Importance of Annealing Step on Dielectric Constant of ZrO$_2$ Layer of Metal-Insulator-Metal Capacitors with Al$_2$O$_3$/ZrO$_2$ and ZrO$_2$/Al$_2$O$_3$ Stack Structures

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Requirements of insulating film for DRAM capacitor

The structure of DRAM capacitor

- Top electrode
- Insulating film
- Bottom electrode
- Contact
- Interlayer

Pillar shape

- Uniform film formation technology for 3D structures

Atomic layer deposition (ALD)

Requirements of insulating film

- High dielectric-constant \((k) \geq 40\) at a process temp. < 650 °C
- Low leakage current density \((J \leq 1.6 \times 10^{-7} \text{ A/cm}^2\) at 0.6V)\(^*2\)

Investigation of ZrO\(_2\)/Al\(_2\)O\(_3\)/ZrO\(_2\) (ZAZ) stack structure

- ZrO\(_2\) has been studied a promising candidate material as an insulating film because of its high \(k\)-value (> 30) at a low fabrication process temperature.
- An amorphous Al\(_2\)O\(_3\) interlayer of the ZAZ structure acts as blocking layer to suppress the leakage current flow through the grain boundaries of a polycrystalline ZrO\(_2\) layer.

*1 Micron HP, Samsung HP, imec IEDM2018, IRDS2017
*2 T. Onaya et al., ECS Trans. 75 667 (2016)

DRAM : Dynamic random access memory
Different properties between 1\textsuperscript{st} and 2\textsuperscript{nd} ZrO\textsubscript{2} layers of ZAZ structure

- There has been not paid attention to the difference in characteristics between 1\textsuperscript{st} and 2\textsuperscript{nd} ZrO\textsubscript{2} layers which was fabricated on BE-TiTaN and Al\textsubscript{2}O\textsubscript{3} layer, respectively.

- To clarify it, two kind of capacitors such as BE-TiTaN/ZrO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}(ZA)/TE-TiTaN and BE-TiTaN/Al\textsubscript{2}O\textsubscript{3}/ZrO\textsubscript{2}(AZ)/TE-TiTaN were prepared.
The purpose of this research

To investigate characteristics of BE-TiN/ZA/TE-TiN and BE-TiN/AZ/TE-TiN capacitors after PDA and PMA at 600°C in N₂.

To discuss about reason why a higher $k$-value of 1st ZrO₂ layer in ZA structure was obtained only after PDA condition.

PDA: Post-deposition annealing  PMA: Post-metallization annealing
Capacitance fabrication flow

- **P+ Si** (<0.01 Ω · cm)
- **BE-TiN** (50 nm)
- **ALD-ZrO₂** (2.9~5.7 nm)
  - $T_g = 300^\circ$C, (C₅H₅)Zr[N(CH₃)₂]₃ & H₂O
- **ALD-Al₂O₃** (2.0 nm)
  - $T_g = 300^\circ$C, Al(CH₃)₃ & H₂O
- **PDA**
  - PDA 600°C in N₂
- **TE-TiN** (50 nm)
- **AZ**
  - **ALD-Al₂O₃** (2.0 nm)
- **AZ**
  - **ALD-ZrO₂** (2.9~5.7 nm)
  - **TE-TiN**
  - **PMA**
  - **PMA 600°C in N₂**
Cross sectional TEM images & EDS of ZA and AZ capacitors

(a) ZA wPDA
- The ZrO$_2$ and Al$_2$O$_3$ layers remained to be ZrO$_2$/Al$_2$O$_3$ stack structure even after PDA.
- From the EDS elemental lines, the ZrO$_2$/Al$_2$O$_3$ stack was also found to be formed without intermixing of Zr and Al atoms.

(b) AZ wPDA
- Same results were observed to be the Al$_2$O$_3$/ZrO$_2$ stack structure without intermixing of ZrO$_2$ and Al$_2$O$_3$ layers.
XRD patterns of ZA and AZ capacitors

(a) ZA

- A sharp peak at $2\theta = 36.4^\circ$ was assigned to (111) plane of TiN.
- In the case of w/o, the ZrO$_2$ layer had an amorphous structure because of no peak.
- In the case of wPDA and wPMA capacitors, a broad peak appeared at $2\theta = 30.0^\circ$ which assigned Cubic (C), Tetragonal (T), and Orthorhombic (O)-phases.

(b) AZ

- The AZ capacitors showed the same data such as an amorphous structure of the ZrO$_2$ layer in w/o and C, T, and O-phases of the ZrO$_2$ layer in the wPDA and wPMA. There is no difference of the XRD pattern between AZ and ZA capacitors.
C-V characteristics of ZA and AZ capacitors

- All capacitors exhibited small tanδ of below 0.2, indicating that ZA and AZ insulators have superior insulating property.

