Interfacial engineering of ZrO$_2$ metal-insulator-metal capacitor using Al$_2$O$_3$/TiO$_2$ buffer layer for improved leakage properties

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ABSTRACT
The continuous scale-down of dynamic random-access memory (DRAM) requires shrinkage of high aspect ratio metal-insulator-metal (MIM) capacitance along with the successful suppression of its leakage current to maintain desired levels of charge storage and retention. As the dimensions of stacked insulating dielectric and metal electrodes in the MIM capacitor are currently <10 nm, interfacial mixing has a large impact on the reliability of the capacitor. This is because defects and secondary interface oxides significantly alter the physicochemical properties of MIM capacitors. The methodology required to characterize ultrathin interfaces in relation to the performance of MIM devices is highly challenging due to its physical and chemical complexities of interface between dielectric and electrode. In this study, a ZrO$_2$-based dielectric film and its interface (with an ultrathin TiO$_2$/Al$_2$O$_3$ buffer layer) are analyzed using angle-resolved X-ray photoelectron spectroscopy (ARXPS), spectroscopic ellipsometry (SE), and temperature dependent I-V analysis for a DRAM MIM capacitor. The composite dielectric layer included either Al$_2$O$_3$ on the bottom or Al$_2$O$_3$/TiO$_2$ between the TiN electrode and ZrO$_2$. This study suggests an effective metrology approach to characterize ultrathin MIM capacitors and the important role of interfacial stabilization using a buffer layer for the effective control of leakage current.

1. Introduction
With the development of the Internet of Things (IoT) and artificial intelligence (AI) technologies, dynamic random-access memory (DRAM) technology has become essential [1–3]. As advanced technology evolves, the amount of information grows exponentially, demanding a reduction in the size of memory charge storage metal-insulator-metal (MIM) cells, and also to improve DRAM performance [4,5]. However, the leakage current in MIM cells increases due to charge tunneling through reduced physical dielectric thickness, trending toward an equivalent oxide thickness of 5 Å [6–8]. This causes the deterioration of charge retention, thus adversely affecting DRAM reliability.

To address this critical issue, a material with a high dielectric constant (k) must be used; many studies have been conducted on electrodes coupled with dielectric film in MIM [9–12]. A promising solution comes in the form of various high-k metal oxides, such as HfO$_2$, ZrO$_2$, La$_2$O$_3$, and Al$_2$O$_3$, that have been investigated as potential candidates for MIM use in recent decades [13–25]. Of these, ZrO$_2$ has received significant interest due to its high bandgap energy, thermal stability, and high permittivity. ZrO$_2$ has three crystal phases with different dielectric constants; the monoclinic phase has a dielectric constant of 17, while the cubic and tetragonal phases have dielectric constants of 37 and 47, respectively [26–31]. Within an MIM capacitor, TiN is often used as an electrode, but this decreases the thickness of the thin dielectric film; the issue of the mixing layer between ZrO$_2$ and TiN is too severe to ignore. TiON, which is formed naturally during ZrO$_2$ deposition, can produce a mixed interfacial complex oxide with ZrO$_2$ that inherently has an interface-induced deep trap level in the ZrO$_2$ dielectric. This is a serious problem as it negatively affects MIM capacitor cells; the volume of the metal/dielectric interface rapidly increases to thicknesses >50% in the scaled-down MIM cell stack, where defects are concentrated around the interface to significantly affect the leakage properties [32–35]. Although there have been many studies that sought to identify the physicochemical properties of the interfacial oxide and their associated defects, the majority of these studies are either indirect electrical characterizations or morphological analyses of limited locations using transmission electron microscopy (TEM). TEM cannot reveal fundamental information regarding defects at the interface and dielectric layers.

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In this study, we report the suppressed leakage current by using double interfacial layers of TiO$_2$ and Al$_2$O$_3$ at the interface of a ZrO$_2$-based MIM capacitor. Initially, Al$_2$O$_3$ was inserted into the TiN and ZrO$_2$ dielectric interface, which showed that it works as an oxygen diffusion-blocking layer by reducing the diffusion of oxygen from ZrO$_2$ toward the TiN electrode, thereby suppressing the formation of secondary interfacial oxides \[36,37\]. Since the materials for this oxygen diffusion-blocking layer for MIM capacitors must have suitable bandgap energy, a high dielectric constant, high thermal stability, and oxygen scavenging ability, Al$_2$O$_3$ is one of the most suitable choices \[38-41\]. However, there is a lattice mismatch between ZrO$_2$ molecules with eightfold oxygen coordination, amorphous Al$_2$O$_3$ with fourfold oxygen coordination, and ionicity difference \[42\]. Such differences in the average bond number per atom and ionicity have been suggested as scaling factors for the density of the interfacial bi-phase oxide bonding defect \[43\]. Interfacial oxide formation is also related to TiON formation at the upper surface of the TiN electrode due to oxidation during the dielectric deposition process; this TiON layer is typically considered to have a negative impact on the MIM capacitor’s reliability \[44,45\].

