Overview of ALD Precursors and Reaction Mechanisms

The Harvard community has made this article openly available. Please share how this access benefits you. Your story matters

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Citable link</td>
<td><a href="http://nrs.harvard.edu/urn-3:HUL.InstRepos:9639954">http://nrs.harvard.edu/urn-3:HUL.InstRepos:9639954</a></td>
</tr>
<tr>
<td>Terms of Use</td>
<td>This article was downloaded from Harvard University’s DASH repository, and is made available under the terms and conditions applicable to Other Posted Material, as set forth at <a href="http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#LAA">http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#LAA</a></td>
</tr>
</tbody>
</table>
Overview of ALD Precursors and Reaction Mechanisms

Roy G. Gordon

Department of Chemistry and Chemical Biology,
Harvard University, Cambridge, MA 02138, U.S.A.

Abstract

Successful use of ALD requires suitable chemical precursors used under reaction conditions that are appropriate for them. There are many requirements for ALD precursors: sufficient volatility, thermal stability and reactivity with substrates and with the films being deposited. In addition, it is easier to produce the required vapors if the precursor is liquid at room temperature, or if it is a solid with melting point below the vaporization temperature, or if it is soluble in an inert solvent with vapor pressure similar to that of the precursor. The precursor vapor should not etch or corrode the substrate or deposited film. Ideally, the precursors should be non-flammable, non-corrosive, non-toxic, simple and non-hazardous to make and inexpensive.

Presenting Author: Roy G. Gordon (gordon@chemistry.harvard.edu)
Introduction to ALD Precursors and Reaction Mechanisms
Outline

• Elements and Materials in ALD Films
• ALD Precursors for Non-Metals
• Types of ALD precursors for Metals
• Types of ALD Reactions
ELEMENTS AND MATERIALS IN ALD FILMS
<table>
<thead>
<tr>
<th></th>
<th>Symbol</th>
<th>Name</th>
<th>Symbol</th>
<th>Name</th>
<th>Symbol</th>
<th>Name</th>
<th>Symbol</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>Ag</td>
<td>Europium</td>
<td>Eu</td>
<td>Manganese</td>
<td>Mn</td>
<td>Antimony</td>
<td>Sb</td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>Al</td>
<td>Fluorine</td>
<td>F</td>
<td>Molybdenum</td>
<td>Mo</td>
<td>Scandium</td>
<td>Sc</td>
<td></td>
</tr>
<tr>
<td>Argon</td>
<td>Ar</td>
<td>Iron</td>
<td>Fe</td>
<td>Nitrogen</td>
<td>N</td>
<td>Selenium</td>
<td>Se</td>
<td></td>
</tr>
<tr>
<td>Arsenic</td>
<td>As</td>
<td>Gallium</td>
<td>Ga</td>
<td>Sodium</td>
<td>Na</td>
<td>Silicon</td>
<td>Si</td>
<td></td>
</tr>
<tr>
<td>Gold</td>
<td>Au</td>
<td>Gadolinium</td>
<td>Gd</td>
<td>Neodymium</td>
<td>Nd</td>
<td>Tin</td>
<td>Sn</td>
<td></td>
</tr>
<tr>
<td>Boron</td>
<td>B</td>
<td>Germanium</td>
<td>Ge</td>
<td>Nickel</td>
<td>Ni</td>
<td>Strontium</td>
<td>Sr</td>
<td></td>
</tr>
<tr>
<td>Barium</td>
<td>Ba</td>
<td>Hydrogen</td>
<td>H</td>
<td>Neon</td>
<td>Ne</td>
<td>Tantalum</td>
<td>Ta</td>
<td></td>
</tr>
<tr>
<td>Beryllium</td>
<td>Be</td>
<td>Helium</td>
<td>He</td>
<td>Nickel</td>
<td>Ni</td>
<td>Terbium</td>
<td>Tb</td>
<td></td>
</tr>
<tr>
<td>Bromine</td>
<td>Br</td>
<td>Hafnium</td>
<td>Hf</td>
<td>Oxygen</td>
<td>O</td>
<td>Tellurium</td>
<td>Te</td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>C</td>
<td>Mercury</td>
<td>Hg</td>
<td>Osmium</td>
<td>Os</td>
<td>Thallium</td>
<td>Tl</td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca</td>
<td>Holmium</td>
<td>Ho</td>
<td>Phosphorus</td>
<td>P</td>
<td>Thulium</td>
<td>Tm</td>
<td></td>
</tr>
<tr>
<td>Cadmium</td>
<td>Cd</td>
<td>Iodine</td>
<td>I</td>
<td>Lead</td>
<td>Pb</td>
<td>Titanium</td>
<td>Ti</td>
<td></td>
</tr>
<tr>
<td>Cerium</td>
<td>Ce</td>
<td>Indium</td>
<td>In</td>
<td>Palladium</td>
<td>Pd</td>
<td>Tungsten</td>
<td>W</td>
<td></td>
</tr>
<tr>
<td>Chlorine</td>
<td>Cl</td>
<td>Iridium</td>
<td>Ir</td>
<td>Praseodymium</td>
<td>Pr</td>
<td>Vanadium</td>
<td>V</td>
<td></td>
</tr>
<tr>
<td>Cobalt</td>
<td>Co</td>
<td>Potassium</td>
<td>K</td>
<td>Platinum</td>
<td>Pt</td>
<td>Xenon</td>
<td>Xe</td>
<td></td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr</td>
<td>Krypton</td>
<td>Kr</td>
<td>Rubidium</td>
<td>Rb</td>
<td>Xenon</td>
<td>Xe</td>
<td></td>
</tr>
<tr>
<td>Cesium</td>
<td>Cs</td>
<td>Lanthanum</td>
<td>La</td>
<td>Rhenium</td>
<td>Re</td>
<td>Yttrium</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>Lithium</td>
<td>Li</td>
<td>Rhodium</td>
<td>Rh</td>
<td>Ytterbium</td>
<td>Yb</td>
<td></td>
</tr>
<tr>
<td>Dysprosium</td>
<td>Dy</td>
<td>Lutetium</td>
<td>Lu</td>
<td>Ruthenium</td>
<td>Ru</td>
<td>Zinc</td>
<td>Zn</td>
<td></td>
</tr>
<tr>
<td>Erbium</td>
<td>Er</td>
<td>Magnesium</td>
<td>Mg</td>
<td>Sulfur</td>
<td>S</td>
<td>Zirconium</td>
<td>Zr</td>
<td></td>
</tr>
</tbody>
</table>
### Periodic Table

