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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-k dielectrics that can passivate III-V surfaces with a low interface state density (D_it). We deposited LaLuO₃ high-k 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 La₂O₃ followed by one cycle of Lu₂O₃ in one complete cycle of LaLuO₃. Both high-resolution XRD analysis and TEM showed that ALD LaLuO₃ 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 LaLuO₃ 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 ~7×10¹¹ cm⁻²eV⁻¹. The amount of lattice mismatch can be engineered by choosing various rare-earth oxides. ALD La₂O₃ 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 Y₂O₃ to the La₂O₃, using yttrium tris(N,N'-diisopropylactamidinate)/H₂O cycles. Perfect zero-mismatched epitaxy was achieved on GaAs(111)A by depositing La₁₋₀.₇₇₇₁₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅₆₅¢
Atomic Layer Epitaxy of Rare Earth Oxide Films on GaAs and Device Properties

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 $\leftrightarrow$ Fermi-level pinning

• Fermi-level unpinning: GaAs(111)A with ALD Al$_2$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</td>
<td>32 (bulk)</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 LaLuO$_3$ films

**ALD process condition for LaLuO$_3$**

<table>
<thead>
<tr>
<th>MO precursors</th>
<th>Oxidant</th>
<th>Bubbler temp.</th>
<th>Deposition temp.</th>
<th>La$_2$O$_3$ : Lu$_2$O$_3$</th>
<th>Exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(iPr$_2$-fAmd)$_3$</td>
<td>DI H$_2$O</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(Et$_2$-fAmd)$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.06 Torr s for H$_2$O</td>
</tr>
</tbody>
</table>
Properties of ALD LaLuO$_3$

- **Composition (RBS)**
  - La:Lu=1:0.9
  - 80% of bulk density
  - C and N not detectable
- **Amorphous on Si with abrupt interface ($\kappa \sim 26$)**
- **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\textsubscript{3} on GaAs(111)A

- High-resolution XRD measurements

![Graph showing XRD patterns]

- 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-LaLuO$_3$ v.s. a-Al$_2$O$_3$ on GaAs(111)A

- Dielectric constant is ~30
- Smaller $V_{FB}$ & frequency dispersions
- Interface state density ($D_{it}$) ~ $7 \times 10^{11}$ cm$^{-2}$ eV$^{-1}$

LaLuO$_3$/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), $\kappa \sim 23$
Lattice mismatch engineering

\[
a_{Y_2O_3} = 1.061 \text{ nm} \\
a_{La_2O_3} = 1.141 \text{ nm} \\
2*a_{GaAs} = 1.130 \text{ nm}
\]

Adjust lattice parameters to get perfect lattice match

- **Metal amidinate precursor for ALD \(Y_2O_3\)**
  - Yttrium tris(\(N,N'\)-diisopropylacetamidinate) or \(Y(\text{Pr}_2\text{-amd})_3\)
  - White solid, less volatile

- **ALD LaYO\(_3\) @300 °C**

<table>
<thead>
<tr>
<th>Subcycle ratio (La_2O_3 : Y_2O_3)</th>
<th>Composition (La_{1.7}Y_{0.3}O_3)</th>
<th>Lattice mismatch</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0</td>
<td>(La_2O_3)</td>
<td>+0.8%</td>
</tr>
<tr>
<td><strong>3:1</strong></td>
<td><strong>(La_{1.7}Y_{0.3}O_3)</strong></td>
<td><strong>0</strong></td>
</tr>
<tr>
<td>1:2</td>
<td>(La_1Y_1O_3)</td>
<td>-2.5%</td>
</tr>
<tr>
<td>0:1</td>
<td>(Y_2O_3)</td>
<td>-6%</td>
</tr>
</tbody>
</table>
Summary

- **Substrate-dependent structures of ALD LaLuO$_3$**
  - Epitaxy on GaAs(111)A
  - Poly. on GaAs(100)
  - Amorph. on Si

- **Promising electrical properties of epi-LaLuO$_3$/GaAs(111)A**
  - High $\kappa$ and low $D_{it}$
  - Fermi-level is unpinned

- **Lattice mismatch engineering**
  - La$_{1.7}$Y$_{0.3}$O$_3$ 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.