Choice of ALD Precursors for Microelectronics and Nanoelectronics

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We review ALD processes that are applicable to the scaling of microelectronic devices to smaller dimensions, as well as to potential structures for future nanoelectronics. Effective candidate materials are given (in parenthesis) for each of the functions listed below:

High-k dielectric on Si (GdScO₃)

High-k dielectric on Ge (HfOₓNᵧ)

High-k dielectric on GaAs (GdₓGa₁₋ₓO₃)

High-k dielectric on noble metals (Ta₂O₅)

Thermally stable metal gates (HfN, TaN)

Replacement metal gates (Ru, WN, CoSi₂, NiSi)

Source/drain contacts (CoSi₂, NiSi)

Pre-metal dielectric (carbon-doped silica)

Sealing the surfaces of porous low-k dielectrics (carbon-doped silica)

Copper diffusion barriers (WN)

Copper adhesion layers (Ru, Co)

Copper seed layers (Cu)

MRAM (Fe, Co, Ni, Ru, MgO)

Insulation for through-die interconnects (doped SiO₂)

Coaxial gated transistors on single-walled carbon nanotubes (any high-k/metal combination, following non-covalent functionalization with NO₂)

The most effective ALD precursors will be discussed for each of these applications. The considerations for each choice are volatility, thermal stability, reactivity, melting point and scalability of chemical synthesis.
Choice of ALD Precursors for Microelectronics and Nanoelectronics

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Outline

High-k Dielectrics

More Stable Precursors for Zirconium and Hafnium

First Precursors for ALD of GdScO$_3$

Interconnects

ALD / CVD Ruthenium Glue Layers

ALD Copper Seed Layers

Electroplating on Cu / Ru / WN
Why More Stable Hf and Zr Precursors?

High-k HfO$_2$ or ZrO$_2$ with very low electrical leakage is needed

Carbon impurity in films increases leakage

Thermal decomposition of organic precursors adds C to films

Thermal decomposition destroys uniformity and conformance

Deposition $T \sim 400$ °C needed for HfAlO$_x$ with ALD Al$_2$O$_3$

Known Hf precursors decompose too quickly (except HfCl$_4$, which makes non-conformal films)
Synthesis of Hf Tetra-Amidinates

Couple methylamine with an alkylnitrile and deprotonate with butyllithium:

\[ 2 \text{H}_2\text{NCH}_3 + \text{RCN} \xrightarrow{1) \text{La(CF}_3\text{SO}_3)_3} \xrightarrow{2) \text{BuLi}} \text{H}_3\text{C}-\text{N} = \text{N}-\text{CH}_3 \]

React the lithium salt with hafnium chloride:

\[ \text{H}_3\text{C}-\text{N} \equiv \text{N}-\text{CH}_3 + \text{HfCl}_4 \rightarrow \]

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Structure of a Zr Tetra-Amidinate

X-ray structure of Zr(isobutyl$_2$-amd)$_4$
Properties of a Hf Amidinate

TG data for Hf(\(\text{Me}_2\text{-amd}\))_4

High thermal stability:
No residue after TG
No change of NMR after heating at 250 °C for 1 week
Melting Points of Hf Amidinates

<table>
<thead>
<tr>
<th>R</th>
<th>Melting Point, °C</th>
<th>TG T½ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>171</td>
<td>221</td>
</tr>
<tr>
<td>CH₂CH₃</td>
<td>80</td>
<td>251</td>
</tr>
<tr>
<td>CH₂CH₂CH₃</td>
<td>&lt;20</td>
<td>246</td>
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</tbody>
</table>

⇒ R = CH₃ (methyl) is the most volatile; soluble in hydrocarbons for use in direct liquid injection

⇒ R = CH₂CH₂CH₃ (propyl) is a liquid Hf precursor

ALD experiments in progress
Advantages of GdScO$_3$ as high-$\kappa$ dielectric

- High dielectric constant ($k \approx 22$) for amorphous phase
- Sharp interface with silicon, and no low-k interlayer
- Stays amorphous and doesn’t form alloys with Si or Ge after respective S/D activation processes
- Conduction band offset w.r.t Si is about 2-2.5eV, helping to achieve low leakage
Amidinate Precursors for Gd and Sc

The $R^n$ are typically alkyl groups: ethyl, isopropyl, etc.