<table>
<thead>
<tr>
<th>Period</th>
<th>Main Group Metals</th>
<th>Transition Metals</th>
<th>Actinides</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Alkali Metals</td>
<td></td>
<td>Ce</td>
</tr>
<tr>
<td>2</td>
<td>Alkaline Earth Metals</td>
<td></td>
<td>Pr</td>
</tr>
<tr>
<td></td>
<td>Metals</td>
<td></td>
<td>Nd</td>
</tr>
<tr>
<td>12</td>
<td>Alkaline Earth Metals</td>
<td></td>
<td>Pm</td>
</tr>
<tr>
<td>13</td>
<td>Halogens</td>
<td></td>
<td>Sm</td>
</tr>
<tr>
<td>14</td>
<td>Metalloids or Semi-metals</td>
<td></td>
<td>Eu</td>
</tr>
<tr>
<td>15</td>
<td>Metals</td>
<td></td>
<td>Gd</td>
</tr>
<tr>
<td>16</td>
<td>Metalloids or Semi-metals</td>
<td></td>
<td>Tb</td>
</tr>
<tr>
<td>17</td>
<td>Non-metals</td>
<td></td>
<td>Dy</td>
</tr>
<tr>
<td>18</td>
<td>Halogens</td>
<td></td>
<td>Dy</td>
</tr>
</tbody>
</table>
Elements in ALD Films

\[ \text{\(M\)} = \text{element in at least one ALD film} \]

Not used in ALD because the elements are

- \(\text{\(\)}\) = low-volatility compounds
- \(\text{\(\)}\) = radioactive
- \(\text{\(\)}\) = highly toxic
- \(\text{\(\)}\) = inert
Combinations of Elements in ALD Films

ALD films have been made with combinations of 2 or more elements within a box

Underlined elements have been deposited as pure, single elements

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>O</td>
<td>O</td>
<td>Te</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>O</td>
<td>F</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rb</td>
<td>O</td>
<td>F</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oxide dielectrics</th>
<th>Oxide conductors or semiconductors</th>
<th>Other ternary oxides</th>
<th>Nitride dielectrics or semiconductors</th>
<th>Metallic nitrides</th>
<th>II-VI semiconductors</th>
<th>II-VI based phosphors</th>
<th>III-V semiconductors</th>
<th>Fluorides</th>
<th>Elements</th>
<th>Other semiconductors</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALD Materials by Type</td>
<td>Al_2O_3, TiO_2, ZrO_2, HfO_2, Ta_2O_5, Nb_2O_5, Sc_2O_3, Y_2O_3, MgO, B_2O_3, SiO_2, GeO_2, La_2O_3, CeO_2, PrO_x, Nd_2O_3, Sm_2O_3, EuO, Gd_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, Yb_2O_3, Lu_2O_3, SrTiO_3, BaTiO_3, NaAlO_2, LaAlO_3, NdAlO_3, GdAlO_3</td>
<td>LaScO_3, LaLuO_3, LaYbO_3, Er_3GaO_13</td>
<td>CuO_x, FeO_x, CrO_x, CoO_x, MnO_x</td>
<td>LaCOO_3, LaNiO_3, LaMnO_3, La_xCa_yMnO_3</td>
<td>TiN, Ti-Si-N, Ti-Al-N, TaN, NbN, MoN, WN, CN, CoN, Sn N</td>
<td>ZnS:ZnSe, ZnTe, CaS, SrS, BaS, CdS, CdTe, MnTe, HgTe</td>
<td>GaAs, AIAs, InP, GaP, InAs</td>
<td>CaF_2, SrF_2, MgF_2, LaF_3, ZnF_2</td>
<td>Ru, Pt, Ir, Pd, Rh, Ag, Cu, Ni, Co, Fe, Mn, Ta, W, Mo, Ti, Al, Si, Ge</td>
<td>PbS, SnS, In_2S_3, Sb_2S_3, CuS, CuGaS_2, WSe_2, SiC, Ge, SnTe, Te</td>
<td>Na_2S_3, Y_2O_3, SiC, Ti_x, Ta_x, TaC, TC, TiC, WC, Ca_3(PO_4)_2, CaCO_3, organics</td>
</tr>
</tbody>
</table>

Adapted from M. Ritala and J. Niinisto, in Chemical Vapor Deposition (Royal Society of Chemistry, 2009)
ALD PRECURSORS FOR NON-METALS

- oxygen
- nitrogen
- fluorine, carbon
- sulfur, selenium, tellurium
- phosphorus, arsenic, antimony
Non-Metals Important in ALD Films

C = Carbon    N = Nitrogen    O = Oxygen    F = Fluorine
P = Phosphorus  S = Sulfur  Se = Selenium

<table>
<thead>
<tr>
<th>Non-Metals</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>He</td>
<td>Li</td>
<td>Be</td>
<td>B</td>
<td>C</td>
<td>N</td>
<td>O</td>
<td>F</td>
<td>Ne</td>
<td>Al</td>
<td>Si</td>
<td>P</td>
</tr>
<tr>
<td>Na</td>
<td>Mg</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>10</td>
<td>11</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>Ca</td>
<td>Sc</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
<td>Co</td>
<td>Ni</td>
<td>Cu</td>
<td>Zn</td>
<td>Ga</td>
</tr>
<tr>
<td>Rb</td>
<td>Sr</td>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
<td>Cd</td>
<td>In</td>
</tr>
<tr>
<td>Cs</td>
<td>Ba</td>
<td>La</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
<td>Hg</td>
<td>Tl</td>
</tr>
<tr>
<td>Fr</td>
<td>Ra</td>
<td>Ac</td>
<td>Rf</td>
<td>Db</td>
<td>Sg</td>
<td>Bh</td>
<td>Hs</td>
<td>Mt</td>
<td>Ds</td>
<td>Rg</td>
<td>Ce</td>
<td>Pr</td>
</tr>
<tr>
<td>Th</td>
<td>Pa</td>
<td>U</td>
<td>Np</td>
<td>Pu</td>
<td>Am</td>
<td>Cm</td>
<td>Bk</td>
<td>Cf</td>
<td>Es</td>
<td>Fm</td>
<td>Md</td>
<td>Lr</td>
</tr>
<tr>
<td>Er</td>
<td>Tm</td>
<td>Yb</td>
<td>Lu</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

13 | 14 | 15 | 16 | 17 | He | Ne | B | C | N | O | F | P | S | Cl | Ar | Br | Kr | I | Xe |
ALD Precursors for Oxygen

Water vapor, H₂O

Hydrogen peroxide, H₂O₂, sometimes more reactive than H₂O (always accompanied by water)

Alcohols, ROH, such as methanol CH₃OH or ethanol C₂H₅OH

Di-oxygen, O₂, the common form of oxygen in the air

Ozone, O₃, a more reactive form of oxygen, made in a plasma, can flow through tubing; (always accompanied by O₂)

Oxygen atoms, created in a plasma close to a substrate surface; so reactive that they can’t travel far through tubing without recombining to form O₂

Nitrogen dioxide, NO₂ (always accompanied by its dimer N₂O₄)
ALD Precursors for Nitrogen

