Overview of ALD Precursors and Reaction Mechanisms

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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

Tutorial for ALD 2011

Roy Gordon
Harvard University
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
List of the Stable Elements by Symbol

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The Periodic Table is a tabular display of chemical elements, organized on the basis of their atomic numbers, electron configurations, and recurring chemical properties. Elements are arranged in order of increasing atomic number from left to right across a period and top to bottom within a group. This organization allows for the identification of patterns and trends among the elements.

- **Main group metals** are typically found on the left side of the periodic table, with elements like lithium (Li), sodium (Na), potassium (K), and calcium (Ca).
- **Alkaline earth metals** are found directly to the right of the main group metals, such as beryllium (Be), magnesium (Mg), calcium (Ca), and strontium (Sr).
- **Transition metals** are elements that are located in the middle of the periodic table, including iron (Fe), nickel (Ni), and cobalt (Co).
- **Metalloids** or semi-metals are found in the middle of each row, such as silicon (Si) and germanium (Ge).
- **Non-metals** are typically found on the right side of the periodic table, including elements like oxygen (O) and sulfur (S).

The periodic table also includes the **halogens** on the far right side, which are highly reactive non-metals like fluorine (F) and chlorine (Cl). The **lanthanides** and **actinides** are groups of elements that are located at the bottom of the periodic table, specifically those with atomic numbers 58 through 71 and 90 through 103, respectively.
Elements in ALD Films

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

Not used in ALD because the elements are

- low-volatility compounds
- radioactive
- highly toxic
- 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.

