Precursors with Metal-Nitrogen Bonds for ALD of Metals, Nitrides and Oxides

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Abstract

To achieve ALD's unique characteristics, ALD precursors must have very specific properties: high and self-limited reactivity with surfaces, high thermal stability and adequate volatility. In addition, their reaction byproducts must not react with the deposited films or the substrates. Precursors with metal-nitrogen bonds have been found to be particularly effective for ALD of metal oxides, nitrides and pure metals: dialkylamides of Al, Sn, Ti, Zr, Hf, Nb and Ta; dialkylamide-alkylimide mixed ligand compounds of Nb, Ta, Mo and W; dialkylacetamidinates of Mg, Ca, Sc, Ti, V, Cr, Mn, Fe, Ru, Co, Rh, Ni, Cu, Bi, Y, La and the other lanthanide metals. As one example, new precursors for ALD of nickel will be presented. Other examples of the materials made from these precursors include high-k dielectric insulators HfO_2, HfON, HfSiON and $LaAlO_3$; electrical conductors of Cu; conducting Cu diffusion barriers of WN and TaN_x; metals Co and Ru that promote strong adhesion between Cu and nitride diffusion barriers; magnetic metals Fe, Co and Ni and their magnetoresistive combinations with Al_2O_3 or MgO; photonic crystals of high-dielectric constant material Ta_3N_5; insulating AlN and Hf_3N_4 for passivating Ge surfaces.

Precursors with Metal-Nitrogen Bonds for ALD of Metals, Nitrides and Oxides

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Outline

How many precursors are needed?

Chemical Types of Precursors for ALD

Precursors with Metal-Nitrogen Bonds

Metals: Ni, Cu

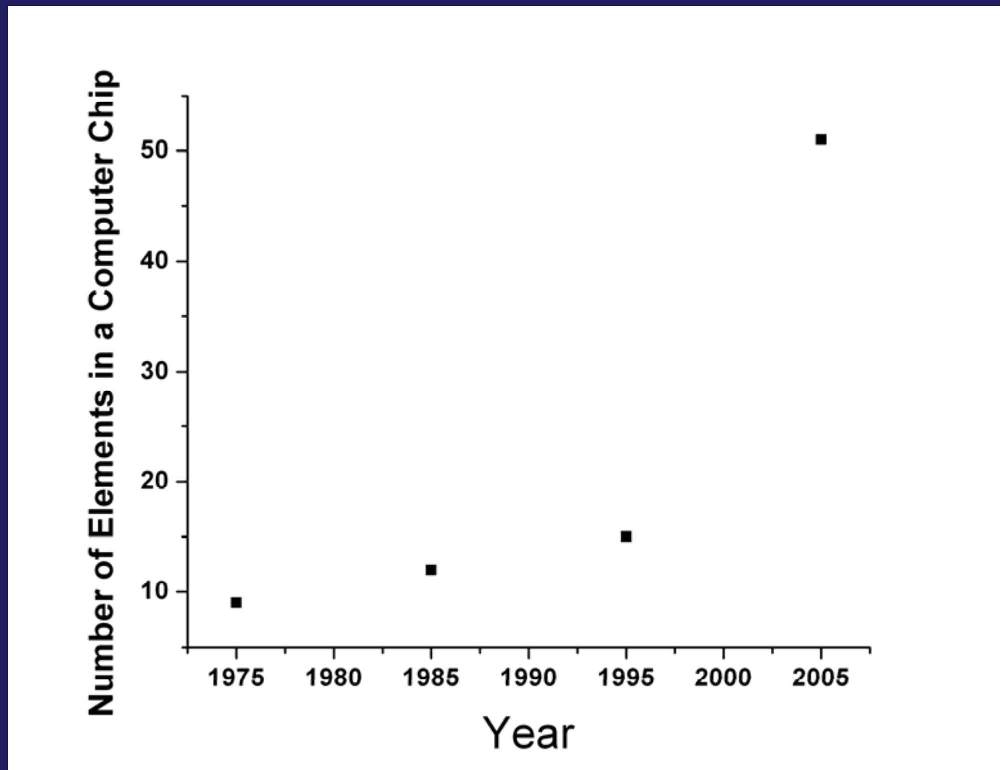
Nitrides: Hf_3N_4 => HfN

Oxides: Lanthanides, Transition metals

How Many Precursors Needed for ALD?

