Impact of Chamber/Annealing Temperature on the Endurance Characteristic of Zr:HfO$_2$ Ferroelectric Capacitor

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Abstract: The endurance characteristic of Zr-doped HfO$_2$ (HZO)-based metal–ferroelectric–metal (MFM) capacitors fabricated under various deposition/annealing temperatures in the atomic layer deposition (ALD) process was investigated. The chamber temperature in the ALD process was set to 120 $^\circ$C, 200 $^\circ$C, or 250 $^\circ$C, and the annealing temperature was set to 400 $^\circ$C, 500 $^\circ$C, 600 $^\circ$C, or 700 $^\circ$C. For the given annealing temperature of 700 $^\circ$C, the remnant polarization ($P_r$) was 17.21 $\mu$C/cm$^2$, 26.37 $\mu$C/cm$^2$, and 31.8 $\mu$C/cm$^2$ at the chamber temperatures of 120 $^\circ$C, 200 $^\circ$C, and 250 $^\circ$C, respectively. For the given/identical annealing temperature, the largest remnant polarization ($P_r$) was achieved when using the chamber temperature of 250 $^\circ$C. At a higher annealing temperature, the grain size in the HZO layer became smaller, and thereby, it enables to boost up $P_r$. It was observed that the endurance characteristics for the capacitors fabricated under various annealing/chamber temperatures were quite different. The different endurance characteristics are due to the oxygen and oxygen vacancies in ferroelectric films, which affects the wake-up/fatigue behaviors. However, in common, all the capacitors showed no breakdown for an externally applied pulse (up to $10^8$ cycles of the pulse).

Keywords: ferroelectric capacitor; hafnium zirconium oxide; chamber temperature; polarization; endurance

1. Introduction

Ferroelectric materials have been widely used/adopted for various types of sensors and devices. Among various ferroelectric materials, HfO$_2$-based ferroelectric devices have attracted great interest [1]. A HfO$_2$-based ferroelectric film with fluorite structure solved the drawbacks in the conventional perovskite–structure ferroelectrics. They have extraordinary compatibility with complementary metal-oxide semiconductors (CMOS) and excellent ferroelectricity at ultra-thin (<10 nm) thickness [2,3]. The ferroelectric properties of HfO$_2$-based film originated from the non-centrosymmetric orthorhombic phase (o-phase), and the stabilization of the o-phase enhances the ferroelectric behavior [4]. The ferroelectric phase can be stabilized through annealing, and it can be characterized differently by various factors, such as dopant, thickness of ferroelectric film, and deposition temperature [5,6].

Various dopants with HfO$_2$ have been studied, and among them, zirconium (Zr) was chosen as the most promising material for memory and logic devices [6,7]. Unlike other dopants remaining stable at much lower concentration, Zr dopants can be stable with the
same percentage as Hf in HZO film. Moreover, ferroelectric properties using Zr dopants can be obtained in much lower annealing temperature ($T_A$) than other dopants.

As a memory device, the ferroelectric films require good endurance properties. The main factor affecting the endurance is the oxygen vacancy ($V_O$) in ferroelectric films. During the electric field cycling, $V_O$ is redistributed, which results in the uniform distribution of $V_O$ in the bulk region of the ferroelectric layer [8]. This phenomenon increases the $P_r$ value by decreasing the built-in field and then decreases the $P_r$ value with additional cycling. This increase in $P_r$ is called the “wake-up effect” and the decrease in $P_r$ is called the “fatigue effect” [9,10]. The breakdown of the films is observed when $V_O$ forms a filament, which results as a leakage path. Therefore, it is very important to control the amount of $V_O$ for the reliability of memory devices.

The characteristics of ferroelectric films can vary through various methods such as adjusting the doping effect and the chamber temperature during ALD [11,12]. Adjusting the temperature of the chamber during ALD changes the deposition rate and the average grain size of the film [6,13]. These factors change the distribution of $V_O$, which can significantly affect the ferroelectricity and the endurance properties. However, studies on the relationship of the effects of chamber temperature and the endurance performance are still lacking.

In this study, the ferroelectric properties of TiN/HZO/TiN capacitors with different chamber temperatures were investigated. The electrical characteristics of each capacitor were analyzed through polarization–voltage (P-V) curves and leakage current–voltage (I-V) curves. Moreover, the endurance performance related to the amount of $V_O$ was investigated under different chamber temperatures.