Ammonia, NH$_3$

Hydrazine, N$_2$H$_4$, is more reactive than NH$_3$, but toxic & explosive

Plasma-activated NH$_3$ is more reactive than NH$_3$

Dinitrogen, N$_2$, is normally unreactive under ALD conditions

Plasma-activated N$_2$ is more reactive than N$_2$

Nitric oxide, NO, can be used for nitrogen-doping of oxides
ALD Precursors for Carbon

Acetylene gas \(\text{H--C\equiv C--H}\)

Formic acid vapor \(\text{H--COOH}\)

Carbon contained in a metal compound

ALD Precursors for Fluorine

Hydrogen fluoride gas, HF

Fluorine contained in a metal compound such as \(\text{WF}_6\)
ALD Precursors for Sulfur, Selenium and Tellurium

Elemental sulfur vapor, $S_n$

Hydrogen sulfide gas, $H_2S$ (poisonous, but sufficient warning by smell, if not chronically exposed)

Hydrogen selenide gas, $H_2Se$ (very poisonous, without sufficient warning by smell)

Bis(triethylsilyl)selenium, $(Et_3Si)_2Se$

Bis(triethylsilyl)tellurium, $(Et_3Si)_2Te$
ALD Precursors for Phosphorus, Arsenic and Antimony

phosphine gas, PH$_3$ (very poisonous)

arsine gas, AsH$_3$ (very poisonous)

antimony trichloride, SbCl$_3$

tris(dimethylamido)antimony
Elemental ALD Precursors

Examples:
Non-metals: O₂, P₄, S₂ or S₈
Metals: Mg, Mn, Zn

Advantage: high purity
Disadvantage: low volatility (metals)
TYPES OF ALD PRECURSORS FOR METALS

pure elements

metal hydrides

metal halides: fluorides, chlorides, bromides, iodides

metal-carbon bonds: alkyls, cyclopentadienyls

metal-oxygen bonds: alkoxides, beta-diketonates

metal-nitrogen bonds: amides, imides, amidinates
Metal Compounds for ALD

Most metal compounds used in ALD have 1 or 2 metal atoms, M, combined with 1 or more “ligands”, L, written as monomers ML_n or dimers M_2L_n, where n = 1, 2, 3, 4, 5 or 6.

The ligands, L, contain 1 or more non-metal atoms.

The metal atoms, M, may be considered to have >1 units of positive charge.

Metals with 1 unit of positive charge M^+ may be written M(I), and are said to be in oxidation state +1.

Metals with 2 units of positive charge M^{2+} may be written M(II), and are said to be in oxidation state +2, etc.

Most ligands used in ALD can be considered to have electrical charge -1. A few ligands, e.g. oxides (O^{2-}) and imides (NC_xH_{2x+1})^{2-}, have charge -2.

The total charges of the metal and ligands in a precursor must add to zero.
## Types of Metal Precursors for ALD

<table>
<thead>
<tr>
<th>Halides, where X = F, Cl, Br, I</th>
<th>Alkoxides</th>
<th>β-diketonates</th>
<th>Alkylimides</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="halide.png" alt="Halide Diagram" /></td>
<td><img src="alkoxide.png" alt="Alkoxide Diagram" /></td>
<td><img src="b-diketonate.png" alt="β-Diketonate Diagram" /></td>
<td><img src="alkylimide.png" alt="Alkylimide Diagram" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Alkylamides</th>
<th>Amidinates</th>
<th>Alkyls</th>
<th>Cyclopentadienyls</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="alkylamide.png" alt="Alkylamide Diagram" /></td>
<td><img src="amidinate.png" alt="Amidinate Diagram" /></td>
<td><img src="alkyl.png" alt="Alkyl Diagram" /></td>
<td><img src="cyclopentadienyl.png" alt="Cyclopentadienyl Diagram" /></td>
</tr>
</tbody>
</table>

R = alkyl group = C\textsubscript{n}H\textsubscript{2n+1}
Elements with Hydride ALD Precursors

Hydrides are compounds of an element X and hydrogen

$$XH_n \quad n = 1, 2, 3 \text{ or } 4$$
Examples of Hydride Precursors

SiH$_4$ = silane

Si$_2$H$_6$ = disilane, more reactive than silane

GeH$_4$ = germane

AlH$_3$ NMe$_3$ = aluminum hydride – trimethylamine

Advantage: very volatile

Disadvantages: usually need plasma activation, pyrophoric and toxic
Halides are compounds of an element M and a halogen $X = F, Cl, Br$ or $I$.

$MX_n$  $n = 1, 2, 3, 4, 5$ or $6$
Examples of Halide ALD Precursors

**WF$_6$** = tungsten hexafluoride

**TiCl$_4$** = titanium tetrachloride

**HfCl$_4$** = hafnium tetrachloride

**SnCl$_4$** = tin tetrachloride

Oxygen can be combined with halide ligands:

**VOCl$_3$** = trichlorooxovanadium
  = vanadium oxide trichloride
  = vanadyl trichloride

**CrO$_2$Cl$_2$** = dichlorodioxochromium
  = chromium dichloride dioxide
  = chromyl dichloride

**Advantages:**
thermally stable
usually inexpensive

**Disadvantages:**
halogen impurities in films
corrosive byproducts
low volatility for some elements

GeCl$_2$·dioxane
Metal Alkyl ALD Precursors

$(\text{CH}_3)_3\text{Al} = \text{trimethylaluminum}$

$(\text{CH}_3\text{CH}_2)_2\text{Zn} = \text{diethylzinc}$

**Advantage:** volatile, highly reactive in ALD

**Disadvantage:** hazardous, burst into flame in air (pyrophoric)

$i\text{Pr}_2\text{Te} = \text{diisopropyltellurium}$
Elements with Alkyl ALD Precursors

![Periodic Table](image-url)
Cyclopentadienyl Ligands

Cp = cyclopentadienyl

MeCp = methylcyclopentadienyl

Me₅Cp = Cp* = pentamethylcyclopentadienyl

EtCp = ethylcyclopentadienyl

iPrCp = isopropylcyclopentadienyl
Examples of Cyclopentadienyl Precursors

\[ \text{Cp}_2\text{Ni} = \text{bis(cyclopentadienyl)nickel(II)} \]

\[ (\text{EtCp})_2\text{Ru} = \text{bis(ethylcyclopentadienyl)ruthenium(II)} \]

\[ (\text{Me}_5\text{Cp})_2\text{Sr} = \text{bis(pentamethylcyclopentadienyl)strontium} \]

\[ (\text{iPrCp})_3\text{La} = \text{tris(isopropylcyclopentadienyl)lanthanum} \]

\[ \text{Cp}_2\text{Me}_2\text{Zr} = (\text{dicyclopentadienyl})(\text{dimethyl})\text{zirconium} \]

\[ (\text{MeCp})(\text{Me})_3\text{Pt} = (\text{methylcyclopentadienyl})(\text{trimethyl})\text{platinum(IV)} \]
## Cyclopentadienyl ALD Precursors

