improved fatigue and retention characteristics are obtained in the 4 nm-thick ZrO₂ FeFET in comparison with the devices with 2.5 nm and 9 nm ZrO₂. The retention test indicates that the 4 nm ZrO₂ transistor keeps an extrapolated 10-year MW of ~ 0.46 V.

Fig. 9a The evolution of $I_{DS}$-$V_{GS}$ curves for the two polarization states for the 2.5, 4, and 9 nm-thick ZrO₂ FeFETs underwent a RTA at 500 °C. b The 4 nm ZrO₂ device has an improved retention performance compared to the transistors with 2.5 and 9 nm-thick ZrO₂.

Authors’ Contributions
HL and YP carried out the experiments and drafted the manuscript. GQH and YL supported the study and helped to revise the manuscript. NZ and CGD helped to do the polarization measurement. YH provided constructive advice in the drafting. All the authors read and approved the final manuscript.

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Availability of Data and Materials
The datasets supporting the conclusions of this article are included in the article.

Competing Interests
The authors declare that they have no competing interests.

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