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### ALD Materials by Type

| Oxide dielectrics | $\text{Al}_2\text{O}_3$, $\text{TiO}_2$, $\text{ZrO}_2$, $\text{HfO}_2$, $\text{Ta}_2\text{O}_5$, $\text{Nb}_2\text{O}_5$, $\text{Sc}_2\text{O}_3$, $\text{Y}_2\text{O}_3$, $\text{MgO}$, $\text{B}_2\text{O}_3$, $\text{SiO}_2$, $\text{GeO}_2$, $\text{La}_2\text{O}_3$, $\text{CeO}_2$, $\text{PrO}_x$, $\text{Nd}_2\text{O}_3$, $\text{Sm}_2\text{O}_3$, $\text{EuO}_x$, $\text{Gd}_2\text{O}_3$, $\text{Dy}_2\text{O}_3$, $\text{Ho}_2\text{O}_3$, $\text{Er}_2\text{O}_3$, $\text{Tm}_2\text{O}_3$, $\text{Yb}_2\text{O}_3$, $\text{Lu}_2\text{O}_3$, $\text{SrTiO}_3$, $\text{BaTiO}_3$, $\text{PbTiO}_3$, $\text{PbZrO}_3$, $\text{Bi}_x\text{Ti}_y\text{O}$, $\text{Bi}_x\text{Si}_y\text{O}$, $\text{SrTa}_2\text{O}_6$, $\text{SrBi}_2\text{Ta}_2\text{O}_9$, $\text{YScO}_3$, $\text{LaAlO}_3$, $\text{NdAlO}_3$, $\text{GdScO}_3$, $\text{LaScO}_3$, $\text{LaLuO}_3$, $\text{LaYbO}_3$, $\text{Er}_3\text{Ga}_5\text{O}_{13}$ |
| Oxide conductors or semiconductors | $\text{In}_2\text{O}_3$, $\text{In}_2\text{O}_3$:Sn, $\text{In}_2\text{O}_3$:F, $\text{In}_2\text{O}_3$:Zr, $\text{SnO}_2$, $\text{SnO}_2$:Sb, $\text{Sb}_2\text{O}_3$, $\text{ZnO}$, $\text{ZnO}:\text{Al}$, $\text{ZnO}:\text{B}$, $\text{ZnO}:\text{Ga}$, $\text{RuO}_2$, $\text{RhO}_2$, $\text{IrO}_2$, $\text{Ga}_2\text{O}_3$, $\text{VO}_2$, $\text{V}_2\text{O}_5$, $\text{WO}_3$, $\text{W}_2\text{O}_3$, $\text{NiO}$, $\text{CuO}_x$, $\text{FeO}_x$, $\text{CrO}_x$, $\text{CoO}_x$, $\text{MnO}_x$ |
| Other ternary oxides | $\text{LaCoO}_3$, $\text{LaNiO}_3$, $\text{LaMnO}_3$, $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ |
| Nitride dielectrics or semiconductors | $\text{BN}$, $\text{AlN}$, $\text{GaN}$, $\text{InN}$, $\text{Si}_3\text{N}_4$, $\text{Ta}_3\text{N}_5$, $\text{Cu}_3\text{N}$, $\text{Zr}_3\text{N}_4$, $\text{Hf}_3\text{N}_4$, $\text{LaN}$, $\text{LuN}$ |
| Metallic nitrides | $\text{TiN}$, $\text{Ti-Si-N}$, $\text{Ti-Al-N}$, $\text{TaN}$, $\text{NbN}$, $\text{MoN}$, $\text{WN}_x$, $\text{WN}_x\text{C}_y$, $\text{Co}_x\text{N}$, $\text{Sn}_x\text{N}$ |
| II-VI semiconductors | $\text{ZnS}$, $\text{ZnSe}$, $\text{ZnTe}$, $\text{CaS}$, $\text{SrS}$, $\text{BaS}$, $\text{CdS}$, $\text{CdTe}$, $\text{MnTe}$, $\text{HgTe}$ |
| II-VI based phosphors | $\text{ZnS:}\text{M}$ ($\text{M}=\text{Mn, Tb, Tm}$); $\text{CaS:}\text{M}$ ($\text{M}=\text{Eu, Ce, Tb, Pb}$); $\text{SrS:}\text{M}$ ($\text{M}=\text{Ce, Tb, Pb}$) |
| III-V semiconductors | $\text{GaAs}$, $\text{AlAs}$, $\text{AlP}$, $\text{InP}$, $\text{GaP}$, $\text{InAs}$ |
| Fluorides | $\text{CaF}_2$, $\text{SrF}_2$, $\text{MgF}_2$, $\text{LaF}_3$, $\text{ZnF}_2$ |
| Elements | $\text{Ru}$, $\text{Pt}$, $\text{Ir}$, $\text{Pd}$, $\text{Rh}$, $\text{Ag}$, $\text{Cu}$, $\text{Ni}$, $\text{Co}$, $\text{Fe}$, $\text{Mn}$, $\text{Ta}$, $\text{W}$, $\text{Mo}$, $\text{Ti}$, $\text{Al}$, $\text{Si}$, $\text{Ge}$ |
| Other semiconductors | $\text{PbS}$, $\text{SnS}$, $\text{In}_2\text{S}_3$, $\text{Sb}_2\text{S}_3$, $\text{Cu}_x\text{S}$, $\text{CuGaS}_2$, $\text{WS}_2$, $\text{SiC}$, $\text{Ge}_2\text{Sb}_2\text{Te}_5$ |
| Others | $\text{La}_2\text{S}_3$, $\text{Y}_2\text{O}_2\text{S}$, $\text{TiC}_x$, $\text{TiS}_2$, $\text{TaC}_x$, $\text{WC}_x$, $\text{Ca}_3\text{(PO}_4)_2$, $\text{CaCO}_3$, organics |

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
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, $\text{NH}_3$

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

Plasma-activated $\text{NH}_3$ is more reactive than $\text{NH}_3$

Dinitrogen, $\text{N}_2$, is normally unreactive under ALD conditions

Plasma-activated $\text{N}_2$ is more reactive than $\text{N}_2$

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

- Acetylene gas: \( \text{H} - \text{C} = \text{C} - \text{H} \)
- Formic acid vapor: \( \text{H}_2\text{C} = \text{O} \)
- Carbon contained in a metal compound

ALD Precursors for Fluorine

- Hydrogen fluoride gas, HF: \( \text{H}_2\text{F} \)
- 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(triethyilsilyl)selenium, $(Et_3Si)_2Se$

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

phosphine gas, $\text{PH}_3$ (very poisonous)

arsine gas, $\text{AsH}_3$ (very poisonous)

antimony trichloride, $\text{SbCl}_3$

tris(dimethylamido)antimony
Elemental ALD Precursors

Examples:
Non-metals: \( \text{O}_2, \text{P}_4, \text{S}_2 \text{ or } \text{S}_8 \)
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$_2$L$_n$, 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 $\geq$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$_x$H$_{2x+1}$)$_2^-$, have charge -2.

