High-$\kappa$ TiCeO MIM Capacitors with a Dual-Plasma Interface Treatment

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In this study, we successfully fabricated high-$\kappa$ Ir/TiCeO/TaN metal-insulator–metal (MIM) capacitors using a dual-plasma treatment on a bottom TaN electrode. The plasma treatment suppressed the growth of the bottom interfacial layer to largely improve capacitor performance at a 400°C thermal budget. The Ir/TiCeO/TaN MIM capacitor achieved a high capacitance density of $\sim 17 \text{ F/\mu m}^2$ at a 22 nm thickness and a low quadratic coefficient of capacitance (VCC-$\alpha$) of 866 ppm/V$^2$ at a 10.3 F/$\mu$m$^2$ density. The good performance is due to the combined effects of a dual-plasma interface treatment, higher-$\kappa$ TiCeO dielectrics, and a high work-function Ir metal.

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There is a continuing demand to increase the capacitance density ($\varepsilon_{\text{eff}}/t_\text{d}$) of the metal–insulator–metal (MIM) capacitors. 1-13 To achieve this, the MIM devices have evolved by using high-$\kappa$ dielectrics, such as SiN, 1,2,3 Al$_2$O$_3$, 1,4 Ta$_2$O$_5$, 5, 6, 7, 8 HfO$_2$, 6-8 and Nb$_2$O$_5$. 9 Tita-

The high-$\kappa$ TiCeO MIM capacitors were fabricated on standard Si wafers. To permit very-large-scale back end integration, the process began with depositing a 2 $\mu$m thick SiO$_2$ isolation layer on the Si substrates. Then, 50 nm TaN was deposited on a 200 nm Ta layer by a sputter system, and the Ta/TaN bilayers were used as a bottom electrode, where thick Ta was chosen to reduce the parasitic resistance of the electrode. After patterning the bottom TaN electrode, the bottom electrode surface was treated first by NH$_3$ plasma to suppress the growth of the bottom interface layer to largely improve capacitor performance at a 400°C thermal budget. The plasma treatment suppressed the growth of the bottom interfacial layer to largely improve capacitor performance at a 400°C thermal budget. The Ir/TiCeO/TaN MIM capacitor achieved a high capacitance density of $\sim 17 \text{ F/\mu m}^2$ at a 22 nm thickness and a low quadratic coefficient of capacitance (VCC-$\alpha$) of 866 ppm/V$^2$ at a 10.3 F/$\mu$m$^2$ density. The good performance is due to the combined effects of a dual-plasma interface treatment, higher-$\kappa$ TiCeO dielectrics, and a high work-function Ir metal.

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Results and Discussion

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× 10⁻⁵ A/cm² at −2 V. The J-V characteristic shows that the asymmetry leakage behavior is attributed to the use of a high-work-function Ir metal as a top electrode to improve the leakage current at a negative bias. However, a large leakage current of ~3 × 10⁻⁵ A/cm² at 1 V from the bottom injection is inevitable due to oxidation of the bottom electrode during dielectric annealing, even though the bottom TaN has been pretreated by the NH₃ plasma. Here, we also fabricated the Ir/CeO₂/TaN capacitor with a 15 nm thickness, and its electrical properties in Fig. 1a exhibit a capacitance density of 12.7 fF/μm² at 500 kHz with a leakage current of 5.3 × 10⁻⁷ A/cm² at −1 V. At the same electric field of 1 MV/cm, a leakage current of 1.2 × 10⁻⁹ for a CeO₂ capacitor is approximately 50 times lower than the TiO₂ capacitor, as shown in Fig. 1b, which is possibly due to higher ΔEc of CeO₂ dielectrics to reduce the gate-injected leakage current. A comparison with other capacitors previously reported is summarized in Table I.