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>He</td>
</tr>
<tr>
<td>Li</td>
<td>B</td>
</tr>
<tr>
<td>Na</td>
<td>Al</td>
</tr>
<tr>
<td>K</td>
<td>Si</td>
</tr>
<tr>
<td>Rb</td>
<td>Cl</td>
</tr>
<tr>
<td>Cs</td>
<td>Ar</td>
</tr>
<tr>
<td>Fr</td>
<td>Ne</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>Ca</td>
<td>Sc</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
<td>Co</td>
<td>Ni</td>
</tr>
<tr>
<td>Sr</td>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
</tr>
<tr>
<td>Ba</td>
<td>La</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
</tr>
<tr>
<td>Ra</td>
<td>Ac</td>
<td>Rf</td>
<td>Db</td>
<td>Sg</td>
<td>Bh</td>
<td>Hs</td>
<td>Mt</td>
<td>Ds</td>
<td>Rg</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
</tr>
<tr>
<td>Ga</td>
<td>Ge</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
</tr>
<tr>
<td>In</td>
<td>Sn</td>
<td>Sb</td>
<td>Te</td>
<td>I</td>
</tr>
<tr>
<td>Sn</td>
<td>Sb</td>
<td>Te</td>
<td>I</td>
<td>Xe</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
</tr>
</tbody>
</table>

### Advantages:
- thermally stable

### Disadvantages:
- some have low reactivity (Ni, Ru)
- some are solids (Ni, Sr, Mg, In, La)
- some have low volatility (La, Sr, Mg)
Alkoxide Compounds

OMe = methoxy

OEt = ethoxy

OiPr = isopropoxy

OiBu = isobutoxy

OisBu = sec-butoxy

O\textsuperscript{t}Bu = \textit{tert}-butoxy

O\textsuperscript{t}Pe = \textit{tert}-pentoxy

mmp = 1-methoxy-2-methyl-2-propoxy

dmae = dimethylamino-ethoxy

dmamp = 1-dimethylamino-2-methyl-2-propoxy
Alkoxide Compounds Used in ALD

\[ \text{Al(OEt)}_3 = \text{tris(ethoxy)aluminum} = \text{aluminum ethoxide} \]

\[ \text{AlMe}_2(\text{OiPr}) = \text{isopropoxydimethylaluminum} \]

\[ \text{B(OMe)}_3 = \text{tris(methoxy)boron} = \text{trimethylborate} \]

\[ \text{Hf(O}^\text{tBu})_4 = \text{tetra(tert-butoxy)hafnium} = \text{hafnium tert-butoxide} \]

\[ \text{Hf(mmp)}_4 = \text{tetra(1-methoxy-2-methyl-2-propoxy)hafnium} \]

\[ \text{Nb(OEt)}_5 = \text{penta(ethoxy)niobium} = \text{niobium ethoxide} \]

\[ \text{Ni(dmamp)}_2 = \text{bis(1-dimethylamino-2-methyl-2-propoxy)nickel(II)} \]

\[ \text{Pb(O}^\text{tBu})_2 = \text{bis(tert-butoxy)lead(II)} = \text{lead(II) tert-butoxide} \]

\[ \text{Si(OEt)}_4 = \text{tetra(ethoxy)silane} = \text{tetraethyl orthosilicate} = \text{TEOS} \]

\[ \text{Si(O}^\text{iBu})_3\text{OH} = \text{tris(tert-butoxy)silanol} \]

\[ \text{Si(O}^\text{iPe})_3\text{OH} = \text{tris(tert-pentoxy)silanol} \]

\[ \text{Ta(OEt)}_5 = \text{penta(ethoxy)tantalum} = \text{tantalum ethoxide} \]

\[ \text{Ti(OMe)}_4 = \text{tetra(methoxy)titanium} = \text{titanium methoxide} \]

\[ \text{Ti(OEt)}_4 = \text{tetra(ethoxy)titanium} = \text{titanium ethoxide} \]

\[ \text{Ti(O}^\text{iPr})_4 = \text{tetra(isopropoxy)titanium} = \text{titanium isopropoxide} \]

\[ \text{VO(O}^\text{iPr})_3 = \text{tris(isopropoxy)oxovanadium} = \text{vanadyl isopropoxide} \]
## Elements with Alkoxide ALD Precursors

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>Li</td>
<td>Be</td>
<td>Mg</td>
<td>Na</td>
<td>K</td>
<td>Ca</td>
<td>Sc</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
<td>Co</td>
<td>Ni</td>
<td>Cu</td>
<td>Zn</td>
<td>Ga</td>
</tr>
<tr>
<td>2</td>
<td>B</td>
<td>C</td>
<td>N</td>
<td>O</td>
<td>F</td>
<td>Ne</td>
<td>Ar</td>
<td>Kr</td>
<td>Xe</td>
<td>Rn</td>
<td>He</td>
<td>Li</td>
<td>Be</td>
<td>B</td>
<td>Al</td>
<td>Si</td>
<td>Ge</td>
<td>Sn</td>
</tr>
<tr>
<td>3</td>
<td>Li</td>
<td>Be</td>
<td>Mg</td>
<td>Na</td>
<td>K</td>
<td>Ca</td>
<td>Sc</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
<td>Co</td>
<td>Ni</td>
<td>Cu</td>
<td>Zn</td>
<td>Ga</td>
<td>Ge</td>
</tr>
<tr>
<td>4</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
<td>Ar</td>
<td>Kr</td>
<td>Xe</td>
<td>Rn</td>
<td>He</td>
<td>Li</td>
<td>Be</td>
<td>B</td>
<td>Al</td>
<td>Si</td>
<td>Ge</td>
<td>Sn</td>
<td>Te</td>
<td>Pb</td>
<td>Bi</td>
</tr>
<tr>
<td>5</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
</tr>
<tr>
<td>6</td>
<td>Cl</td>
<td>Ar</td>
<td>Kr</td>
<td>Xe</td>
<td>Rn</td>
<td>He</td>
<td>Li</td>
<td>Be</td>
<td>B</td>
<td>Al</td>
<td>Si</td>
<td>Ge</td>
<td>Sn</td>
<td>Te</td>
<td>Pb</td>
<td>Bi</td>
<td>Po</td>
<td>As</td>
</tr>
<tr>
<td>7</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
</tr>
<tr>
<td>8</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
</tr>
<tr>
<td>9</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
</tr>
<tr>
<td>10</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
</tr>
<tr>
<td>11</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
</tr>
<tr>
<td>12</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
</tr>
<tr>
<td>13</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
</tr>
<tr>
<td>14</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
</tr>
<tr>
<td>15</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
</tr>
<tr>
<td>16</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
</tr>
<tr>
<td>17</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
</tr>
<tr>
<td>18</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>I</td>
<td>At</td>
<td>Po</td>
<td>As</td>
</tr>
</tbody>
</table>