An additional ALD-grown TiO$_2$ layer was added between Al$_2$O$_3$ and TiN to improve the reliability of the MIM capacitor. Research indicates that this TiO$_2$ layer can suppress TiON formation and block O-diffusion from Al$_2$O$_3$ to TiN \[46\]. It was confirmed that TiON formation and O-diffusion from Al$_2$O$_3$ were both clearly suppressed with the TiO$_2$ interlayer by ARXPS analysis associated with chemical bonding state according to dielectric’s depth \[47\]. This also positively affects the ZrO$_2$ layer, because O-rich Al$_2$O$_3$ that is free of O-diffusion toward the TiN electrode eliminates O-diffusion from ZrO$_2$ toward Al$_2$O$_3$; the TiO$_2$ interlayer promotes chemical stability throughout the MIM stack \[48,49\]. Similarly, from the identified spectroscopic ellipsometry (SE) and 3-phase optical modeling used for the ZrO$_2$/Al$_2$O$_3$/TiN stack, interfacial defect states are significantly reduced and bandgap energy increased, suggesting a higher degree of ZrO$_2$ crystallinity \[50\]. In conjunction with SE data, we evaluated the I-V characteristics and improved the leakage current level with TiO$_2$ use \[51\]. Finally, we propose a carrier injection mechanism in the MIM stack to elucidate the behavior of trap defects in MIM capacitors with high-k dielectric films, which promises reliable control in DRAM charge-storage MIM capacitors.

2. Experimental

2.1. Atomic layer deposition of ZrO$_2$, Al$_2$O$_3$, and TiO$_2$ films

ZrO$_2$, Al$_2$O$_3$, and TiO$_2$ films were deposited using cyclopentadienyltris(dimethylamido)zirconium (IV) (CTDMAZ), trimethylaluminum (TMA), and titanium tetrachloride (TiCl$_4$) as the precursors, and 150 g/m$^3$ of O$_2$ from the ozone generator as the oxidant, using a cold-wall-type atomic layer deposition (ALD) reactor; N$_2$ was used as the precursor carrier and purging gas in the ALD system. The zirconium, aluminum, titanium precursors were injected into the reactor with N$_2$ carrier gas flowing through a bubbler to provide adequate vapor pressure. The gas lines connecting the bubbler and reactor chamber were heated to maintain a temperature of 90°C to avoid vapor condensation of the precursors. The pressure was maintained at 133 Pa throughout the process, and the temperature at deposition was maintained at 300°C. Precursors and reactant injection time were controlled from 1 to 15 s to optimize the ALD process. The purge time was fixed at 20 s. Thin films were annealed after deposition at 500°C with N$_2$ gas for 1 h to enhance crystallinity.

2.2. Interface analysis of deposited films

The ARXPS method was used to analyze the chemical state and interface characteristics of the thin, layered structure of 10 nm or less. This method is a representative method for nondestructive analysis and can analyze the chemical state at various locations while changing the angle of samples. Angle-resolved XPS measurements were performed with FC-XP10, Nexsa (Thermo Fisher Scientific, Waltham, MA, USA), using Al Ka X-ray as a source. A source with a line width of 0.85 eV, a spot size of 400 μm, and a step size of 0.1 eV was used. Casa XPS was used to analyze the obtained XPS data. The XPS peak positions were normalized with the standard C 1s peak related to the C–C bond (~284.5 eV). In angle resolved XPS (ARXPS), the electrons are captured at different angles, which allows for the detection of electrons at different depths. In fact, ARXPS can provide information on the thickness and composition of ultra-thin films without causing damage to the film. By analysis of the peak intensity and mean free path of electrons emitted from layers, a model was used to calculate the thickness. According to the theory behind ARXPS, each element has a different inelastic mean free path (IMFP), which is denoted by lambda ($\lambda$). In ARXPS depth analysis, it is theoretically possible to analyze electrons at a depth of approximately $3\,\lambda$. For accurate analysis, we estimated the maximum depth of Ti and Zr using a software called IMFPWIN; the analysis was thus possible up to approximately $3\,\lambda$ (~10 nm).