Total number of elements known	111
Radioactive elements	- 30
Highly toxic elements: lead, cadmium, mercury, thallium, beryllium	- 5
Noble gases: helium, neon, argon, krypton, xenon	- 5
Maximum number of elements possibly useful in ALD	71

Number of Elements in a Computer Chip



Criteria for ALD Precursors

- Sufficient volatility (> 0.1 Torr)

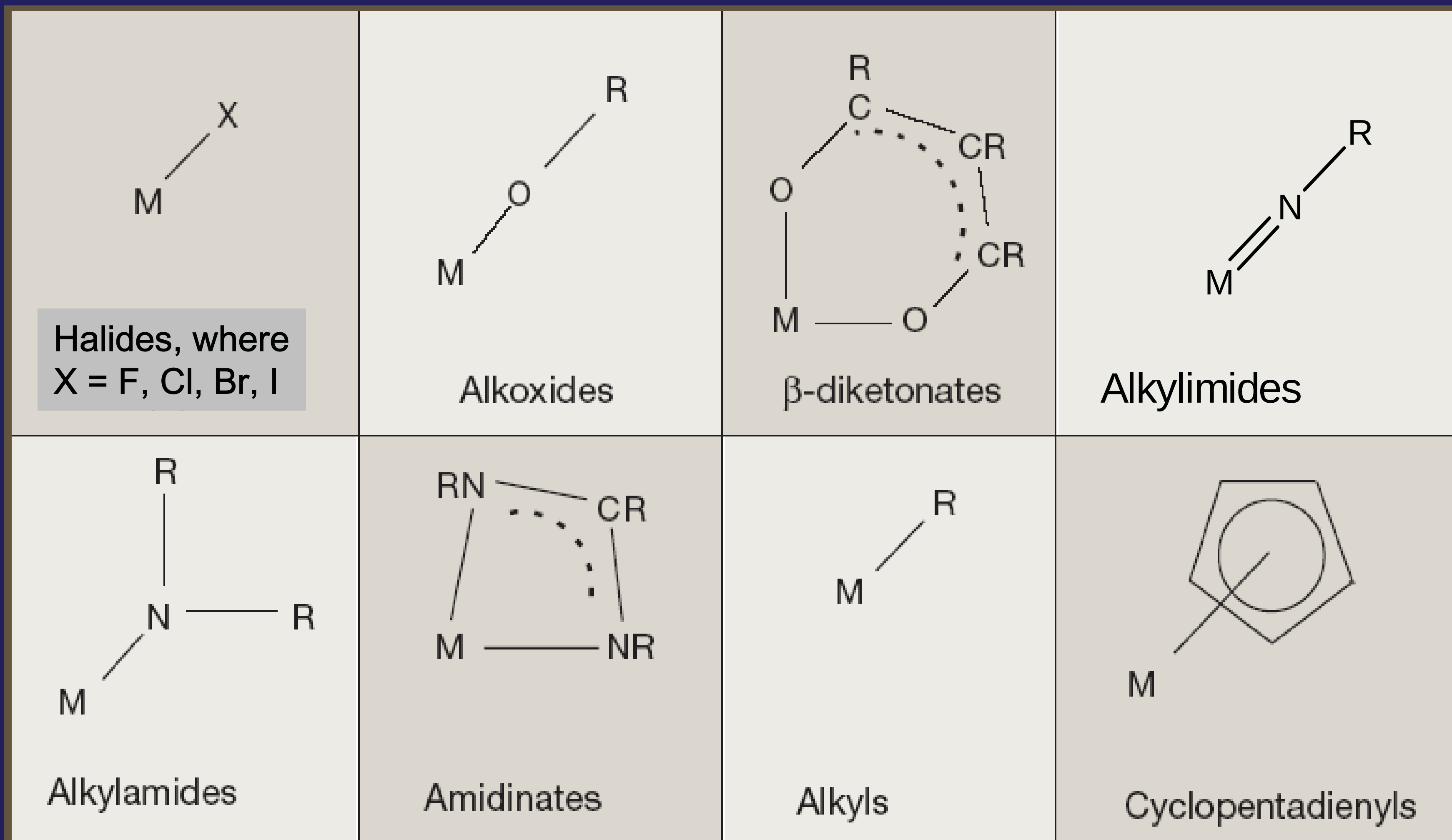
- Sufficient thermal stability

- High, self-limited reactivity with substrates

- High, self-limited reactivity with the surface prepared by the other precursor

- Precursors and byproducts that don’t etch or adsorb on the film or the substrate