In addition, the VCC-α is an important parameter of MIM capacitors for analog/rf applications. The VCC-α characteristic can be obtained by fitting the measured C-V curve with a second-order polynomial equation

\[ C(V) = C_0(1 + VCC - BV + VCC - GAT)^2 \]  

Here, \( C_0 \) is the capacitance density at zero bias and VCC-α and VCC-β represent the quadratic and linear voltage coefficients of capacitance, respectively. Because the linear β term can be compensated by a circuit design, the quadratic α is the main factor in the voltage dependence. The ΔC/C-V characteristics of TiO₂ and CeO₂ MIM capacitors, as shown in Fig. 2, display that the VCC-α of 800 ppm/V for the CeO₂ capacitor is much lower than 5764 ppm/V of the TiO₂ capacitor with 25 nm thickness. Furthermore, in Table I, the VCC-α comparisons for the different high-κ capacitors indicate that the CeO₂ dielectric also shows a much smaller VCC-α, compared with Al₂O₃–HfO₂ (~1900 ppm/V²) and Ti–HfO₂ (~2667 ppm/V²) MIM capacitors at a similar permittivity (~20).

As for the experimental results stated above, the higher-κ TiO₂ dielectric as a dielectric on the TaN substrate suffers the penalty of a large leakage current and a thick interfacial layer due to a very small ΔEc and poor thermal stability. Because the interface layer is a serious issue to influence the MIM capacitor performance and capacitance-equivalent thickness (CET) scaling, the nitrified TaN electrode, by only using an NH₃ plasma as a surface treatment, is not sufficient to impede the dielectric/TaN reaction.

To improve the oxidation of the TaN substrate further, the conventional NH₃ plasma would be replaced by a dual-plasma treat-

Table I. Comparison of MIM capacitors with various dielectrics and metal electrodes.

<table>
<thead>
<tr>
<th>MIM capacitors</th>
<th>Al₂O₃–HfO₂</th>
<th>Tb–HfO₂</th>
<th>TiTaO</th>
<th>TiZrO</th>
<th>TiO₂ (this work)</th>
<th>CeO₂ (this work)</th>
<th>TiCeO (this work)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top electrode</td>
<td>TaN</td>
<td>Ta</td>
<td>Ir</td>
<td>Ni</td>
<td>Ir</td>
<td>Ir</td>
<td>Ir</td>
</tr>
<tr>
<td>Bottom electrode</td>
<td>TaN</td>
<td>TaN</td>
<td>TaN</td>
<td>TaN</td>
<td>TaN</td>
<td>TaN</td>
<td>TaN</td>
</tr>
<tr>
<td>Capacitance density (fF/μm²)</td>
<td>~12.8</td>
<td>13.3</td>
<td>14.3</td>
<td>6.5</td>
<td>16.8</td>
<td>12.2</td>
<td>10.3</td>
</tr>
<tr>
<td>J (A/cm²) at 25°C</td>
<td>8 × 10⁻⁹ (2 V)</td>
<td>1 × 10⁻⁷ (2 V)</td>
<td>2 × 10⁻⁷ (2 V)</td>
<td>6.7 × 10⁻⁸ (–2 V)</td>
<td>3.4 × 10⁻⁷ (–2 V)</td>
<td>9 × 10⁻⁶ (–2 V)</td>
<td>4.7 × 10⁻⁷ (–2 V)</td>
</tr>
<tr>
<td>VCC-α (ppm/V²)</td>
<td>1990</td>
<td>2667</td>
<td>634</td>
<td>248</td>
<td>5055</td>
<td>610</td>
<td>866</td>
</tr>
<tr>
<td>κ value</td>
<td>~18</td>
<td>~20</td>
<td>~45</td>
<td>~28</td>
<td>~48</td>
<td>~21</td>
<td>~44</td>
</tr>
</tbody>
</table>

Figure 1. (a) C-V and J-V characteristics and (b) J vs E plot of Ir/TiO₂ and CeO₂/TaN capacitors with NH₃ plasma on bottom TaN. 

Figure 2. ΔC/C-V characteristics of Ir[TiO₂ and CeO₂]/TaN capacitors with NH₃ plasma on bottom TaN.
ment, which adds an additional oxygen plasma on the nitrided TaN surface, which has been treated by the conventional NH3 plasma.

From the surface roughness of bottom TaN measured by AFM shown in Fig. 3, the roughness values of the bottom interface with and without NH3 plasma treatment are 0.714 and 0.415 nm. The samples with dual-plasma treatment (NH3 and O2) show a smallest root-mean-square (≈0.391 nm). A smoother interface might be helpful for a lower leakage and a higher breakdown field. In the present work, the bottom electrodes of the MIM capacitors were treated by dual-plasma treatment. Subsequently, we introduce the TiCeO dielectric instead of the TiO2 dielectric to fabricate MIM capacitors. The TiCeO MIM capacitors were characterized by C-V and J-V measurements and were shown in the following.