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

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$R = \text{alkyl group} = C_nH_{2n+1}$
Elements with Hydride ALD Precursors

Hydrides are compounds of an element \( X \) and hydrogen

\[ XH_n \quad n = 1, 2, 3 \text{ or } 4 \]

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Examples of Hydride Precursors

\[ \text{SiH}_4 = \text{silane} \]

\[ \text{Si}_2\text{H}_6 = \text{disilane, more reactive than silane} \]

\[ \text{GeH}_4 = \text{germane} \]

\[ \text{AlH}_3 \text{NMe}_3 = \text{aluminum hydride – trimethylamine} \]

**Advantage:**
very volatile

**Disadvantages:**
usually need plasma activation
pyrophoric and toxic
Elements with Halide ALD Precursors

Halides are compounds of an element M and a halogen X = F, Cl, Br or I

\[ MX_n \quad n = 1, 2, 3, 4, 5 \text{ or } 6 \]
Examples of Halide ALD Precursors

WF\textsubscript{6} = tungsten hexafluoride

TiCl\textsubscript{4} = titanium tetrachloride

HfCl\textsubscript{4} = hafnium tetrachloride

SnCl\textsubscript{4} = tin tetrachloride

Oxygen can be combined with halide ligands:

VOCl\textsubscript{3} = trichlorooxovanadium
  = vanadium oxide trichloride
  = vanadyl trichloride

CrO\textsubscript{2}Cl\textsubscript{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\textsubscript{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)

\(\text{iPr}_2\text{Te} = \text{diisopropyltellurium}\)
Elements with Alkyl ALD Precursors

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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
Cyclopentadienyl Ligands

Cp = cyclopentadienyl

MeCp = methylcyclopentadienyl

Me₅Cp = Cp* = pentamethylcyclopentadienyl

EtCp = ethylcyclopentadienyl

iPrCp = isopropylcyclopentadienyl
Examples of Cyclopentadienyl Precursors

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

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

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

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

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

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

<table>
<thead>
<tr>
<th>Advantages:</th>
<th>Disadvantages:</th>
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<tr>
<td>thermally stable</td>
<td>some have low reactivity (Ni, Ru)</td>
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<td>some are solids (Ni, Sr, Mg, In, La)</td>
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<td>some have low volatility (La, Sr, Mg)</td>
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Alkoxide Compounds

OMe = methoxy

OEt = ethoxy

OiPr = isopropoxy

OiBu = isobutoxy

O^iBu = tert-butoxy

O^iPe = tert-pentoxy

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

dmae = dimethylaminoethoxy

dmamp = 1-dimethylamino-2-methyl-2-propoxy

O^sBu = sec-butoxy
Alkoxide Compounds Used in ALD

\[
\begin{align*}
\text{Al(OEt)}_3 &= \text{tris(ethoxy)aluminum = aluminum ethoxide} \\
\text{AlMe}_2(\text{OiPr}) &= \text{isopropoxydimethylaluminum} \\
\text{B(OMe)}_3 &= \text{tris(methoxy)boron = trimethylborate} \\
\text{Hf(OtBu)}_4 &= \text{tetra(tert-butoxy)hafnium = hafnium tert-butoxide} \\
\text{Hf(mmp)}_4 &= \text{tetra(1-methoxy-2-methyl-2-propoxy)hafnium} \\
\text{Nb(OEt)}_5 &= \text{penta(ethoxy)niobium = niobium ethoxide} \\
\text{Ni(dmamp)}_2 &= \text{bis(1-dimethylamino-2-methyl-2-propoxy)nickel(II)} \\
\text{Pb(OtBu)}_2 &= \text{bis(tert-butoxy)lead(II) = lead(II) tert-butoxide} \\
\text{Si(OEt)}_4 &= \text{tetra(ethoxy)silane} = \text{tetraethylorthosilicate = TEOS} \\
\text{Si(OtBu)}_3\text{OH} &= \text{tris(tert-butoxy)silanol} \\
\text{Si(OtPe)}_3\text{OH} &= \text{tris(tert-pentoxy)silanol} \\
\text{Ta(OEt)}_5 &= \text{penta(ethoxy)tantalum = tantalum ethoxide} \\
\text{Ti(OMe)}_4 &= \text{tetra(methoxy)titanium = titanium methoxide} \\
\text{Ti(OEt)}_4 &= \text{tetra(ethoxy)titanium = titanium ethoxide} \\
\text{Ti(OiPr)}_4 &= \text{tetra(isopropoxy)titanium = titanium isopropoxide} \\
\text{VO(OiPr)}_3 &= \text{tris(isopropoxy)oxovanadium = vanadyl isopropoxide}
\end{align*}
\]
## Elements with Alkoxide ALD Precursors