### Advantages:
- Reactive to water vapor => oxides

### Disadvantages:
- Limited thermal stability
- Not suitable for making nitrides
- Not suitable for making pure metals
Beta-diketonate Compounds

4 equivalent ways to represent a metal acetylacetonate (acac):

localized bonding picture 1

localized bonding picture 2

delocalized bonding picture 1

delocalized bonding picture 2
Beta-diketonate Compounds

pentane-2,4-dionate, or acetylacetonate (acac)

1,1,1,5,5,5-hexafluoroacetylacetonate (hfac) (more volatile)

2,2,6,6-tetramethylheptane-3,5-dionate (thd or tmhd) (more bulky)

octane-2,4-dionate (od) (lower melting point)

1-(2-methoxyethoxy)-2,2,6,6-tetramethylheptane-3,5-dionate (methd) (very bulky)
Beta-diketonate ALD Precursors

Ba(thd)$_2$, Ce(thd)$_4$, Co(acac)$_2$, Co(acac)$_3$, Co(thd)$_3$, Cr(acac)$_3$, Cu(hfac)$_2$, Cu(thd)$_2$, Dy(thd)$_2$, Er(thd)$_3$, Eu(thd)$_3$, Fe(acac)$_3$, Fe(thd)$_3$, Gd(thd)$_3$, Ho(thd)$_3$, Ir(acac)$_3$, La(thd)$_3$, Mg(thd)$_2$, Mn(thd)$_3$, Nd(thd)$_3$, Ni(acac)$_2$, Ni(thd)$_2$, Pb(thd)$_2$, Pd(hfac)$_2$, Pd(thd)$_2$, Pt(acac)$_2$, Pt(thd)$_3$, Ru(thd)$_3$, Ru(od)$_3$, Sc(thd)$_3$, Sm(thd)$_3$, Sr(thd)$_2$, Sr(methd)$_2$, Tm(thd)$_3$, Y(thd)$_3$

**Advantages:**
non-reactive to ambient air
high thermal stability

**Disadvantages:**
low vapor pressure (except Cu(hfac)$_2$)
solids with high melting points
low reactivity to water vapor
not suitable for making nitrides
Beta-diketonate ALD Precursors

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>Li</td>
<td>Be</td>
<td>Na</td>
<td>Mg</td>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
<td>Ar</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>Ca</td>
<td>Sc</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
<td>Co</td>
<td>Ni</td>
<td>Cu</td>
<td>Zn</td>
</tr>
<tr>
<td>Rb</td>
<td>Sr</td>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
<td>Cd</td>
</tr>
<tr>
<td>Cs</td>
<td>Ba</td>
<td>La</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
<td>Hg</td>
</tr>
<tr>
<td>Fr</td>
<td>Ra</td>
<td>Ac</td>
<td>Rf</td>
<td>Db</td>
<td>Sg</td>
<td>Bh</td>
<td>Hs</td>
<td>Mt</td>
<td>Ds</td>
<td>Hg</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>C</td>
<td>N</td>
<td>O</td>
<td>F</td>
<td>Ne</td>
</tr>
<tr>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
<td>Ar</td>
</tr>
<tr>
<td>Ga</td>
<td>Ge</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>Kr</td>
</tr>
<tr>
<td>In</td>
<td>Sn</td>
<td>Sb</td>
<td>Te</td>
<td>I</td>
<td>Xe</td>
</tr>
<tr>
<td>Pb</td>
<td>Bi</td>
<td>Po</td>
<td>At</td>
<td>Rn</td>
<td></td>
</tr>
</tbody>
</table>

Ce  Pr  Nd  Pm  Sm  Eu  Gd  Tb  Dy  Ho  Er  Tm  Yb  Lu
Th  Pa  U   Np  Pu  Am  Cm  Bk  Cf  Es  Fm  Md  Lr  No
Amide Ligands

NMe$_2$ = dimethylamino = dimethylamido

NEtMe = ethylmethylamino = ethylmethylamido

NEt$_2$ = diethylamino = diethylamido

N(SiMe$_3$)$_2$ = bis(trimethylsilyl)amido = bis(trimethylsilyl)amino

N$^\dagger$Bu = tert-butylimino = tert-butylimido
Amide and Imide Precursors for ALD

\[ \text{Al(NMe}_2\text{)}_3 = \text{tris(dimethylamido)aluminum} \]
\[ = \text{Al}_2(\text{NMe}_2)_6 = \text{hexakis(dimethylamido)dialuminum} \]
\[ \text{Bi}[\text{N(SiMe}_3\text{)}_2]_3 = \text{tris(bis(trimethylsilyl)amido)bismuth} \]
\[ \text{Hf(NMe}_2\text{)}_4 = \text{tetrakis(dimethylamido)hafnium} \]
\[ \text{Hf(NEtMe}_4\text{)} = \text{tetra(ethylmethylamido)hafnium} = \text{TEMAH} \]
\[ \text{Hf(NEt}_2\text{)}_4 = \text{tetrakis(diethylamido)hafnium} = \text{TDEAH} \]
\[ \text{La}[\text{N(SiMe}_3\text{)}_2]_3 = \text{tris(bis(trimethylsilyl)amido)lanthanum} \]
\[ \text{Pr}[\text{N(SiMe}_3\text{)}_2]_3 = \text{tris(bis(trimethylsilyl)amido)praseodymium} \]
\[ \text{Ta(NMe}_2\text{)}_5 = \text{pentakis(dimethylamido)tantalum} \]
\[ \text{Ta(NEt}_2\text{)}_5 = \text{pentakis(diethylamido)tantalum} \]
\[ \text{Ta(NtBu)(NEt}_2\text{)}_3 = (\text{tert}-\text{butylimido})\text{tris(diethylamido)tantalum} \]
\[ \text{Ti(NMe}_2\text{)}_4 = \text{tetrakis(dimethylamido)titanium} \]
\[ \text{Ti(NEtMe}_4\text{)} = \text{tetra(ethylmethylamido)titanium} = \text{TEMAT} \]
\[ \text{W(NtBu)}_2(\text{NMe}_2)_2 = \text{bis(tert-butylimido)bis(dimethylamido)tungsten} \]
\[ \text{Zn}[\text{N(SiMe}_3\text{)}_2]_2 = \text{bis(bis(trimethylsilyl)amido)zinc} \]
\[ \text{Zr(NMe}_2\text{)}_4 = \text{tetrakis(dimethylamido)zirconium} \]
\[ \text{Zr(NEtMe}_4\text{)} = \text{tetra(ethylmethylamido)zirconium} = \text{TEMAZ} \]
\[ \text{Zr(NEt}_2\text{)}_4 = \text{tetrakis(diethylamido)zirconium} = \text{TDEAZ} \]
## Amide and Imide Precursors for ALD