- ZA wPMA, AZ wPDA and AZ wPMA: The capacitance reasonably decreased as the ZrO$_2$ layer thickness increased.

- ZA wPDA: The degradation of capacitance was very small, as unexpected.

<table>
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<tr>
<th>ZA</th>
<th>wPDA</th>
<th>wPMA</th>
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<tr>
<td>ZrO$_2$ thickness</td>
<td>2.9 nm</td>
<td>3.9 nm</td>
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<tr>
<td>Capacitance (μF cm$^{-2}$)</td>
<td>4.9 nm</td>
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<td>tanδ</td>
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<td>0.00</td>
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</table>
Capacitance and $k$ of ZrO$_2$ vs total thickness of ZA and AZ

The capacitance of the ZA wPMA, AZ wPDA and wPMA decreased as increasing total thickness.

- The ZA wPDA showed same capacitance in the regions of thickness $\geq 6.9$ nm as unexpected.

- The $k$-value of ZrO$_2$ layers in ZA wPMA, AZ wPDA and wPMA increased from $\sim 27$ to $32-37$ as increasing thickness from 4.9 to 6.9 nm and almost saturated.

- On the other hand, the $k$-value of ZrO$_2$ layer in ZA wPDA capacitor dramatically jumped to 44 when their thickness increased to 6.9 nm.

The $k$-value of each ZrO$_2$ layer was estimated when the $k$-value of Al$_2$O$_3$ was 7.7.

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\[ C_{ZA} = \frac{1}{C_{Al2O3}} + \frac{1}{C_{ZrO2}} - \frac{1}{C_{Al2O3}} \]
The hard breakdown electric field exhibited similar values of 4.9-5.1 MV cm\(^{-1}\) for all capacitors.

There was no significant difference of the \(E\)-value between ZA and AZ capacitors.

All capacitors matched the PF model compared to the TAT and FN models.
The Factor affecting the leakage current characteristics

- There was no significant difference of the $E$-value between the ZA and the AZ structures.
- The difference of conduction band offset between TE-TiN and ZrO$_2$ or TE-TiN and Al$_2$O$_3$ was not influenced to the leakage current property.
The \( E \)-values of the wPDA were higher than those of the wPMA.

\[ \downarrow \]

The difference between PDA and PMA treatment may occur the difference of quality in the grain boundary of polycrystalline \( \text{ZrO}_2 \) layer.

As a results, a poor quality of \( \text{ZrO}_2 \) layer after PMA leads to a low \( E \)-value.
The relationship between $k$-value of ZrO$_2$ layer and $E$-value

- The $k$-values of ZA wPMA, AZ wPDA and wPMA gradually increased as $E$-value increased.
- This suggests that the ZrO$_2$ layer needs to have a sufficient thickness to increase of the $k$-value.

- The ZA wPDA exhibited superior characteristics of a high $k$-value and a high $E$-value in the regions of the total thicknesses 6.9-7.7 nm.
Different stress of BE-TiN/ZrO$_2$/Al$_2$O$_3$ under PDA

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<tr>
<td>ZrO$_2$</td>
<td>8.0 ~ 11.0 × 10$^{-6}$ K$^{-1}$</td>
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<tr>
<td>Al$_2$O$_3$</td>
<td>5.4 ~ 8.4 × 10$^{-6}$ K$^{-1}$</td>
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<tr>
<td>TiN</td>
<td>9.4 ~ 10.3 × 10$^{-6}$ K$^{-1}$</td>
</tr>
</tbody>
</table>

• For the ZA wPDA capacitor, the different stress is introduced to the ZrO$_2$ layer due to the coefficients of thermal expansion (CTE) and results in growth of high-$k$ phase.
Conclusion

We studied characteristics of the ZA and AZ capacitors after PDA and PMA at 600°C in N₂.

• In the case of ZA wPMA, AZ wPDA and AZ wPMA capacitors, the $k$-value of ZrO₂ layer were saturated around 32-37 at their total thickness in 6.9 nm.

• On the other hand, the $k$-value of ZA wPDA capacitor dramatically jumped to 44 when their thickness was $\geq$ 6.9 nm.

• The PDA produced an insulating film with better electrical properties than the PMA.

• For the ZA wPDA capacitor, the different stress is introduced to the ZrO₂ layer due to the coefficients of thermal expansion (CTE) and results in growth of high-$k$ phase.

When we fabricated ZAZ insulator of DRAM capacitor, the PDA treatment should perform after 1st-ZrO₂/Al₂O₃ layer deposition to obtain a high dielectric constant ZrO₂.
This work was partially supported by JSPS KAKENHI (Nos. JP20H02189 and JP18J22998). The authors thank all staff members of the Nanofabrication Group of NIMS for their support in the fabrication of the TiN/ZA/TiN capacitors.