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### 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):

1. Localized bonding picture 1
   ![Localized bonding picture 1](image)

2. Localized bonding picture 2
   ![Localized bonding picture 2](image)

3. Delocalized bonding picture 1
   ![Delocalized bonding picture 1](image)

4. Delocalized bonding picture 2
   ![Delocalized bonding picture 2](image)
Beta-diketonate Compounds

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

1,1,1,5,5,5-hexafluoro-acetylacetonate (hfac)

2,2,6,6-tetramethyl-heptane-3,5-dionate (thd or tmhd)

octane-2,4-dionate (od)

1-(2-methoxyethoxy)-2,2,6,6-tetramethyl-heptane-3,5-dionate (methd)
Beta-diketonate ALD Precursors

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

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Amide Ligands

NMe₂ = dimethylamino = dimethylamido

NEtMe = ethylmethylamino = ethylmethylamido

NEt₂ = diethylamino = diethylamido

N(SiMe₃)₂ = bis(trimethylsilyl)amido = bis(trimethylsilyl)amino

NᵀBu = tert-butylimino = tert-butylimido
Amide and Imide Precursors for ALD

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

- **Advantages:**
  - Highly reactive
  - Suitable for oxides and nitrides

- **Disadvantages:**
  - Limited thermal stability
  - Silicon impurity from silylamides

---

<table>
<thead>
<tr>
<th>Period</th>
<th>Group</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Li, Be</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Na, Mg</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>K, Ca</td>
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<td></td>
<td>5</td>
<td>Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu</td>
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<tr>
<td></td>
<td>6</td>
<td>Zn, Ga, Ge, As, Se, Br, Kr</td>
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<tr>
<td></td>
<td>7</td>
<td>Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>Cs, Ba, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Rn</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>Fr, Ra, Ac, Rf, Db, Sg, Bh, Hs, Mt, Ds, Rg</td>
</tr>
</tbody>
</table>

---

**Period**: 1-18
**Group**: 1-18

---

**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
- **Localized bonding**, picture 2
- **Delocalized bonding**, picture 1
- **Delocalized bonding**, picture 2

R\(^1\), R\(^2\) and R\(^3\) are non-metals, usually alkyl groups C\(_x\)H\(_{2x+1}\); other non-metals, such as silicon or nitrogen may be included.
Some Amidinate Ligands

N,N’-dimethyl-formamidinate (Me₂fmd)
N,N’-diethyl-formamidinate (Et₂fmd)
N,N’-diisopropyl-formamidinate (iPr₂fmd)
N,N’-di-sec-butyl-acetamidinate (sBu₂amd)
N,N’-dimethyl-acetamidinate ('Bu₂amd)

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

Ag\(_2\)(^{t}Bu\(_2\)-amd)\(_2\)
Ca\(^{t}Bu\(_2\)-amd)\(_2\)
Co\(^{i}Pr\(_2\)-amd)\(_2\)
Co\(^{t}BuEt-amd)\(_2\)
Cr(Et\(_2\)-amd)\(_3\)
Cu\(_2\)(^{i}Pr\(_2\)-amd)\(_2\)
Cu\(_2\)(^{s}Bu\(_2\)-amd)\(_2\)
Er\(^{t}Bu\(_2\)-amd)\(_3\)
Fe(^{i}Pr\(_2\)-amd)\(_2\)
Fe\(^{t}BuEt-amd)\(_2\)
Ga(Et\(_2\)-amd)\(_3\)
Gd\(^{i}Pr\(_2\)-amd)\(_3\)
Hf(Me\(_2\)-fmd)\(_4\)
Hf(Me\(_2\)-pmd)\(_4\)
Hf(Me\(_2\)-bmd)\(_4\)
La\(^{i}Pr\(_2\)-fmd)\(_3\)
La\(^{t}Bu\(_2\)-fmd)\(_3\)