The choices of $R^n$ affect the reactivity, stability and volatility.
Some Amidinate Ligands

- tert-butyl$_2$-acetamidinate
- isopropyl$_2$-acetamidinate
- ethyl-tert-butyl-acetamidinate
- n-propyl$_2$-acetamidinate

Increasing ligand bulk
## Structures of Metal(III) Amidinates

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Al</th>
<th>Ga</th>
<th>Cr</th>
<th>V</th>
<th>Ti</th>
<th>Ru</th>
<th>Sc</th>
<th>Lu</th>
<th>Y</th>
<th>Gd</th>
<th>Pr</th>
<th>La</th>
<th>Bi</th>
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<tbody>
<tr>
<td>tert-butyl₂</td>
<td>c</td>
<td>m</td>
<td>m</td>
<td>m</td>
<td>m</td>
<td>m</td>
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<td>m</td>
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<td>m</td>
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<tr>
<td>isopropyl₂</td>
<td>m</td>
<td>m</td>
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<tr>
<td>Et-tert-Bu</td>
<td>m</td>
<td>m</td>
<td>m</td>
<td>m</td>
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<td>m</td>
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<td>m</td>
</tr>
<tr>
<td>n-propyl₂</td>
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<td>m</td>
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<td>m</td>
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<td>m</td>
<td>m</td>
<td>d</td>
<td>m</td>
<td>d</td>
<td>d</td>
<td>m</td>
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</tr>
</tbody>
</table>

Increasing size of metal atom →

- c = too crowded to make
- m = monomer
- d = dimer

=> Can’t make precursor if ligands are too bulky for a metal
=> Dimers are nearly as volatile as monomers
### Reactivity of Metal(III) Amidinates with $H_2O$

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Al</th>
<th>Ga</th>
<th>Cr</th>
<th>V</th>
<th>Ti</th>
<th>Ru</th>
<th>Sc</th>
<th>Lu</th>
<th>Y</th>
<th>Gd</th>
<th>Pr</th>
<th>La</th>
<th>Bi</th>
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<tbody>
<tr>
<td>$tert$-butyl$_2$</td>
<td>n</td>
<td>n</td>
<td>n</td>
<td>n</td>
<td>n</td>
<td>n</td>
<td>n</td>
<td>n</td>
<td>n</td>
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<tr>
<td>isopropyl$_2$</td>
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<td>s</td>
<td>s</td>
<td>s</td>
<td>s</td>
<td>r</td>
<td>r</td>
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<td>r</td>
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<td>r</td>
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<tr>
<td>Et-^t^Bu</td>
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<td>r</td>
<td>r</td>
<td></td>
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</tr>
<tr>
<td>$n$-propyl$_2$</td>
<td></td>
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<td></td>
<td>r</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

- **n** = no reaction
- **s** = slow reaction
- **r** = rapid reaction

Increasing size of metal atom →

=> Too bulky ligands slow or stop reactions
Precursors for GdScO₃ ALD

Tris-diisopropylacetamidinato Gadolinium (III)

\[ \text{Gd}(\text{N}_2\text{C}_8\text{H}_{17})_3 \quad \text{Gd}^{(\text{iPr-amd})}_3 \]

Bubbler Temp. : 140 °C
Thermally Stable to 320 °C

Both precursors nucleate well on hydrogenated Si surfaces and show high reactivity with H₂O.
No need for chemical oxide interlayer to initiate growth

Tris-diethylacetamidinato Scandium (III)

\[ \text{Sc}(\text{N}_2\text{C}_6\text{H}_{13})_3 \quad \text{Sc}^{(\text{Et-amd})}_3 \]

Bubbler Temp. : 140 °C
Thermally Stable to 350 °C

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**ALD of GdScO₃ films**

1 cycle:

<table>
<thead>
<tr>
<th></th>
<th>Sc</th>
<th>Purge</th>
<th>H₂O</th>
<th>Purge</th>
<th>Gd</th>
<th>Purge</th>
<th>H₂O</th>
<th>Purge</th>
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</thead>
<tbody>
<tr>
<td>time</td>
<td>6s</td>
<td>15s</td>
<td>4s</td>
<td>40s</td>
<td>6s</td>
<td>15s</td>
<td>4s</td>
<td>40s</td>
</tr>
</tbody>
</table>