2. Fabrication

The illustrated cross-sectional view and fabrication flow of TiN/HZO/TiN capacitors are shown in Figure 1a,b, respectively. First, a p$^+$-doped silicon wafer was cleaned by a SPM cleaning, which was followed by the conventional RCA method (i.e., SC-1 cleaning and SC-2 cleaning). Then, the 50 nm-thick TiN bottom electrode was deposited on the Si substrate by using DC sputtering. The 10 nm-thick HZO thin film was deposited by thermal atomic layer deposition (ALD). The tetrakis (ethylmethylamino) hafnium (TEMAH), tetrakis (ethylmethylamino) zirconium (TEMAZ), and $H_2O$ source precursor were used for the ALD process to deposit the HZO film. The Hf and Zr was deposited using an ALD supercycle [14]. The aforementioned fabrication was identically completed but at three different chamber temperatures ($T_{CH}$) of 120 $^\circ$C, 200 $^\circ$C, and 250 $^\circ$C. As shown in Figure 1c, the growth per (super)cycle of HZO film decreased as the chamber temperature ($T_{CH}$) increased. The total number of supercycles to make 10 nm-thick HZO thin film was set to 56, 61, and 68 for $T_{CH}$ of 120 $^\circ$C, 200 $^\circ$C, and 250 $^\circ$C, respectively. The 50 nm-thick TiN top electrode on the HZO layer was deposited using the DC sputtering used for bottom electrodes. Then, the HZO capacitors were patterned to have the electrode area of 6400 $\mu$m$^2$.

Finally, the post-metallization annealing (PMA) was completed by rapid thermal annealing (RTA) at 400, 500, 600, and 700 $^\circ$C for 30 s in N$_2$ atmosphere to crystallize the HZO films.

To investigate the electrical characteristics of HZO capacitors, P-V curves and I-V curves were measured using semiconductor parameter analyzer (Keithley 4200-SCS). The X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and energy-dispersive X-ray spectroscopy (EDS) were used to characterize the HZO capacitor.
was physically originated from a few reasons, as follows: (1) The number of supercycles which is due primarily to the decreasing contribution of surface exchange reaction [13].

This is mainly because the ratio of o-phase in the HZO layer was increased at the higher temperature, which is due primarily to the decreasing contribution of surface exchange reaction [13]. Note that the growth per cycle is decreased with increasing the chamber temperature, which is due primarily to the decreasing contribution of surface exchange reaction [13].

3. Results and Discussion

3.1. Electrical Characteristics

Figure 2a–c show the measured P-V curves of the TiN/HZO/TiN capacitors with a few annealing temperatures (i.e., 400, 500, 600, and 700 °C) at $T_{CH}$ of 120 °C, 200 °C, and 250 °C, respectively. The measured $P_r$ was increased at a higher $T_A$ for all the capacitors. This is physically originated from a few reasons, as follows: (1) The number of supercycles increases at a higher $T_{CH}$ because the deposition rate of HZO film is decreased at a higher $T_{CH}$ (see Figure 1c). This leads to increasing the number of HfO$_2$/ZrO$_2$ nanolaminates, resulting in the improved $P_r$ [15]. (2) The average grain size of HZO film becomes smaller at a higher deposition temperature, if H$_2$O is used as the oxygen source in ALD [13]. The smaller average grain size enables us to boost up the ferroelectric polarization [10,16]. This is primarily originated from the tetragonal phase (t-phase) and the orthorhombic phase (o-phase), which are easily stabilized in smaller grain regions. (3) Because defects (noted as $V_O$) are likely to be accumulated along the grain boundaries, the smaller grain size is likely to build more grain boundaries for a given volume. This would distort the distribution of $V_O$. Herein, it is noteworthy that the well-balanced distribution of $V_O$ in HZO films should help stabilize the ferroelectric phase, and thereby, the ferroelectric polarization would be enhanced [10,17].