Lu(Et\(_2\)-fmd)\(_3\)
Lu(Et\(_2\)-amd)\(_3\)
Mg\(^{t}Bu\(_2\)-amd)\(_2\)
Mg\(^{i}Pr\(_2\)-amd)\(_2\)
Mn\(^{t}Bu\(_2\)-pemd)\(_2\)
Ni\(^{t}Bu\(_2\)-amd)\(_2\)
Pr\(^{i}Pr\(_2\)-amd)\(_3\)
Sc(Et\(_2\)-amd)\(_3\)
Sr\(^{t}Bu\(_2\)-amd)\(_2\)
Ti\(^{i}Pr\(_2\)-amd)\(_3\)
V(Et\(_2\)-amd)\(_3\)
V\(^{i}Pr\(_2\)-amd)\(_3\)
Y\(^{i}Pr\(_2\)-amd)\(_3\)
Zn\(^{i}Pr\(_2\)-amd)\(_2\)
Zr(Me\(_2\)-fmd)\(_4\)
Zr(Me\(_2\)-pmd)\(_4\)
Zr(Me\(_2\)-bmd)\(_4\)

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
## 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>d</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>p</td>
<td>p</td>
<td></td>
</tr>
<tr>
<td>n-propyl₂</td>
<td></td>
<td>d</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

- **t** = volatile monomer
- **d** = volatile dimer
- **p** = non-volatile polymer

Increasing size of metal atom →

Increasing ligand bulk →

Increasing size of metal atom →

m = volatile monomer  

**d** = volatile dimer  

**p** = non-volatile polymer
# Structures of Metal(III) Acetamidinates

<table>
<thead>
<tr>
<th>Ligand</th>
<th>tert-butyl₂</th>
<th>isopropyl₂</th>
<th>Et-tBu</th>
<th>n-propyl₂</th>
<th>Et₂</th>
<th>Al</th>
<th>Cr</th>
<th>Ga</th>
<th>V</th>
<th>Ti</th>
<th>Ru</th>
<th>Sc</th>
<th>Lu</th>
<th>Er</th>
<th>Y</th>
<th>Gd</th>
<th>Eu</th>
<th>Nd</th>
<th>Pr</th>
<th>Ce</th>
<th>La</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increasing bulk</td>
<td>m</td>
<td>m</td>
<td>r</td>
<td>d</td>
<td>r</td>
<td>d</td>
<td></td>
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</tr>
<tr>
<td>Increasing size of metal atom</td>
<td>n = non-existent?</td>
<td>m = more crowded, less reactive monomer, reacts with water, H₂O, &amp; ammonia, NH₃</td>
<td>r = more reactive monomer, reacts with ozone, O₃</td>
<td>d = volatile dimer</td>
<td>d = low-volatility dimer</td>
<td></td>
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</tr>
</tbody>
</table>

- m: more crowded, less reactive monomer, reacts with water, H₂O, & ammonia, NH₃
- r: more reactive monomer, reacts with ozone, O₃
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 => metal oxides

ozone $O$-transfer reactions => metal oxides

silanol $H$-transfer reactions => metal silicates

ammonia $H$-transfer reactions => metal nitrides

$H$-reduction reactions => transition metals

oxygen $O$-transfer reactions => noble metals (Pt, Ru, Ir)

fluoride to silicon reactions => tungsten or molybdenum

chloride to trialkylsilyl reactions => selenides or tellurides

ethanolamine $H$-transfer reactions => 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:

\[
\begin{align*}
\text{Hf(NMe}_2\text{)}_4 + 2 \text{H}_2\text{O} + 2 \text{Me}_2\text{NHNMe}_2 & \rightarrow \text{Me}_2\text{N} + \text{HNMe}_2 \\
\end{align*}
\]

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

Trimethylaluminum reacts with ozone to make aluminum oxide:

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

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

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

Water may not be detected because it reacts with other surface CH$_3$ groups
Metal Silicates from Silanol