2.3. Spectroscopic ellipsometry analysis

The shifts in the electrical bandgap and interfacial defect states were measured using rotating analyzer enhanced spectroscopic ellipsometry (SE) (VASE model; J.A. Woollam Co.). The photon energy of
incident monochromatic light generated by a xenon lamp was swept from 1.5 to 6 eV at an incidence angle of 67.08°. The optical parameters or pseudo-dielectric functions obtained from the SE measurement were used as the input data for 3-phase (i.e. air/thin film/substrate) optical modeling [52]. In this 3-phase optical modeling, the pseudo-dielectric function for the clean TiN/SiO$_2$/Si sample was used as the substrate layer (i.e. the 1st layer), and the dielectric function of the overlayer, consisting of the interface and dielectric layer (i.e. the 2nd layer) was extracted either from the measured data of the sample or from ZrO$_2$ dielectrics with the buffer layer (Al$_2$O$_3$ and TiO$_2$) using the iteration method to find the exact optical Hamiltonian (n and k). Compared to the conventional oscillator fitting method, this yields a true dielectric function of the overlayer in both the strong absorption range (i.e. photon energy > bandgap) and the semi-transparent range (i.e. photon energy < bandgap). Therefore, this is the only suitable approach to identify the real sub-band defect states both at the interface and dielectrics with low optical absorption using SE. In fact, the overlayer is chemically complex, with a main ZrO$_2$ layer along with additional TiO$_2$, Al$_2$O$_3$, and TiON buffer layers. However, these layers are all mixed with each other in a significant portion of the MIM stack; therefore, it is acceptable to consider a single layer when drawing a relative comparison between the same type of sample sets.

2.4. Electrical property analysis of deposited films

To analyze the electrical properties of the dielectric film, current-voltage (I–V) measurements were conducted using a Keithley 4200. The results revealed in-depth charge transport-like effects on the dielectric film and insertion of Al$_2$O$_3$ and TiO$_2$ at the interface. Based on the observed I–V characteristics, direct tunneling, trap-assisted tunneling (TAT), Fowler-Nordheim tunneling (FN tunneling), and Poole-Frenkel emission (PF emission) were confirmed as the conduction mechanisms at different voltage ranges. To avoid any role of the environmental conditions, the electric measurements were performed with low humidity, under dark, and at similar temperature of 293 K.

3. Result and discussion

3.1. Device geometry

Samples R1 and R2 represent reference samples in which the dielectric layer(s) (Al$_2$O$_3$ and/or TiO$_2$) are not deposited. The R1 sample had a TiN/SiO$_2$/Si structure, and the R2 sample had a TiO$_2$/TiN/SiO$_2$/Si structure, as shown in Figure S1 (Supporting Information). In addition, sample S1 has a basic geometry of an MIM capacitor with a TiN electrode and a ZrO$_2$ layered structure, whereas the S2 sample has an Al$_2$O$_3$ interlayer between the TiN and ZrO$_2$ films. Further, in sample S3, a TiO$_2$ layer was deposited on the TiN electrode using ALD, and Al$_2$O$_3$ and ZrO$_2$ were then sequentially deposited (see Figure 1).

3.2. ARXPS results

A Lorentzian/Gaussian curve was used as the line shape to fit the raw data, and correction was performed by shifting the data with respect to the 1s peak at 284.5 eV [53,54]. Initially, to examine the effect of the ultra-thin TiO$_2$ layer (~7 Å), a comparison of the reference sample (i.e. ZrO$_2$/TiN) without the TiO$_2$ and/or Al$_2$O$_3$ layer was done. In a sample with a dielectric (ZrO$_2$) film, it was difficult to accurately analyze Ti 2p electrons because of the strong influence of interference. The ARXPS data of the reference samples that do not contain a dielectric (ZrO$_2$) film are shown in Figure 2(a,b). Fitting was conducted by referring to previous data of TiO$_2$ 2p$_{3/2}$ peaks. The peak at 458.2 corresponds to the TiO$_2$ formation, whereas the peaks at 456.9 eV and 454.8 eV can be attributed to the presence of TION formation and due to underneath TiN, respectively [55]. Figure 2(a,b) shows that the relative intensity of TiO$_2$ increases, when the R2 sample is deposited with TiO$_2$. In the case of deposited TiO$_2$ (i.e. R2 sample), it was clearly confirmed that the intensity and area of the TiO$_2$ peak increased, which was due to the deposition of interfacial TiO$_2$ (~7 Å). To understand this further, the peak intensities corresponding to TiO$_2$, TION, and TiN phase as a function of depth for the S1, S2, and S3 samples are plotted in Figure 2(c–e), respectively. It is evident from Figures 2(c–e) that there is no significant difference in the intensity between the