Types of Precursors for ALD



R = alkyl group = C_xH_y

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Limitations of Precursor Types for ALD

Halides: corrosive and competitive adsorption of byproducts

Alkoxides: limited thermal stability

Beta-diketonates: low reactivity and high melting points

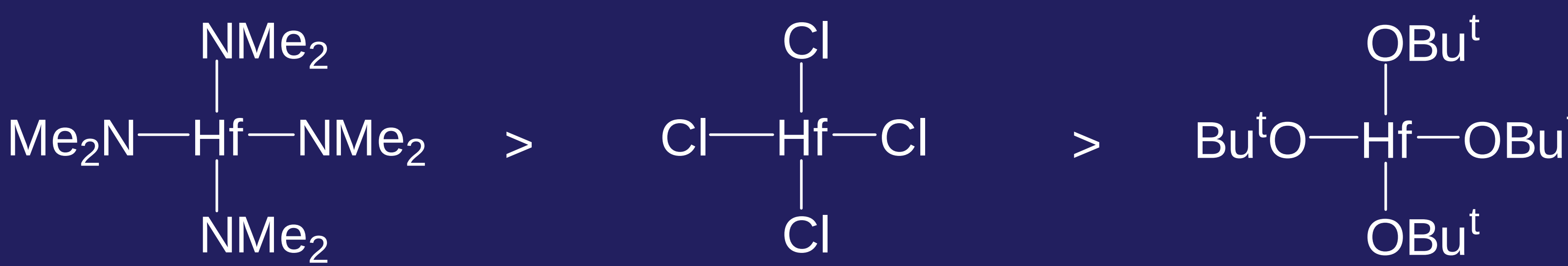
Alkyls: good for Al and Zn, but few other elements

Cyclopentadienyls: low reactivity and high melting points

Amides and imides: some have limited thermal stability

Amidinates: high melting points for trivalent metals

Reactivity of Hafnium Precursors



Hafnium dimethylamide   Hafnium chloride   Hafnium *tert*-butoxide

$Hf(NMe_2)_4$ has highest reactivity with water and ammonia, leading to the

- **Purest films (<0.1% impurities)**
- **Smoothest films (roughness same as substrate)**
- **Highest step coverage (>200:1 aspect ratios)**
- **Lowest deposition temperature (~50 ºC)**

Precursors with Nitrogen-Based Ligands

Green = at least one volatile N-based precursor known

Red = Radioactive

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
			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	No	Lr	

53 metals

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ALD of transition metals from amidinate precursors

Thermal ALD with molecular hydrogen, H_2

Film	Precur. Temp.	Depos. Temp.	Growth Rate	Metal Dose	Hydrogen Dose	Metal Exposure	Hydrogen Exposure
	°C	°C	Å/cycle	$nmol/cm^2$	$\mu mol/cm^2$	Torr-sec	Torr-sec
Mn	85	250					
Fe	75	250	0.6	2	4	0.04	40
Co	65	350	0.2	2	0.9	0.05	20
Ni	95	270	0.2 to 0.5	2	4	0.05	40
Cu[1]	105	170	0.1 to 2.0	4	3	0.09	60
Ru[2]	130	270	0.1 to 0.5				
Rh							

[1]Zhengwen Li, ALD 2005, Tuesday 1:45

[2]Huazhi Li, ALD 2005, Tuesday 2:15

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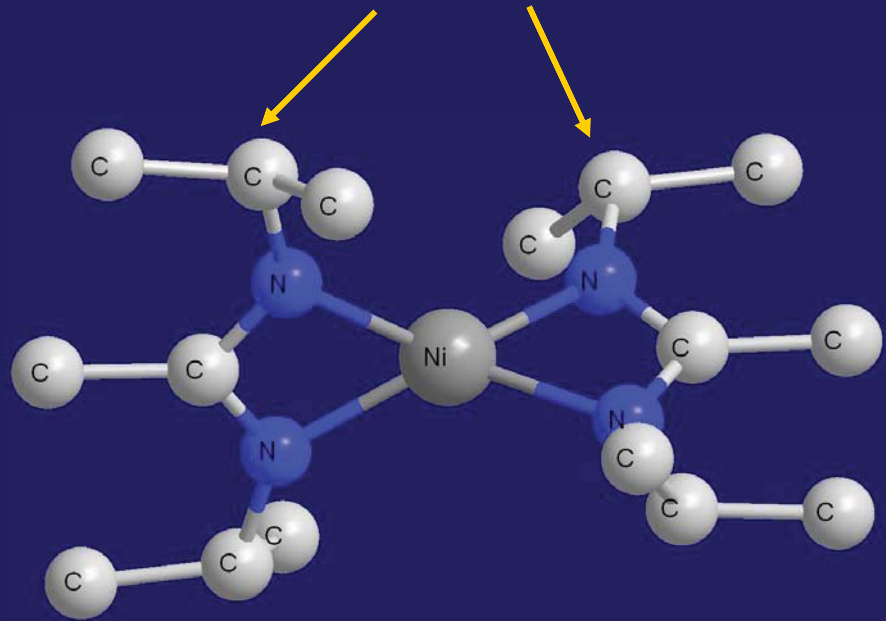
Structures of 2 Ni acetamidinate precursors

