ALD Capabilities at MRC UT Austin

Marylene Palard *, J. H. Yum, T. Akyol, B Fallahazad, E Tutuc, J Lee, S Banerjee

*Research associate, MRC NNIN coordinator
ALD reactors at MRC – Savannah-100

Savannah-100 Cambridge ALD (2007)

• Precursors – as Nov 2012

0= water  
1= trimethyl Al (TMA). RT

2= MgO- amidinate (2-28-10)  
3= BeO (Liquid 2-6-12)  
Patent  
4= tetrakis(dimethylamino) Hf TDMHf. 115C. - 0.97Å/cycle

5= ammonia gas

• N2 carrier
ALD reactors at MRC – Savannah-xxx

Savannah Cambridge ALD (2009)

0= water  1= Al – 0.92A/cycle  2= Hf  3= La -150C

Pure La2O3 absorbs moisture quickly, so LaAlO is preferred.

4= Zr. 73C - 0.9A/cycle  ZrO2 did not form good interface with III-V.

ZrAlO was preferred instead.

5= ammonia

• N2 carrier
ALD reactors at MRC - Fiji

Fiji ALD Cambridge (2010)

- Precursors:
  0 = water
  1 = Al
  2 = Ti (TDMAT) - 75°C
  3 = Hafnium (TDMHf) - 115°C
  4 = Empty. (Set up for low vapor pressure precursor, w/ extra carrier gas input)
- ICP RF plasma assisted source gases: Ar, N2, H2, NH3, O2
- Ozone generator
- Ar carrier
Al₂O₃ on Si

- Precursors: H₂O/TMA
- Chamber temperature: 250/200 °C
- Substrate: lightly doped p-Si (10-20 Ω·cm). HF cleaned

MOS test structure to characterize the Al₂O₃ deposited by ALD

![Graph showing thickness vs. number of deposition cycles]

![Graph showing capacitance vs. voltage for different frequencies]
**Al₂O₃ on Si: Dielectric Constant (k)**

![Diagram showing the model for calculating the dielectric constant](image)

**Model**

\[ C^{-1} = C^{-1}_{\text{int}} + \frac{t_{\text{Al₂O₃}}}{k \cdot \varepsilon_0} \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric constant (k)</td>
<td>8.4</td>
</tr>
<tr>
<td>(C_{\text{it}}) ((\mu F/cm^2))</td>
<td>4.14</td>
</tr>
</tbody>
</table>
Al$_2$O$_3$ on Graphene

- A nucleation layer is required for ALD of dielectrics on graphene
- The nucleation layer has a significant impact on the dielectric constant and morphology of the subsequently grown ALD dielectric

B. Fallahazad et al, Appl. Phys. Lett. 100, 093112 (2012);
HfO$_2$ on Graphene

- Top dielectric stack
  - Interface: Oxidized Al (15Å)
  - Precursor: H$_2$O/TEMAH
  - Chamber Temperature: 200/200 °C

Dielectric Constant ($k$): 16

TEMAH: Tetrakis(EthylMethylamino)Hafnium
ALD of AlN?

- Precursors: TDMAA/Ammonia
- Temperature: 200-300 C
- Deposition rate: very low (less than 0.1Å /cycle)
- Deposited film very leaky

TDMAA: Tris(DimethylAmido)Aluminum
ALD BeO precursor synthesis

Dimethylberyllium (solid)  Diethylberyllium (liquid)

- As-received
- Be(CH₃)₂
- Et₂O

Black: measured
Red: simulated

Grinard metathesis:
BeCl₂ + 2CH₃MgBr → Be(CH₃)₂ + 2BrCl
Ether (solvent): C₂H₅OC₂H₅
(very stable liquid)

- ALD BeO precursors were successfully synthesized.
- After multiple rounds of sublimation, ether impurities were much reduced.
Successful Deposition of ALD BeO

(a) Raman spectrum, (b) XPS of Be 1s, (c) XPS of C 1s.

- From Raman and XPS, ALD BeO film is successfully deposited.
- ALD BeO shows slightly higher carbon impurities due to low quality of synthesis.
TEM images of ALD BeO Film

- As-grown ALD BeO on Si and GaAs shows high crystallinity.
- ALD BeO shows a relatively distinct interface.
TEM images of ALD BeO Film

ALD BeO on Ge substrate

- As-grown ALD BeO on Ge shows high crystallinity.
- ALD BeO shows a relatively distinct interface.
ALD BeO shows negligible frequency dispersion and hysteresis.
The dielectric constants of the BeO film are $k = 6.5$ before annealing and $k = 6.8$ after annealing.
The Al$_2$O$_3$ dielectric constant changes significantly by annealing, from $k = 6.4$ to 7.2.
NMOSFETs $I_d$-$V_g$ characteristics of SiO$_2$/HfO$_2$, Al$_2$O$_3$/HfO$_2$, and BeO/HfO$_2$ gate stacks.

- With the slightly lower EOT, the BeO/HfO$_2$ stack exhibits more positive $V_{th}$ (0.66 V), higher drive current at $V_g = 2$ V.
- From literature, interface charge (including interface trapped charge and interface fixed charge) is “+” value. So BeO IPL may reduce the interface charge and result in a higher threshold voltage.
Si MOSFETs characteristics

I_d-V_d characteristics of SiO_2/HfO_2, Al_2O_3/HfO_2 and BeO/HfO_2 gate stacks.

- BeO/HfO_2 gate stack shows significant increased drive current compared to SiO_2/HfO_2 and Al_2O_3/HfO_2 gate stacks.
# Conclusions

## BeO vs Al₂O₃ vs HfO₂

<table>
<thead>
<tr>
<th></th>
<th>BeO</th>
<th>Al₂O₃</th>
<th>HfO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Thermal stability</td>
<td>Better</td>
<td>Middle</td>
<td>Poor</td>
</tr>
<tr>
<td>2. $E_g$ &amp; $\Delta E_c$</td>
<td>Larger</td>
<td>(8.5eV, &lt;1.9eV)</td>
<td>Lower</td>
</tr>
<tr>
<td>(10.6eV, 2.3eV)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Diffusion barrier</td>
<td>Better</td>
<td>Middle</td>
<td>Poor</td>
</tr>
<tr>
<td>4. Self-cleaning effect</td>
<td>Better</td>
<td>Middle</td>
<td>Poor</td>
</tr>
<tr>
<td>5. Structural defects</td>
<td>lower</td>
<td>middle</td>
<td>Larger</td>
</tr>
<tr>
<td>6. Orbitals</td>
<td>No filled “P” orbital</td>
<td>“P” orbital</td>
<td>“d” orbital</td>
</tr>
<tr>
<td>7. Thermal conductivity</td>
<td>High</td>
<td>Poor</td>
<td>Poor</td>
</tr>
</tbody>
</table>

Energy bandgap↑ $\rightarrow$ Quantum tunneling current↓ $\rightarrow$ Defect generation↓
Cation and Anion similar $\rightarrow$ Stacking fault energy↓ $\rightarrow$ Intrinsic defects↓
Temperature ↑ $\rightarrow$ Phonon scattering ↑ $\rightarrow$ Thermal conductivity ↓
Bonding distance ↓ $\rightarrow$ Orbital splitting ↑ $\rightarrow$ Energy bandgap↑(10.6eV)
Bonding distance ↓ $\rightarrow$ Binding energy ↑ $\rightarrow$ High melting point