![Figure 1](image-url). (a) Device schematics of ZrO$_2$/TiN device (named S1), (b) with in insertion of interfacial (Al$_2$O$_3$) layer between ZrO$_2$ and TiN (named S2), and (c) structure schematic with both Al$_2$O$_3$ and TiO$_2$ layer (named S3).
three samples at 0° and 20°. This is because the analysis at low angle provides information from the TiN region, which is below the dielectric layers [56]. However, a significant difference was observed for measurements performed at 40°. In the case of S1 sample, the appropriate TiO₂ intensity was confirmed at the TiN/ZrO₂ interface; the relative intensity of TiO₂ decreased for sample S2, which is due to the influence of Al₂O₃. On the other hand, sample S3 clearly confirmed that the TiO₂ intensity was the highest, and it was possible to confirm that TiO₂ (~7 Å) had a significant effect. Furthermore, at higher angles, such as 60° and 80°, the analysis of Ti 2p electrons was impossible owing to the influence of dielectric film interference. Relatively high intensity for TiO₂ peak in S3 sample is due to the TiO₂ thin layer deposited by ALD.

Moreover, XPS analysis of the Zr 3d fitting is depicted in Figure 3(a). Referring to the available research and the National Institute of Standards and Technology (NIST), the binding energy of ZrO₂ was fixed at 182.05 eV [57,58]. In addition, to fit the raw data, a low binding energy peak at 181.6 eV was added, and the interval between the 3d₅/₂ and 3d₃/₂ peaks was fixed at 2.38 eV due to spin-orbital coupling [59]. Figures S2a, S2b, and S2c are the result of the peak intensity plot according to the presence or absence of Al₂O₃ and TiO₂, respectively (see Supporting Information). In all the cases of S1, S2, and S3 samples, it was confirmed that the intensities at 60° and 80° were relatively small. As the incident X-rays are inclined, their thin-film penetration depth decreases and the resultant decrease in intensity is natural. In addition, the oxygen peaks are shown in Figure S3 (Supporting Information).

The concept of binding tendency was used to analyze the chemical state of the dielectric film. Binding tendency indicates that the Zr⁺⁺ (x < 4) subpeak area was over the total Zr 3d peak area. In other words, it is considered as the ratio of area with a lower oxidation state than stoichiometric Zr⁺⁺ in the ZrO₂ film [60]. This process is similar to calculating the oxygen vacancy ratio at the oxygen 1s peak [61–63]. Through this

Figure 2. ARXPS spectra of (a) TiN/SiO₂/Si at 0°, (b) TiO₂/TiN/SiO₂/Si at 0°, ARXPS intensity of (c) S1 sample according to angle, (d) sample S2 sample for different angles, and (e) ARXPS intensity variation of S3 sample for different X-ray angles.
Figure 3. (a) ARXPS spectra of Si/SiO$_2$/ZrO$_2$ at 0°, (b) binding tendency of S1 sample according to angle, (c) binding tendency of S2 sample according to angle, and (d) binding tendency of S3 sample according to angle.

analysis, the deviation in the composition of dielectric film was confirmed from stoichiometric full oxidation, according to depth. The Zr$^{4+}$ and Zr$^{6+}$ intensity plots are shown in Figures S2d and S2e (see Supporting Information).