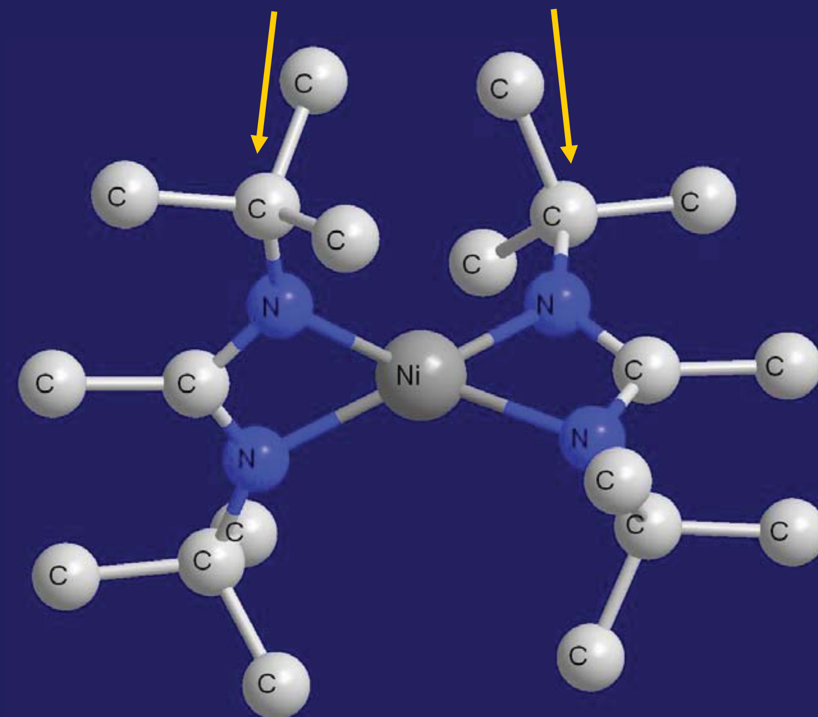
isopropyls
on each N



Ni(^{i}Pr-amd)$_2$

(N,N'-diisopropylacetamidinato)$_2$Ni

tert-butyls
on each N



Ni(^{t}Bu-amd)$_2$

(N,N'-di-*tert*-butylacetamidinato)$_2$Ni

(for clarity, hydrogens not shown)

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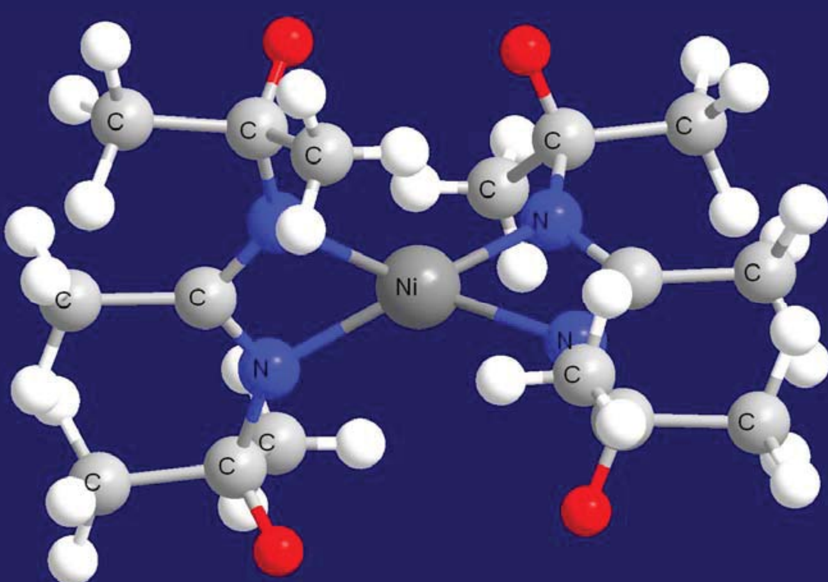
Stabilities of these two Ni precursors are very different