### Periodic Table

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>Li</td>
<td>B</td>
<td>C</td>
<td>N</td>
<td>O</td>
<td>F</td>
<td>Ne</td>
</tr>
<tr>
<td>Na</td>
<td>Mg</td>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
<td>Ar</td>
</tr>
<tr>
<td>K</td>
<td>Ca</td>
<td>Sc</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
</tr>
<tr>
<td>Rb</td>
<td>Sr</td>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
</tr>
<tr>
<td>Cs</td>
<td>Ba</td>
<td>La</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
</tr>
<tr>
<td>Fr</td>
<td>Ra</td>
<td>Ac</td>
<td>Rf</td>
<td>Db</td>
<td>Sg</td>
<td>Bh</td>
<td>Hs</td>
</tr>
</tbody>
</table>

### Advantages:
- highly reactive
- suitable for oxides and nitrides

### Disadvantages:
- limited thermal stability
- silicon impurity from silylamides
Amidinate Compounds

4 equivalent ways to represent a metal amidinate:

- **Localized bonding**
  - Picture 1
  - Picture 2

- **Delocalized bonding**
  - Picture 1
  - Picture 2

\[ \begin{align*}
R^1, R^2 \text{ and } R^3 & \text{ are non-metals, usually alkyl groups } C_xH_{2x+1}; \\
\text{other non-metals, such as silicon or nitrogen may be included.}
\end{align*} \]
Some Amidinate Ligands

N,N’-dimethyl-formamidinate (Me$_2$fmd)
N,N’-diethyl-formamidinate (Et$_2$fmd)
N,N’-diisopropyl-formamidinate (iPr$_2$fmd)
N,N’-di-sec-butyl-acetamidinate (sBu$_2$amd)
N,N’-dimethyl-acetamidinate (tBu$_2$amd)

Increasing steric bulk →

N’-tert-butyl-N-ethyl-acetamidinate ('BuEt-amd)
N’-tert-butyl-N-ethyl-propionamidinate ('BuEt-pmd)
N’-tert-butyl-N-ethyl-butyramidinate ('BuEt-bmd)
N-ethyl-N’-tert-butyl-pentylamidinate ('BuEt-pemd)

Increasing flexibility leads to decreasing melting points and liquids →
Amidinate Compounds Used in ALD

Advantages:
- high reactivity to water => oxides
- high reactivity to ammonia => nitrides
- high reactivity to H$_2$S => sulfides
- reactive to hydrogen gas H$_2$ => metals

Disadvantages:
- several different ligands needed
- some are solids, not liquids
Amidinate ALD Precursors

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>Li</td>
<td>Be</td>
<td>Na</td>
<td>Mg</td>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
<td>Ar</td>
<td>K</td>
<td>Ca</td>
<td>Sc</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
</tr>
</tbody>
</table>
# Structures of Metal(II) Acetamidinates

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Ni</th>
<th>Co</th>
<th>Cr</th>
<th>Fe</th>
<th>Mg</th>
<th>Mn</th>
<th>Ca</th>
<th>Sr</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>tert-butyl₂</td>
<td>m</td>
<td>m</td>
<td>m</td>
<td>m</td>
<td>m</td>
<td>m</td>
<td>m</td>
<td>d</td>
<td>d</td>
</tr>
<tr>
<td>isopropyl₂</td>
<td>m</td>
<td>m</td>
<td>m</td>
<td>d</td>
<td>d</td>
<td>d</td>
<td>d</td>
<td>d</td>
<td>p</td>
</tr>
<tr>
<td>tBu-Et</td>
<td>m</td>
<td>d</td>
<td>d</td>
<td>d</td>
<td></td>
<td></td>
<td></td>
<td>p</td>
<td>p</td>
</tr>
<tr>
<td>n-propyl₂</td>
<td></td>
<td></td>
<td></td>
<td>d</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Increasing size of metal atom →

Increasing size of metal atom

- **m** = volatile monomer
- **d** = volatile dimer
- **p** = non-volatile polymer
# Structures of Metal(III) Acetamidinates

<table>
<thead>
<tr>
<th>tert-butyl$_2$</th>
<th>n</th>
<th>m</th>
<th>m</th>
<th>m</th>
<th>m</th>
<th>m</th>
<th>m</th>
<th>m</th>
<th>d</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>isopropyl$_2$</td>
<td>m</td>
<td>m</td>
<td>m</td>
<td>m</td>
<td>m</td>
<td>m</td>
<td>m</td>
<td>r</td>
<td>r</td>
<td>r</td>
</tr>
<tr>
<td>Et-^t^Bu</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>r</td>
<td>d</td>
<td>d</td>
</tr>
<tr>
<td>n-propyl$_2$</td>
<td>m</td>
<td>m</td>
<td></td>
<td></td>
<td>r</td>
<td>d</td>
<td>d</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Et$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>r</td>
<td>d</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

## Increasing Ligand Bulk

- **n** = non-existent?
- **m** = more crowded, less reactive monomer, reacts with water, H$_2$O, & ozone, O$_3$
- **r** = more reactive monomer, reacts with ammonia, NH$_3$
- **d** = volatile dimer
- **d** = low-volatility dimer

## Increasing Size of Metal Atom
TYPES OF ALD REACTIONS

ALD reactions usually transfer **one atom** from a surface-bound group to a vapor group, or from a vapor group to a surface-bound group (the reverse direction).

The transferred atoms are usually **hydrogen, oxygen, fluorine or chlorine**.

A few reactions transfer a **whole group of atoms**, not just a single atom.
Examples of ALD Reactions

- Water $H$-transfer reactions $\Rightarrow$ metal oxides
- Ozone $O$-transfer reactions $\Rightarrow$ metal oxides
- Silanol $H$-transfer reactions $\Rightarrow$ metal silicates
- Ammonia $H$-transfer reactions $\Rightarrow$ metal nitrides
- $H$-reduction reactions $\Rightarrow$ transition metals
- Oxygen $O$-transfer reactions $\Rightarrow$ noble metals (Pt, Ru, Ir)
- Fluoride to silicon reactions $\Rightarrow$ tungsten or molybdenum
- Chloride to trialkylsilyl reactions $\Rightarrow$ selenides or tellurides
- Ethanolamine $H$-transfer reactions $\Rightarrow$ incorporated organic groups
Oxides by Hydroxyl Exchange & Hydrolysis

Tetrakis(dimethylamido)hafnium reacts with water to make hafnium dioxide

\[ \text{Hf(NMe}_2\text{)}_4 + 2 \text{H}_2\text{O} \Rightarrow \text{HfO}_2 + 4 \text{HNMe}_2 \]

Chemisorption by hydrogen transfer to ligands to form dimethylamine gas:

Transfer of hydrogen from water to surface-bound dimethylamide ligands:
Oxides by Oxidation with Ozone