ARXPS data corresponding to 0° and 20° inclination angles were not meaningful, because they contain the dominant chemical properties of TiN substrates. However, the data corresponding to 40°, 60°, and 80° were mainly influenced by the dielectric film. As shown in Figure 3(b), the binding tendency inside the dielectric film was irregular in the case of S1 sample. This is because when ZrO$_2$ was deposited directly on the bottom TiN, the oxygen from ZrO$_2$ filled the voids of TiON that formed naturally on the TiN surface, leading to a lack of oxygen in the ZrO$_2$ thin film. A possible reason for the large binding tendency in the S1 sample, especially at 60°, is that oxygen in the ZrO$_2$ thin film diffused to the lower TiN electrode and oxygen is insufficient in the ZrO$_2$ thin film. On the other hand, in S2 sample, Al$_2$O$_3$ is inserted between the lower electrode and ZrO$_2$ thin film. As shown in Figure 3(c), a high binding tendency was observed in the lower part of ZrO$_2$. This is because Al$_2$O$_3$ has a strong oxygen affinity; therefore, Al$_2$O$_3$ takes oxygen from the ZrO$_2$ thin film [64–66].

It was confirmed that S3 sample (i.e. with TiO$_2$/Al$_2$O$_3$ layers) had the smallest and relatively depth-uniform binding tendency of the dielectric film (see Figure 3(d)). This is because Al$_2$O$_3$ grows well without oxygen deficiency following the deposition of TiO$_2$ layers (~7 Å) with ALD. Therefore, when ZrO$_2$ was deposited, Al$_2$O$_3$ could partially bring oxygen to ZrO$_2$; however, the diffusion of oxygen was expected to be the least. As shown in Figure 3(d), in the case of sample S3, it was confirmed that the binding tendency value at 40° indicates that the interface between the bottom electrode and the dielectric film was the smallest compared to other samples. This means that the interfacial mixing arising from ZrTi$_2$O$_7$ between the ZrO$_2$ and TiN bottom electrode was minimized by the TiO$_2$/Al$_2$O$_3$ double layer of S3 sample.
**Figure 4.** Al, Zr, O atomic% of (a) S1, (b) S2, and (c) S3 sample.

**3.3. Spectroscopic ellipsometry results**

**Figure 5** shows the absorption coefficient plot of the S1, S2, and S3 samples. As explained in the experimental section, these absorption spectra are subject to an overlayer consisting of an interfacial oxide and 

ZrO$_2$/buffer oxide stack extracted by 3-phase optical modeling with the TiN substrate pseudo-dielectric function data. The absorption spectra revealed three distinctive energy ranges: (1) interface oxide (TiO$_x$, TiON, or ZrTi$_x$O$_y$) and buffer layer (TiO$_2$) region at <5 eV, (2) sub-band defect states of ZrO$_2$ dielectric (5–5.5 eV), and (3) conduction band of ZrO$_2$ dielectric (>5.5 eV). Compared to S1 without the buffer layer, the buffer insertion of Al$_2$O$_3$ and Al$_2$O$_3$/TiO$_2$ reduced sub-band defect states (5–5.5 eV), resulting in lower absorption. This is ascribed to the relatively low oxygen vacancies or low Zr$^{n+}$ (n<4) bonding states, which agree with the data from ARXPS. The bandgaps for S1, S2, and S3 measured by linear fitting of the strong onset in the imaginary dielectric function.

**Figure 5.** Absorption coefficient spectra of overlayer consisting of interface, buffer, and ZrO$_2$ dielectrics in S1, S2, and S3 samples, extracted by 3-phase optical modeling using TiN substrate optical data.
spectra were 5.37, 5.32, and 5.67, respectively. The conventional Tauc-plot to evaluate the bandgap is incorrect here, because the dielectric morphology is not well crystallized but is almost amorphous-like short-range-ordered. The bandgap value increased significantly with a steeper absorption onset for S3, indicating that the TiO$_2$ buffer layer improved the Zr$^{4+}$ bond dominating stoichiometric ZrO$_2$ with fewer suboxides. In the energy ranges <5 eV, absorption features are clearly differentiated at <4.8 eV among samples. For S3, this is due to the intentionally grown TiO$_2$ (and a minor ZrTi$_2$O$_7$ contribution) absorption; however, the stronger absorption feature for S2 is due to ZrO$_2$-Al$_2$O$_3$ bonding defects, which is not typical in the ZrO$_2$/Al$_2$O$_3$ stack. Based on the ARXPS analysis and other reports, the Al$_2$O$_3$ buffer layer effectively blocks O diffusion from ZrO$_2$ to TiN, which is more likely due to the ZrO$_2$ dielectric bulk defect rather than the interfacial defect. This is related to the non-optimized Al$_2$O$_3$ process (or O out-diffusion at the interface) for the ZrO$_2$ overlayer. S1 shows much less absorption features <4.8 eV since the interfacial TiON after ZrO$_2$ growth is ultrathin (<1 nm). Consequently, SE analysis confirmed that the double buffer layer of TiO$_2$/Al$_2$O$_3$ not only diminished the sub-band defects of dielectrics but also stimulated stoichiometric ZrO$_2$ formation.