Hydrogen atom transfer from surface hydroxyls to dimethylamide ligands:

\[
\begin{align*}
\text{Hf} & + \text{Me}_2\text{N} = \text{Me}_2\text{N} \\
\text{Me}_2\text{N} & + \text{Hf} = \text{Me}_2\text{N} \\
\text{Me}_2\text{N} & + \text{Me}_2\text{N} = \text{Me}_2\text{N} \\
\text{Me}_2\text{N} & + \text{Me}_2\text{N} = \text{Me}_2\text{N}
\end{align*}
\]

Hydrogen atom transfer from silanol to surface-bound dimethylamides:

\[
\begin{align*}
\text{Me}_2\text{N} & + \text{Bu}^\text{t} \text{O} \text{Si} = \text{Bu}^\text{t} \text{O} \text{Si} \\
\text{Bu}^\text{t} \text{O} \text{Si} & + \text{Hf} = \text{Bu}^\text{t} \text{O} \text{Si} \\
\text{Bu}^\text{t} \text{O} \text{Si} & + \text{Bu}^\text{t} \text{O} \text{Si} = \text{Bu}^\text{t} \text{O} \text{Si}
\end{align*}
\]

Regeneration of surface hydroxyls by hydrogen from tertiary butyl groups:

\[
\begin{align*}
\text{H}_3\text{C} \text{O} & + \text{OC} \text{(CH}_3\text{)}_3 \\
\text{OC} \text{(CH}_3\text{)}_3 & + \text{Hf} = \text{OC} \text{(CH}_3\text{)}_3 \\
\text{OC} \text{(CH}_3\text{)}_3 & + \text{OC} \text{(CH}_3\text{)}_3 = \text{OC} \text{(CH}_3\text{)}_3
\end{align*}
\]
Al-doped SiO$_2$ from AlMe$_3$ and (tBuO)$_3$SiOH

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

Hydrogen atom transfer from surface hydroxyl to methyl ligands:

$$\text{H} \quad \text{H} \quad \text{O} \quad \text{O} \quad + \quad (\text{CH}_3)_3\text{Al} \quad \rightarrow \quad \text{H} \quad \text{H} \quad \text{O} \quad \text{O} \quad + \quad 2 \quad \text{HCH}_3$$

Hydrogen atom transfer from silanols to methyl ligands:

$$\quad (\text{tBuO})_3\text{SiOH} \quad + \quad \text{CH}_3 \quad \rightarrow \quad \text{O} \quad \text{O} \quad + \quad \text{HCH}_3$$
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 ($^{t}$BuO)$_3$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 SiO$_2$ from AlMe$_3$ and (tBuO)$_3$SiOH

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:

\[
\begin{array}{c}
\text{H} \quad \text{H} \\
\text{N} \quad \text{N} \\
\text{N} \quad \text{N}
\end{array}
\]

\[
\begin{array}{c}
\text{Cl} \quad \text{Cl} \\
\text{Cl} \quad \text{Cl}
\end{array}
\]

\[
\begin{array}{c}
\text{Ti} \\
\text{C} \quad \text{C}
\end{array}
\]

\[
\begin{array}{c}
\text{N} \quad \text{N} \\
\text{N} \quad \text{N}
\end{array}
\]

\[
\begin{array}{c}
\text{N} \quad \text{N} \\
\text{N} \quad \text{N}
\end{array}
\]

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

\[
\begin{array}{c}
\text{Cl} \quad \text{Cl} \\
\text{Cl} \quad \text{Cl}
\end{array}
\]

\[
\begin{array}{c}
\text{H}_2\text{N} \quad \text{NH}_2
\end{array}
\]

\[
\begin{array}{c}
\text{H}_2\text{N} \quad \text{NH}_2
\end{array}
\]

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

\[
\begin{array}{c}
\text{H}_2\text{N} \quad \text{NH}_2 \\
\text{N} \quad \text{N}
\end{array}
\]

\[
\begin{array}{c}
\text{NH}_2
\end{array}
\]

\[
\begin{array}{c}
\text{N} \quad \text{N}
\end{array}
\]