Trimethylaluminum reacts with ozone to make aluminum oxide:

\[(\text{CH}_3)\text{Al} + \text{O}_3 \rightarrow \text{Al}_2\text{O}_3 + \text{CH}_4 + \text{H}_2\text{O} + \text{CO}_2\]

Hydrogen atom transfer from surface hydroxyl to ligand to form methane:

\[
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{H} \\
\end{array}
+ \text{Al(\text{CH}_3)_3} \rightarrow
\begin{array}{c}
\text{CH}_3 \\
\text{O} \\
\text{O} \\
\end{array}
+ 2 \text{HCH}_3
\]

Oxygen atom transfer to surface ligand to form water and carbon dioxide:

\[
\begin{array}{c}
\text{CH}_3 \\
\text{Al} \\
\text{O} \\
\text{O} \\
\end{array}
+ \text{O}_3 \rightarrow
\begin{array}{c}
\text{OH} \\
\text{Al} \\
\text{O} \\
\text{O} \\
\end{array}
+ \text{H}_2\text{O} + \text{CO}_2
\]

Water may not be detected because it reacts with other surface CH\textsubscript{3} groups.
Metal Silicates from Silanol

Hydrogen atom transfer from surface hydroxyls to dimethylamide ligands:

\[
\begin{align*}
\text{H}_2\text{O} + \text{Me}_2\text{N}_2\text{HfNMe}_2 & \rightarrow \text{Me}_2\text{N}_2\text{HfNMe}_2 + 2\text{HNMe}_2 \\
\text{Me}_2\text{N}_2\text{HfNMe}_2 + \text{H}_2\text{O} & \rightarrow \text{Me}_2\text{N}_2\text{HfNMe}_2 + 2\text{HNMe}_2
\end{align*}
\]

Hydrogen atom transfer from silanol to surface-bound dimethylamides:

\[
\begin{align*}
\text{Me}_2\text{N}_2\text{HfNMe}_2 + \text{Bu}^\text{t}O\text{Si}(\text{Bu}^\text{t})_2 & \rightarrow \text{Bu}^\text{t}O\text{Si}(\text{Bu}^\text{t})_2 + 2\text{HNMe}_2
\end{align*}
\]

Regeneration of surface hydroxyls by hydrogen from tertiary butyl groups:

\[
\begin{align*}
\text{COCH}^\text{t}\text{Bu}_3 + \text{H}_2\text{O} & \rightarrow \text{COCH}^\text{t}\text{Bu}_3 + 2\text{HNMe}_2
\end{align*}
\]
Al-doped SiO₂ from AlMe₃ and (tBuO)₃SiOH

=> very large growth per cycle, up to 15 nm, > 50 monolayers

Hydrogen atom transfer from surface hydroxyl to methyl ligands:

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]  
\[+ (\text{CH}_3)_3\text{Al} \quad \rightarrow \quad
\begin{align*}
\text{CH}_3 \\
\end{align*}
\]

Hydrogen atom transfer from silanols to methyl ligands:

\[
\begin{align*}
(\text{tBuO})_3\text{SiOH} & \quad + \quad \text{CH}_3 \\
\end{align*}
\]

\[\rightarrow \quad
\begin{align*}
\text{Al} \\
\end{align*}
\]

\[+ \quad \text{HCH}_3 \]

\[\text{(tBuO)}_3\text{SiOH} \quad + \quad \text{CH}_3 \quad \rightarrow \quad \text{HCH}_3 \]

50
Al-doped SiO₂ from AlMe₃ and (tBuO)₃SiOH

Repeated insertions of (tBuO)₃SiOH into an Al-O bond produces a siloxane polymer tethered to the surface:
Al-doped SiO$_2$ from AlMe$_3$ and (tBuO)$_3$SiOH

Elimination of isobutene by $\beta$-hydrogen transfer:
Al-doped SiO$_2$ from AlMe$_3$ and ($^t$BuO)$_3$SiOH

Siloxane polymer chains cross-link by elimination of tert-butanol:

Complete crosslinking produces a solid silica layer that is impervious to diffusion of more silanol up to the aluminum catalyst, so reaction stops.
Al-doped SiO₂ from AlMe₃ and (ᵣBuO)₃SiOH

Elimination of water also cross-links polymer chains:

Complete crosslinking produces a solid silica layer that is impervious to diffusion of more silanol up to the aluminum catalyst, so reaction stops.
Nitrides by Chloride Exchange and Reduction

Titanium(IV) tetrachloride plus ammonia makes titanium(III) nitride:

\[ \text{TiCl}_4 + \text{NH}_3 \rightarrow \text{TiN} \]

Hydrogen atom transfer from surface amides to chlorides on precursor:

\[
\begin{array}{c}
\text{H} \quad \text{H} \\
\text{N} \quad \text{N} \\
\text{N} \\
\text{N}
\end{array}
\quad +
\quad \begin{array}{c}
\text{Cl} \quad \text{Cl} \\
\text{Ti} \\
\text{Cl} \quad \text{Cl}
\end{array}
\rightarrow
\quad \begin{array}{c}
\text{Cl} \quad \text{Cl} \\
\text{Ti} \\
\text{Cl} \quad \text{Cl}
\end{array}
\quad +
\quad 2 \text{HCl}
\]

Hydrogen atom transfer from ammonia to surface-bound chloride ligands:

\[
\begin{array}{c}
\text{Cl} \quad \text{Cl} \\
\text{Ti} \\
\text{N} \quad \text{N}
\end{array}
\quad +
\quad 2 \text{HNH}_2
\rightarrow
\quad \begin{array}{c}
\text{H}_2\text{N} \\
\text{NH}_2
\end{array}
\quad +
\quad 2 \text{HCl}
\]

Titanium in oxidation state +4 is reduced to +3 by elimination reactions:

\[
\begin{array}{c}
\text{H}_2\text{N} \\
\text{Ti} \\
\text{NH}_2
\end{array}
\rightarrow
\quad \begin{array}{c}
\text{N} \\
\text{N}
\end{array}
\quad + \quad ? \text{ N}_2, \text{H}_2, \text{and/or N}_2\text{H}_4 ?
\]
Tungsten Nitride by Exchange and Catalysis

Hydrogen transfer from surface imides to dimethylamides on precursor:

\[
\begin{align*}
\text{BuN} & \quad \text{BuN} \\
\text{Me}_2\text{N} & \quad \text{NMe}_2 \\
\text{NH} & \quad \text{NH}
\end{align*}
\]

\[\text{Me}_2\text{NH} + \text{H} \] + \text{BuN} \\
\[
\begin{align*}
\text{BuN} & \quad \text{BuN} \\
\text{Me}_2\text{N} & \quad \text{NMe}_2 \\
\text{NH} & \quad \text{NH}
\end{align*}
\]

Hydrogen transfer to imides from ammonia or from tert-butyl imido group?