Ni(^{i}Pr-amd)$_2$

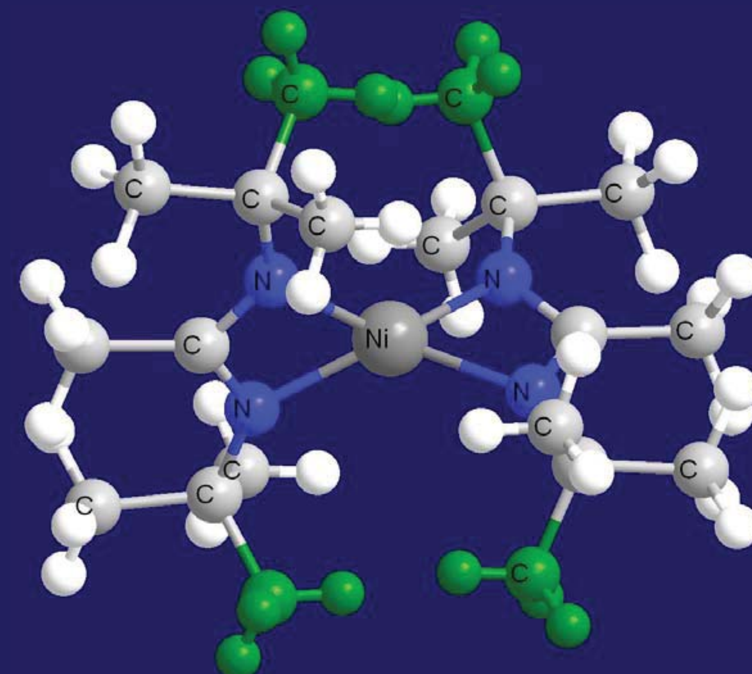
Less stable, decomposes during distillation.
TG residue 27%



Hydrogens on the carbons directly attached to nitrogen => less stable

Ni(tBu-amd)$_2$

More stable, distills without decomposition.



No hydrogens on carbons directly attached to nitrogen

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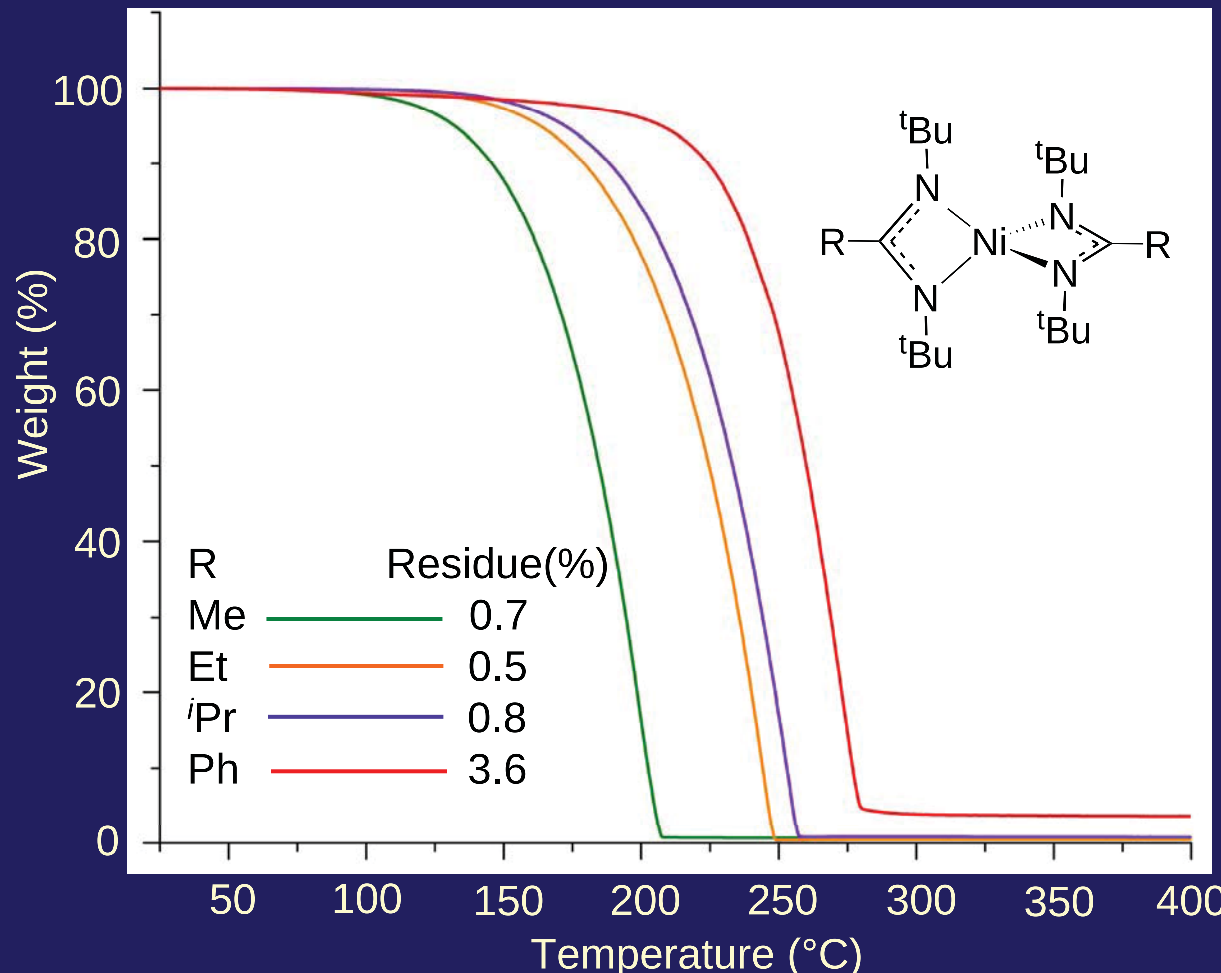
Nickel Precursors with Various Alkyl Groups