In Figure 2d, the leakage current of TiN/HZO/TiN capacitors fabricated at different $T_A$ and $T_{CH}$ was measured. It turned out that for a given $T_{CH}$ ($T_A$), the leakage current increases at a higher $T_A$ ($T_{CH}$). In the MFM ferroelectric capacitor, the leakage current is mostly originated from $V_O$ (i.e., the higher $V_O$ is, the more the leakage current flows [15]). In Section 3.2, with TEM, XPS, and EDS data, it is investigated how $V_O$ is varied at different $T_{CH}$.
thereby, the V$_O$ in HZO film is increased [17]. Hence, the increased V$_O$ means that the oxygen (and therefore, indicating the presence of vacancies). The peak describes the bonds such as Hf-O and Zr-O, of which the binding energy is located in 532 eV. The sub-oxide peak indicates oxygen in a lattice, which does not contain its full complement of oxygen (i.e., lattice oxygen peak and sub-oxide peak). The lattice oxygen peak describes the bonds such as such as oxygen interstitial and oxygen vacancy (V$_O$), of which the binding energy locates at $\approx$534 eV.

3.2. XPS, TEM, and EDS

Figure 3 shows the XPS depth profile of the TiN/HZO/TiN capacitor at $T_A$ of 700 °C under three different $T_{CH}$ values. The atomic percent clearly reveals the TiN/HZO/TiN device structure. Among many atoms in the profile, the O 1s in the HZO layer is deconvoluted to figure out the oxygen bonds in great detail (see Figure 4). Notice that the intensities of each net peak were normalized to the same scale. The O 1s was divided into two peaks (i.e., lattice oxygen peak and sub-oxide peak). The lattice oxygen peak describes the bonds such as Hf-O and Zr-O, of which the binding energy is located in $\approx$532 eV. The sub-oxide peak indicates oxygen in a lattice, which does not contain its full complement of oxygen (and therefore, indicating the presence of vacancies). The peak describes the bonds such as oxygen interstitial and oxygen vacancy (V$_O$), of which the binding energy locates at $\approx$534 eV.

Figure 2. Measured polarization vs. electric field of TiN/HZO/TiN capacitor in which the HZO layer was deposited at the chamber temperature of (a) 120 °C, (b) 200 °C, and (c) 250 °C. Note that four different annealing temperatures ($T_A = 400$–$700$ °C) were used for better implementing the ferroelectric characteristics of the HZO layer. (d) Measured leakage current-vs.-annealing temperature for three different chamber temperatures. Note that the leakage current was measured with the voltage of $-3$ V across the ferroelectric capacitor.

Figure 3. Measured XPS depth profiles of TiN (50 nm)/HZO (10 nm)/TiN (50nm) capacitor, which was fabricated at three different chamber temperatures: (a) 120 °C, (b) 200 °C, and (c) 250 °C.
The amount of O 1s in Figures 3 and 4a confirms that there was a difference in the ratio of O 1s in HZO film, depending on three different T_{CH}. The intensity of peak amplitude is decreased at a higher T_{CH}. In addition, the atomic percent of Ti and N is decreased at a lower T_{CH} (see Figure 3). In other words, the formation of the dead layer (i.e., TiO_{2} and TiON) between the HZO layer and the TiN electrode was suppressed at a lower T_{CH}, which reduces the amount of V_{O} in the HZO layer. It was confirmed that the ratio of V_{O} increases if the dead layer between the HZO layer and the TiN electrode is formed [18].

It was observed that the percentage of sub-oxide bonding is increased at a higher T_{CH} (see Figure 4a). This also indicates that the ratio of V_{O} increases. In other words, the oxygen should move from the HZO layer to the electrodes to make the interfacial layer, and thereby, the V_{O} in HZO film is increased [17]. Hence, the increased V_{O} means that the larger amount of oxygen has moved toward the interfacial layer. In addition, in the XPS for Hf 4f spectra, it was confirmed that the sub-oxide means the oxygen vacancy in the HZO layer [19]. As shown in Figure 4b, it was observed that the ratio of sub-oxide in Hf 4f spectra is increased when T_{CH} is increased, which leads to a higher V_{O}. In summary, the ratio of oxygen in the HZO layer becomes smaller at a higher T_{CH}, which is closely associate with the amount of V_{O}. A higher T_{CH} would make the ratio of V_{O} higher. This is well agreed to the increase in leakage current at a higher T_{CH} because of the increased V_{O} (see Figure 2d).