\[
\begin{align*}
\text{(H}_3\text{C})_3\text{CN} & \quad \text{NC(CH}_3)_3 \\
\text{W} & \quad \text{W} \\
\text{N} & \quad \text{N}
\end{align*}
\]

\[\text{NH}_3 \quad + \text{H} \] + \text{Me}_2\text{CNH}_2 \quad \text{or} \quad \text{Me}_2\text{C=CH}_2
\]

Reductive elimination of nitrogen to reduce W(VI) to W(III)

\[\text{WN}_2 \quad \Rightarrow \quad \text{WN} \quad + \quad \frac{1}{2} \text{N}_2\]
Metals by Reduction with H Atoms

Titanium from titanium tetrachloride and hydrogen atoms in a plasma

\[ \text{TiCl}_4 + 4 \text{H} \rightarrow \text{Ti} + 4 \text{HCl} \]

Hydrogen atoms on surface transfer to chlorides on precursor:

\[ \begin{array}{c}
\text{H} \\
\downarrow
\end{array} + \begin{array}{c}
\text{H} \\
\downarrow
\end{array} \rightarrow \begin{array}{c}
\text{Cl} \\
\downarrow
\end{array} + \begin{array}{c}
\text{Ti} \\
\downarrow
\end{array} + 2 \text{HCl} \]

Hydrogen atoms from plasma remove chlorine as hydrogen chloride gas:

\[ \begin{array}{c}
\text{Cl} \\
\downarrow
\end{array} + 4 \begin{array}{c}
\text{H} \\
\downarrow
\end{array} \rightarrow \begin{array}{c}
\text{H} \\
\downarrow
\end{array} + \begin{array}{c}
\text{Ti} \\
\downarrow
\end{array} + 2 \text{HCl} \]
Metals by Reduction with H₂ Molecules

Dissociative chemisorption of copper amidinate on a copper surface:

\[
\text{Cu—Cu—Cu—Cu—Cu—Cu—Cu} \quad \rightarrow \quad \text{Cu—Cu—Cu—Cu—Cu—Cu—Cu}
\]

Hydrogen transfer to amidinate ligands to make copper & amidine vapor:

\[
\text{Cu—Cu—Cu—Cu—Cu—Cu—Cu} + \text{H}_2 \quad \rightarrow \quad \text{Cu—Cu} + \text{RNN} + \text{RNN} + \text{RNN}
\]
Oxygen atoms chemisorb on noble metals (platinum, ruthenium, etc.):

\[ \text{M–M–M–M–M} + \text{O}_n \rightarrow \text{M–M–M–M–M} \]

Adsorbed oxygen atoms burn ligands to form carbon dioxide and water:

\[ \text{O–O–O–O–O} + \text{ML}_n \rightarrow \text{M–M–M–M–M} \rightarrow \text{M–M–M–M–M} + \text{CO}_2 + \text{H}_2\text{O} \]
Tungsten Metal by Fluoride Exchange

Overall reaction: \( WF_6 + Si_2H_6 \Rightarrow W + 2 SiF_3H + 2 H_2 \)

a F atom moves from \( WF_6 \) vapor to liberate Si from surface:

\[
\text{surface-WSiF}_2H + WFF_5 \Rightarrow \text{surface-WWF}_5 + \text{SiFF}_2H
\]

3 F atoms move from W on surface to break up \( Si_2H_6 \) vapor:

\[
\text{surface-WWF}_2F_3 + Si_2H_6 \Rightarrow \text{surface-WWSiF}_2H + SiF_3H + 2 H_2
\]

A very complex reaction, breaking 1 Si-Si, 5 W-F and 4 Si-H bonds while forming a new W-Si bond, 5 new Si-F bonds and 2 new H-H bonds.
Tellurides by Chloride Exchange Reactions

Chlorine atoms on surface move to trialkylsilyl groups on tellurium:

\[
\begin{align*}
\text{Cl-Cl-Cl-Cl-Cl} & \quad \text{Ge-Ge-Ge-Ge-Ge} + (R_3\text{Si})_2\text{Te} \\
& \quad \Rightarrow \quad \text{Ge-Ge-Ge-Ge-Ge} + R_3\text{SiCl}
\end{align*}
\]

Chlorine atoms on germanium remove surface trialkylsilyl groups:

\[
\begin{align*}
R_3\text{Si-Si-Si-Si-Si} & \quad \text{Te-Te-Te-Te-Te} \quad \text{Ge-Ge-Ge-Ge-Ge} + \text{GeCl}_2 \\
& \quad \Rightarrow \quad \text{Ge-Ge-Ge-Ge-Ge} + R_3\text{SiCl}
\end{align*}
\]
Adding Organic Components to ALD Films

A) trimethylaluminum
B) ethanolamine
C) maleic anhydride

Adds flexibility to brittle inorganic films

from S. M. George, Chem. Rev. 110, 111 (2010)
Problems When the Chemistry is Wrong

Thermal decomposition
destroys the self-limiting property of surface reactions
thickness uniformity, step coverage and film purity degraded

Incomplete surface reactions can incorporate ligands as impurities
slow kinetics can be alleviated by longer exposure times, or
too low thermodynamic driving force => change precursors

Incomplete step coverage
need longer exposure time or higher precursor vapor pressure
but may be limited by decomposition or desorption of precursor

Etching by precursor or reaction byproducts
mostly from halide precursors (chlorides, bromides)
Summary

ALD precursors are available for most non-radioactive elements

Suitable reactant pairs are known for ALD of

some pure elements
oxides of most elements
nitrides of many elements
sulfides, selenides and tellurides of some elements
phosphides and arsenides of a few elements
fluorides of a few elements

ALD reactions usually involve

exchange reactions between surface groups and vapor groups
exchanged atoms are usually hydrogen, oxygen or halogen
Summary

Recent Reviews of ALD Chemistry


M. Ritala and J. Niinisto, in Chemical Vapor Deposition (Royal Society of Chemistry, 2009)


Acknowledgements

Students and Post-docs who worked on ALD in Gordon’s Lab

Titta Aaltonen        Yiqun Liu
Sean Barry           Hisashi Nakagawa
Jill Becker          Jun Ni
Mike Coulter         Dawen Pang
Damon Farmer         Jin-Seong Park
Dennis Hausmann      Antti Rahtu
Adam Hock            P. Venkateswara Rao
Jaeyeong Heo         Leo Rodriguez
Daewon Hong          Philippe de Rouffignac
Esther Kim           Prasert Sinsermsuksakul
Kyoung-ha Kim        Amethyst Smith
Jean Sebastien Lehn  Seigi Suh
Booyong S. Lim       Hongtao Wang
Don Keun Lee         Shenglong Wang
Huazhi Li            Xinwei Wang
Zhengwen Li          Sheng Xu
Xinye Liu            Andrew P. Yousef

Supported by the US National Science Foundation, Dow, IBM and Intel