### 3.4. Current–voltage (I–V) analysis

Figure 6 shows the electrical properties of an MIM device based on ZrO$_2$. The I–V curves for all three devices were measured and analyzed with respect to the device geometry. The I–V curves collected in the range from 0 to +2.0 V are depicted in Figure 6(a), which is used to investigate the leakage current of each sample. To avoid breakdown and to have accurate analysis, measurement was taken up to +2.0 V voltage range. Primary results of I–V analysis confirm that the leakage current changes significantly depending on whether Al$_2$O$_3$ and TiO$_2$ were deposited or not. A comparison of S1 and S2 in Figure 6(a) reveals that the presence of Al$_2$O$_3$ film has several effects on the suppression of leakage current. In the case of S2, the comparison of the leakage currents of S1 and S2, as shown in Figure 6(b), a low leakage current of approximately 30 times less was recorded at 1 V, which is consistent with the XPS analysis. As shown in Figure 4(b), the deposited Al$_2$O$_3$ blocks the spatially distributed formation of a mixing layer of ZrTi$_3$O$_7$. At the same time, it can also be confirmed that the presence of Al$_2$O$_3$ affects the leakage current, comparing S1 with S2.

In the case of S3, as shown in Figure 6(b), the leakage current was approximately four times lower than that of S2; this is most likely due to the double-
blocking layer effect. This result is also in agreement with ARXPS analysis, and Al2O3 formed in the TiO2 film has a relatively stable chemical composition ratio. The reduced leakage current can be explained by the deposition of Al2O3 and TiO2. First, as shown in Figure 6(b), the deposition of Al2O3 blocks the formation of ZrTiOx between ZrO2 and TiN. Second, oxygen vacancies which may be generated by the diffusion of oxygen from ZrO2 to Al2O3 are relatively reduced. The deposition of Al2O3 has a greater influence on reducing the leakage current than the additional deposition of TiO2, when compared to the leakage currents of S1, S2, and S3 in Figure 6(b). Consequently, substantial changes in leakage current are induced by ZrTiOx, and the formation of the Al2O3 film is more effective for an important role in suppressing the formation of the ZrTiOx interface.

Furthermore, I–V measurements were performed to analyze the ongoing conduction mechanism for each device for different voltage scan ranges. Figure 6(d–f) shows the I–V curve analysis of the major mechanisms according to voltage. Direct tunneling ranging from 0 to +1.0 V was considered as the major leakage current mechanism. Figure S4, S5, and S6 show ln (J/E2) vs 1/V plot, which depicts that direct tunneling is the dominating charge transport mechanism in this section (see Supporting Information). In fact, the ln (J/E2) varies linearly with 1/V, which confirms that the direct tunneling is the main governing conduction mechanism for this device (Supporting Information). By fitting the ln (J/E2) vs 1/V plots linearly as per equation (1), it is revealed that the direct tunneling range of voltage for each sample varies from 0 to 0.66 V, 0 to 0.8 V, and 0 to 0.94 V for S1, S2, and S3 devices, respectively. For direct tunneling, it is also noted that direct tunneling is inversely proportional to the thickness of the dielectric film in the low-field region (<1.0 V).

\[
J = \frac{q^2}{8\pi\hbar\epsilon_0}C(V_G, V, t, \theta_b) \times \exp \left\{ -8\pi\sqrt{2m^*\epsilon_0} \left( \frac{q\epsilon_0}{\hbar} \right)^{3/2} \left[ 1 - \frac{1}{1 - \frac{|V|}{\theta_b}} \right] \right\} 
\]

\[
C(V_G, V, t, \theta_b) = \frac{20}{\theta_b} \left[ \frac{\epsilon_0 - \theta_b}{\epsilon_0} + 1 \right]^{\alpha} \cdot \left( 1 - \frac{|V|}{\theta_b} \right) \cdot \frac{V_G}{T} \cdot N
\]