+ ? \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:

\[
\text{HN} \quad \text{HN} \\
\text{Me}_2\text{N} \quad \text{NMe}_2
\]

\[
\text{HN} \quad \text{HN} \\
\text{Me}_2\text{N} \quad \text{NMe}_2
\]

\[
\text{HN} \quad \text{HN} \\
\text{Me}_2\text{N} \quad \text{NMe}_2
\]

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

\[
\text{HN} \quad \text{HN} \\
\text{Me}_2\text{N} \quad \text{NMe}_2
\]

\[
\text{HN} \quad \text{HN} \\
\text{Me}_2\text{N} \quad \text{NMe}_2
\]

\[
\text{HN} \quad \text{HN} \\
\text{Me}_2\text{N} \quad \text{NMe}_2
\]

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

\[
\text{W}N_2 \quad \Rightarrow \quad \text{WN} \quad + \quad \frac{1}{2} \text{N}_2
\]
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:

\[ \text{H} + 2\text{HCl} + \text{TiCl}_4 \rightarrow \text{Cl}_2\text{Ti} + 2\text{HCl} \]

Hydrogen atoms from plasma remove chlorine as hydrogen chloride gas:

\[ \text{H}_4 + 4\text{H} + \text{Cl}_2\text{Ti} \rightarrow \text{H}_2\text{Ti} + 2\text{HCl} \]
Metals by Reduction with H₂ Molecules

Dissociative chemisorption of copper amidinate on a copper surface:

\[
\begin{align*}
\text{Cu–Cu–Cu–Cu–Cu–Cu–Cu} & \quad + \\
\text{R'N} & \quad \text{R'N} \\
\text{RN} & \quad \text{RN} \\
\text{Cu} & \quad \text{Cu} \\
\end{align*}
\]

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

\[
\begin{align*}
\text{Cu–Cu–Cu–Cu–Cu–Cu–Cu} & \quad + \quad \text{H₂} \\
\text{R'N} & \quad \text{R'N} \\
\text{RN} & \quad \text{RN} \\
\text{Cu} & \quad \text{Cu} \\
\end{align*}
\]

\[
\begin{align*}
\text{Cu–Cu–Cu–Cu–Cu–Cu–Cu} & \quad + \\
\text{R'N} & \quad \text{R'N} \\
\text{RN} & \quad \text{RN} \\
\text{Cu} & \quad \text{Cu} \\
\end{align*}
\]
Noble Metals by Oxidation Reactions

Oxygen atoms chemisorb on noble metals (platinum, ruthenium, etc.):

\[ M\cdots M\cdots M\cdots M\cdots M + O_n \rightarrow M\cdots M\cdots M\cdots M\cdots M \]

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

\[ M\cdots M\cdots M\cdots M\cdots M + M\text{L}_n \rightarrow M\cdots M\cdots M\cdots M\cdots M + CO_2 + H_2O \]
Tungsten Metal by Fluoride Exchange

Overall reaction: \( WF_6 + \text{Si}_2\text{H}_6 \rightarrow W + 2 \text{SiF}_3\text{H} + 2 \text{H}_2 \)

A \( F \) atom moves from \( WF_6 \) vapor to liberate \( \text{Si} \) from surface:

\[
\text{surface-WSiF}_2\text{H} + \text{WFF}_5 \rightarrow \text{surface-WWF}_5 + \text{SiFF}_2\text{H}
\]

3 \( F \) atoms move from \( W \) on surface to break up \( \text{Si}_2\text{H}_6 \) vapor:

\[
\text{surface-WWF}_2\text{F}_3 + \text{Si}_2\text{H}_6 \rightarrow \text{surface-WWSiF}_2\text{H} + \text{SiF}_3\text{H} + 2 \text{H}_2
\]

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

Chlorine atoms on surface move to trialkylsilyl groups on tellurium:

\[
\text{Ge-Ge-Ge-Ge-Ge} + (R_3\text{Si})_2\text{Te} \rightarrow \text{Ge-Ge-Ge-Ge-Ge} + R_3\text{SiCl}
\]

Chlorine atoms on germanium remove surface trialkylsilyl groups:

\[
R_3\text{SiSiSiSiSiSi} + \text{GeCl}_2 \rightarrow \text{GeGeGeGeGeGe} + R_3\text{SiCl}
\]
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)


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