Figure 5a–c show the TEM image of TiN/HZO/TiN capacitors fabricated at three different chamber temperatures (T_{CH}) with T_{A} of 500 °C. It was observed that the thicknesses of the HZO films were all the same: 10 nm. Figure 5d shows the EDS image of the TiN/HZO/TiN capacitor fabricated with T_{A} of 700 °C. The ratio of elements in each layer can be determined through the EDS analysis (see Table 1). For example, the largest (smallest) atomic rate of oxygen in HZO films was implemented with T_{CH} of 120 °C (250 °C), which was consistent with the XPS analysis. The amount of oxygen vacancy (V_{O}) was increased, as the oxygen was decreased with increasing T_{CH}. However, the discrepancy of the ratio of elements exists between the XPS and EDS analysis. Note that the purpose of the EDS analysis in this work was to confirm/verify the change of oxygen atoms.
Figure 5. The transmission electron microscopy (TEM) image of the TiN/HZO/TiN capacitor, which was fabricated at three different chamber temperatures: (a) 120 °C, (b) 200 °C, and (c) 250 °C. (d) The energy-dispersive spectroscopy (EDS) images for titanium, hafnium, zirconium, and oxygen in the HZO capacitor at the chamber temperature of 250 °C.

Table 1. Energy-dispersive spectrometer (EDS) quantification of elements in HZO layer.

| Chamber Temperature (T_{CH}) (°C) | Atomic Percent (%) |
|----------------------------------|--------------------|
|                                  | Ti  | N   | Hf  | Zr  | O   | Si  |
| 120                              | 4.50| 9.76| 20.90| 18.16| 30.44| 16.24|
| 200                              | 9.20| 4.49| 24.95| 21.00| 23.32| 17.03|
| 250                              | 10.74| 10.80| 24.75| 21.18| 19.38| 13.15|

3.3. Endurance

The endurance (especially, affected by an electric field cycling) in TiN/HZO/TiN capacitors was investigated. Figure 6 shows the pulsing scheme for evaluating the endurance of the capacitors. The electric field cycling was completed with using a trapezoidal pulse, and the number of cycling was applied up to $10^8$. After the cycling pulses were applied, a triangular pulse was applied to measure the P-V characteristic of the capacitor. Note that both pulses have the same peak amplitude of 3 V. The P-V characteristic of each capacitor was compared to each other (see Figure 7).

Figure 6. Illustrated pulsing scheme for analyzing the wake-up and fatigue behaviors of TiN/HZO/TiN capacitor. The cycling was first completed using the trapezoidal pulse with the ramp time (T_{ramp}) of 1 µs and the hold time (T_{hold}) of 1 µs. Afterwards, the P-V measurement was made using the triangular pulse. Note that the amplitude for both pulses is set to 3 V.
The remnant polarization ($P_r$) of each HZO capacitor in pristine state is as follows: In case of $T_{CH}$ of 120 °C, $P_r$ of 0.28 µC/cm$^2$, 1.17 µC/cm$^2$, 2.68 µC/cm$^2$, and 17.21 µC/cm$^2$ was observed for $T_A$ of 400 °C, 500 °C, 600 °C, and 700 °C, respectively. In case of $T_{CH}$ of 200 °C, $P_r$ of 5.66 µC/cm$^2$, 6.88 µC/cm$^2$, 13.43 µC/cm$^2$, and 26.37 µC/cm$^2$ was observed for $T_A$ of 400 °C, 500 °C, 600 °C, and 700 °C, respectively. Finally, in case of $T_{CH}$ of 250 °C, $P_r$ of 16.38 µC/cm$^2$, 20.46 µC/cm$^2$, 25.3 µC/cm$^2$, and 31.8 µC/cm$^2$ was observed for $T_A$ of 400 °C, 500 °C, 600 °C, and 700 °C, respectively. Regardless of $T_{CH}$, it turned out that $P_r$ was increased with increasing $T_A$. For a given/identical $T_A$, $P_r$ can be improved with

![Figure 7. Measured polarization vs. electric field (PE) characteristics of TiN/HZO/TiN capacitors fabricated at various chamber temperatures (i.e., 120 °C, 200 °C, and 250 °C) as well as at various annealing temperatures ($T_A$): (a) 400 °C, (b) 500 °C, (c) 600 °C, and (d) 700 °C. Note that the different numbers of cycles were used to explore the endurance characteristics of the ferroelectric capacitor.](image-url)
higher $T_{CH}$. This is primarily because the amount of ferroelectric phase was increased with increasing either $T_A$ or $T_{CH}$ [2,9].