All these precursors evaporate cleanly, except phenyl-substituted

The methyl precursor is the most volatile, so it was used for ALD.

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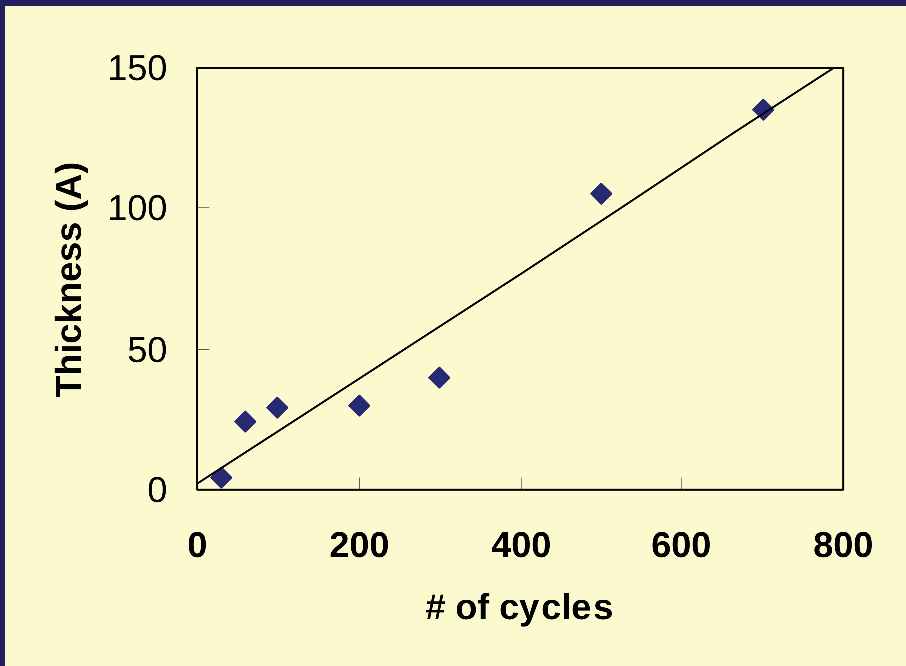
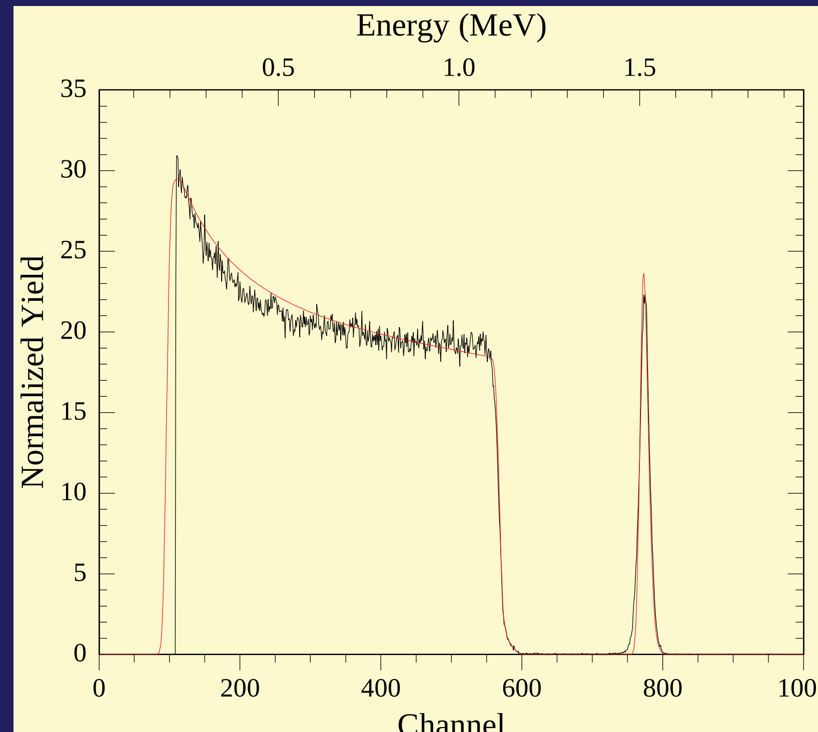
ALD of Nickel on Si





