Atomic layer epitaxy of rare earth oxide films on GaAs(111)A and their device properties

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The aggressive scaling of MOSFETs has created interest in using high-mobility III-V channel materials to replace traditional strained Si. However, it has been challenging to form high-$\kappa$ dielectrics that can passivate III-V surfaces with a low interface state density ($D_{it}$). We deposited LaLuO$_3$ high-$\kappa$ dielectric layer by ALD on sulfur-passivated GaAs substrates. The precursors lanthanum tris($N,N'$-diisopropylformamidinate), and lutetium tris($N,N'$-diethylformamidinate) reacted with water vapor at 350 °C. The compositional ratio of La:Lu was about 1:1 by using one cycle of La$_2$O$_3$ followed by one cycle of Lu$_2$O$_3$ in one complete cycle of LaLuO$_3$. Both high-resolution XRD analysis and TEM showed that ALD LaLuO$_3$ formed epitaxially on GaAs(111)A substrates, as shown in Figures 1 and 2, respectively. The epitaxial layer exhibited a cubic structure with a lattice constant smaller than GaAs by 3.8%. The LaLuO$_3$ film had a high degree of crystalline perfection and was relaxed and not strained. Electrical characterizations showed the measured dielectric constant of around 30, which is close to its bulk crystalline value. The interface had a low interface state density ($D_{it}$) of $\sim 7 \times 10^{11}$ cm$^{-2}$eV$^{-1}$. The amount of lattice mismatch can be engineered by choosing various rare-earth oxides. ALD La$_2$O$_3$ formed cube-on-cube epitaxy on GaAs(111)A with a lattice constant just $+0.9\%$ larger than that of the substrate. The mismatch can be reduced to zero by adding some Y$_2$O$_3$ to the La$_2$O$_3$, using yttrium tris($N,N'$-diisopropylactamidinate)/H$_2$O cycles. Perfect zero-mismatched epitaxy was achieved on GaAs(111)A by depositing La$_{1.7}$Y$_{0.3}$O$_3$, as shown in Figure 3. The effects of mismatch on the electrical properties of epi-LaYO$_3$ on GaAs(111)A were studied. These results suggest that atomic layer epitaxy of rare-earth oxides/GaAs(111)A is a promising structure for future generations of high-power/high-frequency analog devices or high-speed logic devices.

Figure 1 (a) High-resolution X-ray omega-two theta scan for LaLuO$_3$ film on GaAs(111)A. (b) and (c) The rocking curves of the LaLuO$_3$ (222) peak and the GaAs(111) peak, respectively.

Figure 2 (a) Cross-sectional TEM of LaLuO$_3$/GaAs(111)A heterostructure. (b) A magnified image of the interface.

Figure 3. Cross-sectional TEM of La$_{1.7}$Y$_{0.3}$O$_3$/GaAs(111)A. The mismatch is zero for this composition with 15% Y$_2$O$_3$. 
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2011 ALD Meeting

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Motivation

• High-κ and high mobility for future scaling

• GaAs: high electron mobility

• Issue: small $I_{DS}$ in GaAs NMOSFET $\leftarrow$ Fermi-level pinning

• Fermi-level unpinning: GaAs(111)A with ALD $\text{Al}_2\text{O}_3$*

  *(Prof. Ye’s group at Purdue)*

### High-κ on GaAs for EOT scaling

<table>
<thead>
<tr>
<th>on GaAs</th>
<th>κ</th>
<th>Band gap (eV)</th>
<th>ΔEc (eV)</th>
<th>ΔEv (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>8</td>
<td>6.5</td>
<td>1.8</td>
<td>3.4</td>
</tr>
<tr>
<td>HfO₂</td>
<td>12</td>
<td>6.2</td>
<td>1.8</td>
<td>3</td>
</tr>
<tr>
<td>LaAlO₃</td>
<td>15</td>
<td>5.8</td>
<td>1.6</td>
<td>2.8</td>
</tr>
<tr>
<td>GdScO₃</td>
<td>22</td>
<td>5.7</td>
<td>2</td>
<td>2.3</td>
</tr>
<tr>
<td>LaScO₃</td>
<td>23</td>
<td>5.6</td>
<td>2</td>
<td>2.3</td>
</tr>
<tr>
<td>LaLuO₃ (bulk)</td>
<td>32</td>
<td>5.6</td>
<td>2.1</td>
<td>2.2</td>
</tr>
</tbody>
</table>

ALD process for LaLuO$_3$ films

• Metal amidinate precursor for ALD La$_2$O$_3$:
  • Lanthanum tris($N,N'$-diisopropylformamidinate) or La($^{i}$Pr$_2$-fAmd)$_3$
  • white solid
  • most volatile La compound known, 60 mTorr at 100 °C
  • high reactivity to H$_2$O, O$_2$ and NH$_3$

• Metal amidinate precursor for ALD Lu$_2$O$_3$:
  • Lutetium tris($N,N'$-diethylformamidinate) or Lu(Et$_2$-fAmd)$_3$
  • more volatile than La($^{i}$pr$_2$-fAmd)$_3$
ALD process for LaLuO₃ films

Furnace Heater (350 °C)

Oven (118 °C)