As shown in Figure 8, all the capacitors did not show any breakdown up to $10^8$ cycles. However, depending on $T_{CH}$, the number of cycles at which the fatigue begins (i.e., $P_r$ is about to decrease) is varied. Regardless of $T_{CH}$, higher $P_r$ was observed with higher $T_A$. This is primarily originated from a well-distributed $V_O$ in bulk region of HZO film at a higher $T_A$ [10].

![Figure 8](image)

**Figure 8.** Measured representative ferroelectric characteristics (i.e., remnant polarization ($2P_r$) and/or coercive electric field ($2E_c$)) versus cycles, for given three different chamber temperatures, (a,d) $120^\circ C$, (b,e) $200^\circ C$, and (c,f) $250^\circ C$ with four different annealing temperatures ($T_A$ from $400^\circ C$ to $700^\circ C$). The yellow–colored circle indicates the max point of $2P_r$.

It is known that the ferroelectric characteristics (notably, represented by $P_r$) can be improved as the number of cycles increases (a.k.a., wake-up effect). However, the ferroelectric characteristics should not be ever enhanced because of fatigue. The maximum value of $2P_r$ and the number of cycles at which fatigue begins (a.k.a. critical number of cycles) are summarized in Figure 9. It turned out that the value of $2P_r$ increases with increasing $T_A$. (However, only for $T_{CH}$ of $120^\circ C$, $T_A$ of $400^\circ C$ shows insufficient ferroelectricity, which results in a low $2P_r$.) Compared to the other $T_{CH}$ of $200^\circ C$ and $250^\circ C$, the measured $P_r$ was significantly degraded for $T_{CH}$ of $120^\circ C$. When H$_2$O reactant is used as an oxygen source in ALD, the lowest $T_{CH}$ (i.e., $120^\circ C$) forms the largest average grain size. This causes more formation of monoclinic phase (m-phase), which is non-ferroelectric phase, and it makes the depolarization field stronger [20,21]. Therefore, for $T_{CH}$ of $120^\circ C$, the sudden decrease in $P_r$ in the HZO capacitor was understood with less m-phase.

![Figure 9](image)

**Figure 9.** (a) Maximum remnant polarization ($2P_r$) and (b) critical number of cycles at which fatigue begins for given three different chamber temperatures, $120^\circ C$, $200^\circ C$, and $250^\circ C$, with four different annealing temperatures ($T_A$ from $400^\circ C$ to $700^\circ C$).
In Figure 9, it was also observed that the critical number of cycles (i.e., the number of cycles at which fatigue begins) decreases at a higher $T_{CH}$ for the same $T_A$. As shown in Figures 2d and 4, more $V_O$ in the ferroelectric layer was observed at a higher $T_{CH}$, and thereby, so is the leakage current in HZO capacitor (this is because the excessive amount of $V_O$ makes undesirable conducting paths in the HZO film [10,22]). The more $V_O$ in the ferroelectric film should cause the ferroelectricity of the film to be fatigued at a rapid pace.

4. Conclusions

In this work, the impact of chamber/annealing temperatures in the atomic layer deposition (ALD) process on the ferroelectric property of the HZO layer in a TiN/HZO/TiN capacitor was investigated. Regardless of the chamber temperature ($T_{CH}$), a higher remnant polarization ($P_r$) was achieved with a higher annealing temperature ($T_A$). For a given $T_A$, $P_r$ was increased with increasing $T_{CH}$. This ferroelectricity was well retained up to the cycles of $10^8$. However, the capacitors fabricated under the three different $T_{CH}$ showed different endurance performances in terms of the critical number of cycles. This is due primarily to the oxygen and oxygen vacancies in the HZO layer (which was quantitatively analyzed and confirmed by XPS and EDS analysis). The more oxygen vacancies ($V_O$) at a higher $T_{CH}$ enabled for $P_r$ to be improved, but they made an undesirable conducting path in the HZO film, resulting in decreasing the critical number of cycles.

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