- Flow-through type tube reactor
- Substrate temperature 310 °C
- Linear growth rate ~ 2.0 Å/cycle
- Slight inhibition (~10 cycles) on HF-last Si
Structural Properties of GdScO$_3$ Films

- XRD and TEM indicate the films are amorphous as deposited and stay amorphous up to 950 °C

- Stoichiometry of a 25nm thick film by RBS: Gd$_{1}$Sc$_{1.07}$O$_3$ with 1:1 dosing of Gd and Sc

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Advantages of WN as a Gate Metal

- Excellent diffusion barrier for oxygen and metal atoms
- Can be etched easily
- Good thermal stability
- Good adhesion to oxides as well as metals
ALD of Tungsten Nitride, WN

- Precursor: Bis(tert-butylimido)bis-(dimethylamido)tungsten(VI)
- Vapor pressure ~ 37 mTorr at 30 °C
- Liquid at room temperature
- NH₃ gas is used as a co-reactant
- Growth Rate at 385 °C ~ 2.0 Å / cycle
- Resistivity of W after anneal > 750 °C ~ 10⁻⁴ Ω-cm

Films are very uniform over a wide area.

GdScO$_3$ is amorphous as deposited.

Interfaces are sharp and smooth.
Electrical Properties of a Low EOT Film

WN / GdScO$_3$ / Si (100) Capacitors

- EOT ~ 1 nm
- Flatband Voltage ~ +0.35 V
- Hysteresis $\Delta V < 60$ mV
- Leakage Current density at 1V ~ $10^{-3}$ A/cm$^2$

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Equivalent Oxide Thickness vs. Physical Thickness

\[ \kappa \approx 21.5, \text{ interfacial layer } \approx 1.5 \, \text{Å} \]
Fixed Charge Density and Work Function of WN

- Fixed Charge Density $\sim 2.4 \times 10^{11}$ cm$^{-2}$
- Work Function of WN $\sim 4.6$ eV (midgap metal)
Interface Trap Density by Conductance Method

- Interface Trap Density $\approx 2.8 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$
Leakage Current vs. EOT

- leakage current $\sim 10^{-3}$ A cm$^{-2}$ at EOT = 1 nm
- leakage current $\sim 10^{-7}$ A cm$^{-2}$ at EOT = 2 nm
- $\sim 10^4$ times lower than SiO$_2$
Summary of GdScO$_3$

- Ultrathin amorphous GdScO$_3$ films were deposited on HF-last Si substrates by ALD using Gd and Sc amidinate precursors.
- ALD WN / GdScO$_3$ gate stacks show promising electrical properties for future MOSFET and DRAM applications
  - High $\kappa$ (k~ 21.5) and Low EOT (~ 1 nm)
  - Low leakage current ( < 10$^{-3}$ A/cm$^2$ at 1V for EOT ~ 1 nm)
  - Reasonably low fixed charge and interface trap density
Outline of Cu / Ru / WN for Interconnects

Ru(amidinate) precursor
  structure
  deposition conditions

Properties of Ruthenium films
  conformal and complete coverage
  smooth surface
  low resistance
  strong adhesion to WN

Copper seed layers
  conformal and complete coverage
  low resistance
  electrochemical deposition of Cu
  survive CMP of Cu
Motivation for using Ruthenium or Cobalt instead of Tantalum as an adhesion layer

Tantalum has low adhesion to CVD or ALD copper

Ta, Ru and Co all have these required properties:

• **Low solubility in copper**

• **Strong interfacial adhesion to copper**
  - Ta $>6 \text{ J m}^{-2}$
  - Ru $\sim4 \text{ J m}^{-2}$
  - Co $>30 \text{ J m}^{-2}$

• **Low electrical resistivity**
  - Ta $13.4 \mu\Omega\cdot\text{cm}$
  - Ru $7.4 \mu\Omega\cdot\text{cm}$
  - Co $5.8 \mu\Omega\cdot\text{cm}$
Ru Precursor Ru(\textsuperscript{t}Bu-amd\textsubscript{2})(CO\textsubscript{2})