In Fig. 4a, we show the C-V and J-V characteristics of TiCeO MIM capacitors with or without an additional O2 plasma treatment on the bottom electrode. For the samples with the second O2 plasma treatment, the capacitance density slightly increases from 16 to 17 fF/m2, which may be attributed to less electrode oxidation. Moreover, the leakage performance demonstrates that the samples with an additional O2 plasma treatment can be largely improved by 2 orders of magnitude. In addition, the samples with the second O2 plasma show a close leakage performance, whose low leakage currents of 3.9 × 10−7 A/cm2 at −1 V and 4.1 × 10−7 A/cm2 at 1 V are measured under different polarities, respectively. Apparently, the leakage current under the bottom injection is lower than that of the 17 fF/m2 density Ir/TiO2/TaN capacitors. This improved leakage current, at a comparable capacitance density, is due to the TiCeO dielectric with a higher ΔEC and dual-plasma treatment, which lowers the leakage current exponentially.

To more deeply investigate the current conduction mechanism, we plot ln(J) vs E1/2 for the Ir/TiCeO/TaN MIM capacitors

\[ J \propto \exp \left( \frac{\gamma E^{1/2} - V_b}{kT} \right) \]

\[ \gamma = \left( \frac{e^3}{\eta \pi \varepsilon_e K_n} \right)^{1/2} \]

Here, \( K_n \) is the high frequency dielectric constant (≈n2). The ideal refractive index \( n \) is 2.6 or 2.3 for TiO2 or CeO2, and \( \eta \) is 1 or 4 for Schottky emission (SE) or Poole–Frenkel (PF) conduction, respectively. From the ln(J/F)–E1/2 plot in Fig. 4b, the conduction mechanism of the leakage current seems to be dominated by SE at a low electric field and PF emission at a high electric field. The comparison of J-V characteristic between Ir and Ni top electrode in the inset of Fig. 4c demonstrates that Ir electrodes could effectively reduce leakage currents from the low to high electrical field compared with the Ni case. Furthermore, a small change in J-V characteristic in Fig. 4c also indicates that the thermal stability is acceptable.

According to the TiZrO MIM capacitors reported before, the VCC-a can be improved with increasing dielectric thickness. Therefore, a 37 nm thick TiCeO MIM capacitor was fabricated for the improved voltage nonlinearity simultaneously. A capacitance density

\[ C_V-V \text{ characteristic of Ir/TiCeO/TaN capacitors with NH3 or/and O2 plasma on bottom TaN. A J-V characteristic of Ni/TiCeO/TaN device is shown, for comparison, in the inset of (c).} \]
of 10.3 fF/μm² at 500 kHz is measured, along with a low VCC-α of 866 ppm/V² shown in Fig. 5a. The 37 nm thick TiCeO dielectric measured by SEM spectroscopy indicates a κ value of 44 at a capacitance density of 10.3 fF/μm². Correspondingly, the leakage current at −3 V decreases from 2.6 × 10⁻⁵ to 7.7 × 10⁻⁷ A/cm² with increasing the film thickness from 22 to 37 nm, as shown in Fig. 5b. Besides, we also show the C-V and J-V characteristics of TiO₂ and CeO₂ films with dual-plasma treatment in Fig. 5b. The leakage currents for the two control samples could also be improved. Therefore, by using an additional oxygen plasma treatment, the interfacial reaction and growth are reduced, leading to a lower leakage current. The experimental results indicate the importance of an additional oxygen plasma treatment on the bottom TaN electrode. To compare with the reported MIM capacitors, we plotted the VCC-α as a function of capacitance density in Fig. 6. The results show that the TiCeO dielectric with a higher-κ value is more suitable than TiZrO dielectrics for the CET scaling and the control of voltage nonlinearity.

**Conclusion**

In this study, by using a dual-plasma interface treatment, the penalty of interface reaction was reduced at the dielectric/TaN interface. This effectively reduced the interface reaction and growth, leading to a lower leakage current and its voltage nonlinearity. Thus, the Ir/TiCeO/TaN MIM capacitors could appear to have a high capacitance density, low leakage current, and small voltage nonlinearity.

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**References**