Lu(Et₂-fAmd)₃

La(ᵢPr₂-fAmd)₃

N₂ purge

N₂ carrier

H₂O

ALD process condition for LaLuO₃

<table>
<thead>
<tr>
<th>MO precursors</th>
<th>Oxidant</th>
<th>Bubbler temp.</th>
<th>Deposition temp.</th>
<th>La₂O₃ : Lu₂O₃</th>
<th>Exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(ᵢPr₂-fAmd)₃</td>
<td>DI H₂O</td>
<td>118 °C</td>
<td>300-350 °C</td>
<td>1:1</td>
<td>0.003 Torr s for metal precursor</td>
</tr>
<tr>
<td>Lu(Et₂-fAmd)₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.06 Torr s for H₂O</td>
</tr>
</tbody>
</table>
Properties of ALD LaLuO₃

• Composition (RBS)
  • La:Lu=1:0.9
  • 80% of bulk density
  • C and N not detectable
• Amorphous on Si with abrupt interface (κ ~26)
• Highly conformal (90% step coverage)

Properties of ALD LaLuO$_3$ on GaAs(111)A

- Lattice mismatch $\sim-4\%^{*}$
- Relaxed
- Epitaxy: cubic, not orthorhombic!

* defined as $(a_{\text{oxide}} - 2a)/2a$

Quality of ALD epi-LaLuO$_3$ on GaAs(111)A

- High-resolution XRD measurements

\[ \omega - 2\theta \text{ (}^\circ\text{)} \]

- Mismatch $\sim$3.8%
- Crystalline uniformity
- FWHM of the film peak

The quality of epitaxy is comparable to GaAs
Substrate-dependent crystal structures

- Cubic polycrystalline with (110) preferential orientation on GaAs(100)

Substrate-dependent crystal structures

- Amorphous on Si (0.18% mismatch)
  - Silicate IL formation → Disturb ordering of substrate.

Epi-LaLuO$_3$/GaAs(111)A: no amorphous IL desirable for EOT scaling

Electrical properties

- Epi-LaLuO₃ v.s. a-Al₂O₃ on GaAs(111)A

![Graphs showing capacitance (C) vs. gate bias (V) at different temperatures and frequencies for LaLuO₃ and a-Al₂O₃ on GaAs(111)A.]

- Dielectric constant is ~30
- Smaller V₉B & frequency dispersions
- Interface state density (Dₗt) ~ 7×10¹¹ cm⁻² eV⁻¹

LaLuO₃/GaAs(111)A: better interface
Lattice mismatch engineering

- ALD La$_2$O$_3$ on GaAs(111)A
  - nearly zero lattice mismatch (+0.8%)
  - cubic phase (*not tetragonal*), κ~23

![STEM image of La$_2$O$_3$ and GaAs(111)A with a scale bar of 5 nm.](image1.png)

![Selected area electron diffraction (SAED) pattern with zones axes [111] and (440) of La$_2$O$_3$ and (220) of GaAs.](image2.png)
Lattice mismatch engineering

Adjust lattice parameters to get perfect lattice match

- Metal amidinate precursor for ALD Y$_2$O$_3$
  - Yttrium tris($N,N'$-diisopropylacetamidinate) or Y(iPr$_2$-amd)$_3$
  - White solid, less volatile

- ALD LaYO$_3$ @300 °C

<table>
<thead>
<tr>
<th>Subcycle ratio</th>
<th>Composition</th>
<th>Lattice mismatch</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_2$O$_3$ : Y$_2$O$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:0</td>
<td>La$_2$O$_3$</td>
<td>+0.8%</td>
</tr>
<tr>
<td><strong>3:1</strong></td>
<td>La$<em>{1.7}$Y$</em>{0.3}$O$_3$</td>
<td><strong>0</strong></td>
</tr>
<tr>
<td>1:2</td>
<td>La$_1$Y$_1$O$_3$</td>
<td>-2.5%</td>
</tr>
<tr>
<td>0:1</td>
<td>Y$_2$O$_3$</td>
<td>-6%</td>
</tr>
</tbody>
</table>
Summary

- **Substrate-dependent structures of ALD LaLuO₃**
  - Epitaxy on GaAs(111)A
  - Poly. on GaAs(100)
  - Amorph. on Si

- **Promising electrical properties of epi-LaLuO₃/GaAs(111)A**
  - High κ and low Dᵢᵣ
  - Fermi-level is unpinned

- **Lattice mismatch engineering**
  - La₁.₇Y₀.₃O₃ on GaAs(111)A: perfect lattice match
Acknowledgements

• Prof. Roy Gordon and all group members

• Prof. Peide D. Ye and Min Xu

• Dr. Jun-Jieh Wang prepared Lu precursor

• Dow Chemical provides La and Y precursor

• Center for Nanoscale Systems (CNS) at Harvard
Electrical properties

• Effect of sulfur passivation

All devices: RTA in N₂ at 700 °C before Ni electrodes were patterned on the devices.
Electrical properties

- **GaAs(111)A** v.s. **GaAs(100)**

Fermi-level is **partially pinned** and $D_{it}$ is higher on GaAs(100).

Fermi-level is **unpinned** on GaAs(111)A.