Chemical formula

Molecular structure by x-ray crystallography

- vapor pressure >0.05 Torr at 130 °C
- low evaporation residue 0.14% by TG
- air and moisture stable
ALD/CVD of Ru

Conditions:

- Bubbler: 130 °C
- Substrate: 200 - 300 °C
- co-reactant: NH₃
- Pressure: 1 ~ 2 Torr
- ~1.5 Angstrom/cycle at 300 °C
- No saturation of growth/cycle

=> Mostly surface controlled CVD, only partly ALD

\[
\text{Ru}^{t}\text{Bu-amd)}_2(\text{CO})_2 \rightarrow \text{Ru} + \text{N} \quad \text{N} \quad \text{N} + 2 \text{CO}
\]
High Conformality of ALD/CVD Ru/WN/SiO2

> 2% rms roughness

Smooth films: by AFM

80% conformal in trench with 40:1 aspect ratio

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Electrical Conductivity of CVD Ru / SiO₂

Conductivity matches pure Ru films sputtered onto Ta

Grain Boundary Scattering Model

\[ \rho/\rho_0 = 1 + 1.5\{R/(1-R)\} \left( \frac{\lambda}{g} \right) \]

where the average grain size \( g \) is estimated as the film thickness scattering coefficient for electrons at grain boundaries \( R = 0.58 \)

bulk scattering length \( \lambda = 10 \text{ nm} \)

bulk resistivity \( \rho_0 = 7.1 \mu\Omega\text{-cm} \)
2 nm ALD/CVD Ru completely covers WN

- no pinholes seen by vertical TEM:
- an etch solution $\text{H}_2\text{O}_2/\text{NH}_4\text{OH}$, which normally dissolves a WN film within one minute, does not etch the WN under a 2 nm Ru film even after one hour.
- Ru films are strongly adherent to freshly-deposited WN adhesion energy $\sim 4 \text{ J/m}^2$ by 4-point bend test.
Nucleation of Cu(3nm) on Ru(2nm) / WN(3nm) / Si₃N₄

Vertical TEM shows complete coverage

Chemical test for completeness of coverage by copper:
Ru catalyzes $\text{H}_2\text{O}_2$ decomposition rapidly forming bubbles of oxygen
Cu bubbles very slowly
Cu / Ru also bubbles very slowly

Electrical Resistance of ALD Cu on Ru

Continuous layer just 3 Cu atoms thick!

Grain Boundary Scattering Model

\[ \frac{\rho}{\rho_0} = 1 + 1.5 \frac{R}{(1-R)} \left( \frac{\lambda}{g} \right) \]

where the average grain size \( g \) is estimated as the film thickness scattering coefficient for electrons at grain boundaries \( R = 0.3 \)

bulk scattering length \( \lambda = 39 \) nm

bulk resistivity \( \rho_0 = 1.7 \, \mu\Omega\cdot\text{cm} \)

ALD Cu resistivity matches pure sputtered Cu films


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Conformality and Sheet Resistance of Cu / Ru / WN

SEM of copper film at bottom of hole with aspect ratio 40:1 and > 90% step coverage

Cu(3nm)/Ru(2nm)/WN(2nm) has sheet resistance ~ 50 Ω/sq

Suitable for electroplating

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Cross Section of Electroplated Cu/Ru/WN/SiO$_2$

Electroplated by Tom P. Moffat
CMP by Christian Witt
SEM by Daniel Josell, NIST

=> Adhesion strong enough to survive CMP
Interconnect Summary

ALD of SiO$_2$ pore sealant / WN barrier / Ru glue / Cu seed

- Extendable to the end of the roadmap
- No deposition on chamber walls $\Rightarrow$ no chamber cleaning
- No plasma damage to substrates
- Simplified equipment design because no plasma needed
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TEM: Damon Farmer; SEMATECH

Adhesion measurements: Joost Vlassak, Youbo Lin

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In-situ Deposited WN Gate vs. Ex-situ Deposited Pt Gate

- **In-situ** WN gate stack shows 18% increase in capacitance

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