where t is the thickness of the dielectric, V is the voltage across the dielectric, \( \theta_b \) is the effective barrier height, and E is the electrical field. In addition, higher direct tunneling section from S2 and S3 in comparison to the sample S1 is due to an increase in the thickness of the oxide film because of the Al2O3 and TiO2 films. On the other hand, the PF emission mechanism occurred at similar voltages (~1.0 V) in all three samples. Figures S5, Figure S6 (Supporting Information), and Figure 6 explain the existence of the Schottky emission mechanism at a low electric field, as shown by the graph of ln(J/T2) ~ E1/2 (see Supporting Information). In fact, from the graph of ln (J/E2) to E1/2, it is most likely that there is a major mechanism through the slope of the linear section. Since the slope of the linear interval and the refractive index of ZrO2 do not match, it is concluded that Schottky emission is not a major mechanism. The interval between the direct tunneling section and the PF emission section was explained as the trap-assisted tunneling (TAT) section. We confirmed that the TAT section of S1 had a larger bias span than S2 and S3, as shown in Figure 6. Owing to the deposition of Al2O3, it was explained that interface mixing could occur less between ZrO2 and TiN, and the defect was reduced. As a result, the deposition of Al2O3 induces decreasing in the defect density and leakage current related to TAT. To confirm that the PF emission is the major mechanism of the leakage current, a linear section was confirmed by a graph of ln (J/E) to E1/2, as shown in Figures S4, S5, and S6 (see Supporting Information). Equation (3) shows the current density due to PF emission:

\[
J = q\mu N_c \exp \left[ -\frac{q(V_G - \sqrt{qE/\pi\epsilon_0\epsilon_0})}{kT} \right]
\]

where \( \mu \) is the electronic drift mobility, \( N_c \) is the density of states in the conduction band, and \( \theta_b \) is the trap energy level. The slope value of ln (J/E) vs E1/2 can be used to confirm whether reliable data can be obtained for a PF emission. If the refractive index has an approximately squared dielectric constant, this result is attributed to a major mechanism for PF emission. When the refractive index is calculated through the slope of each sample, between 2.29 and 2.66, it fits very well with the known value of the refractive index of ZrO2 such as 2.5 [67]. It is well known that the PF emission depends on the concentration of trap centers, so that the lower leakage current of samples S2 or S3 is explained by the fact that the mixing layer containing the trap center in the dielectric film is suppressed. However, in the higher electrical field such as between 1.3 V and 1.7 V, this does not match the refractive index of ZrO2; this is because FN tunneling, and PF emissions occur simultaneously. FN tunneling is a major mechanism at more than 1.7 V. To confirm this (see Figure S4, S5, and S6d), ln (J/E2) vs 1/E should be fit by a linear line at more than 1.7 V (see Supporting Information). From this, FN tunneling is dominant in the voltage section of 1.7 V or more for each sample. As shown in Figure 6(c), sample S3 shows the lowest leakage current. As a result, the double blocking layer is more effective in reducing the leakage current at higher voltages. This is because FN tunneling is based on band-to-
band tunneling; electrons suffer from more energy barrier heights for tunneling through the double blocking layer. This proves that the double blocking layer strategy is highly effective for the suppression of leakage current in all low bias (PF emission), medium bias (TA), and high bias regimes (FN), because it reduces defect-associated charge traps and increases tunneling barrier heights.

4. Conclusion
This paper identifies that interface mixing, O-diffusion, and ZrTiO₃ formation can occur in the dielectric film of a ZrO₂-based DRAM capacitor that is getting thinner; this suggests a possible solution for inserting a double blocking layer. We inserted a TiO₂/Al₂O₃ double-blocking layer in the MIM capacitor to prevent interfacial defects induced by chemical mixing between the dielectric film and the bottom electrode, as well as to secure a stable chemical state of the dielectric film. Through ARXPS analysis, it was confirmed that the double blocking layer stabilized the chemical state of the dielectric layer, and reduced the leakage current, as confirmed by I–V analysis. This study clearly suggests that the chemical mixing features between the dielectric layer and the bottom electrode in the MIM capacitor, probed by both XPS and SE, are strongly associated with the electrical properties of the capacitor. We propose an engineered solution that can solve the interface mixing problem through the insertion of a TiO₂/Al₂O₃ double-blocking layer. This is highly applicable, not only to aggressive scaled-down DRAM MIM capacitors but also to other thin-film stacked device structures with ZrO₂-based dielectrics.

Disclosure statement
No potential conflict of interest was reported by the author(s).

Funding
This work was supported by Samsung Electronics Co., Ltd (IO191218-06937-01).

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