- 95 ºC source (liquid)
- 270ºC substrate
- Growth : ~0.2 Å/cycle

with either H_2 or NH_3

RBS spectrum (700 cycles)

Thickness ~ 14 nm

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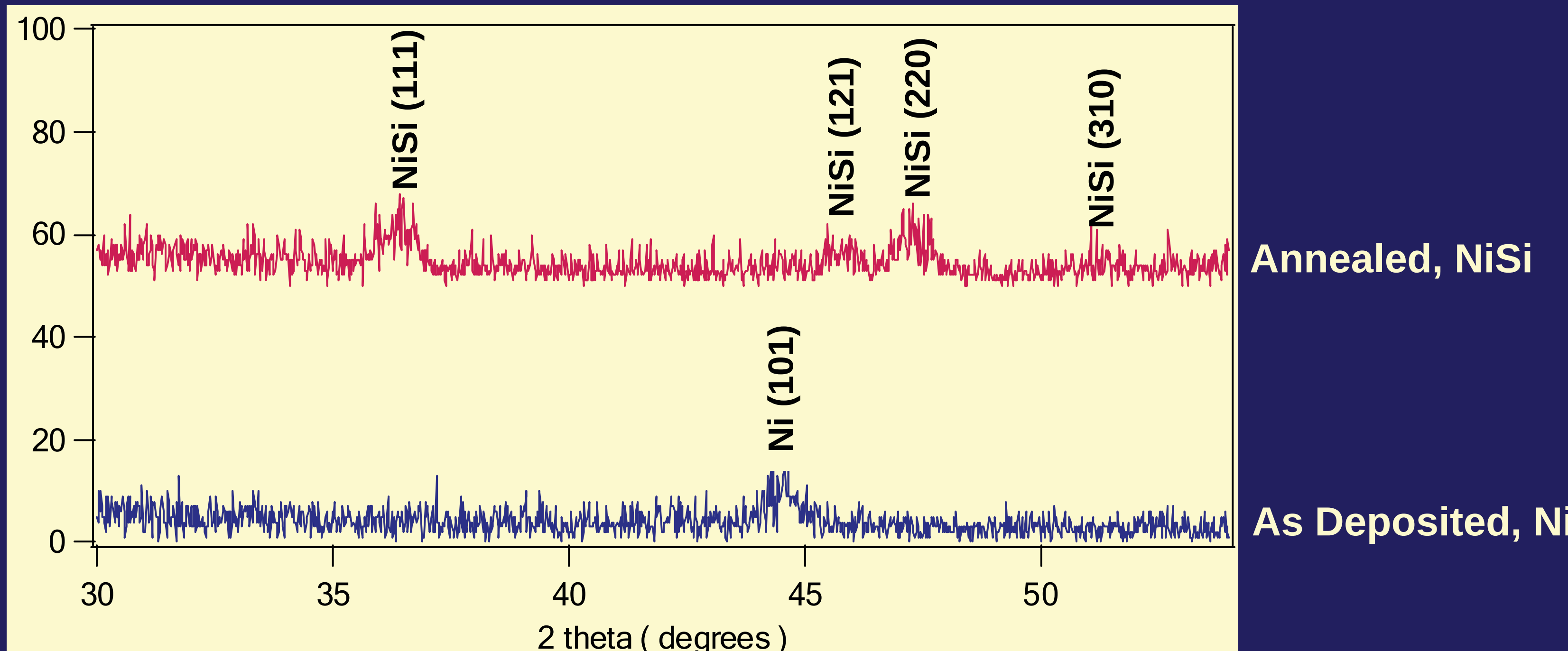
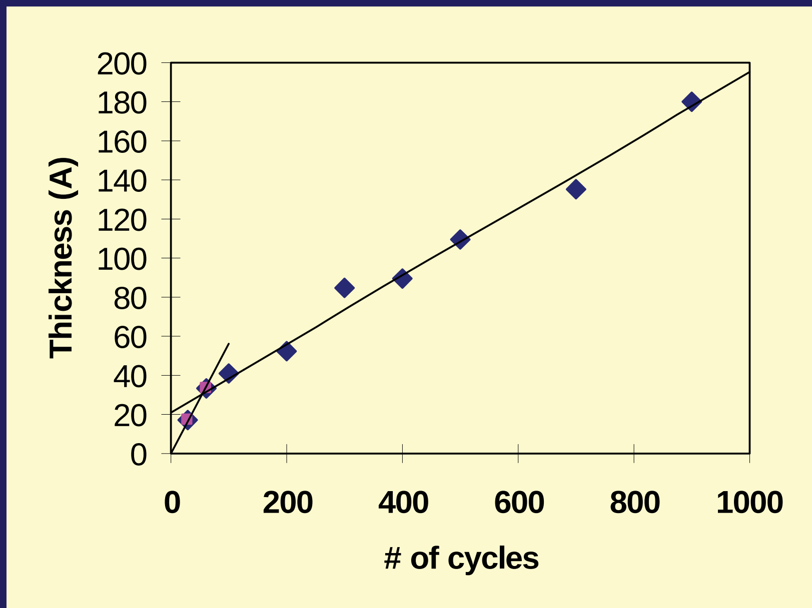
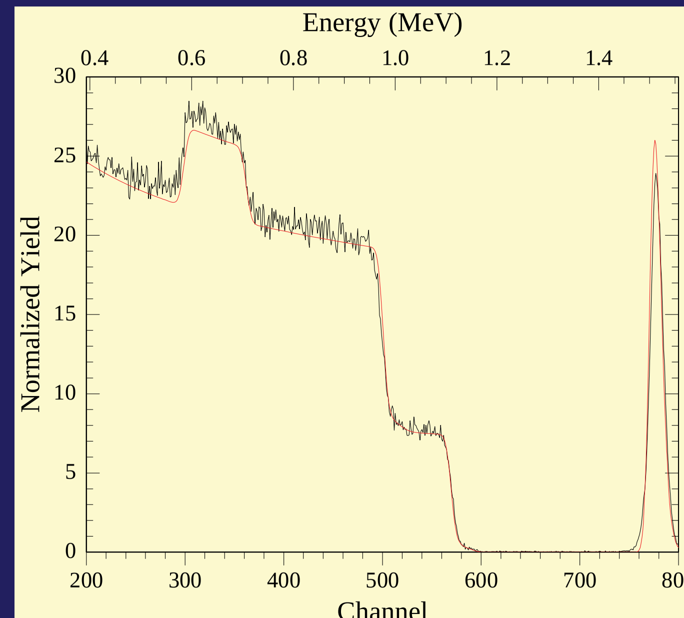
XRD of Nickel on Si



- Silicidation using RTA : 550 ^{o}C, 5 min in forming gas (low pressure)
- Sheet resistance of Ni as deposited ~ 90 Ω/□, 14 nm
- Sheet Resistance of NiSi after annealing ~ 4.2 Ω/□

ALD of Nickel on SiO_2





- Deposition Conditions: 270ºC/ 95 ºC
- Growth before 60 cycles ~ 0.6 Å / cycle
- Growth after 60 cycles ~ 0.2 Å/cycle
- Resistivity ~ 68 μΩ-cm (900 cycle, 18 nm, Sheet Resistance ~ 38 Ω/□)

- RBS spectrum for 700 cycles
- Thickness ~ 14 nm

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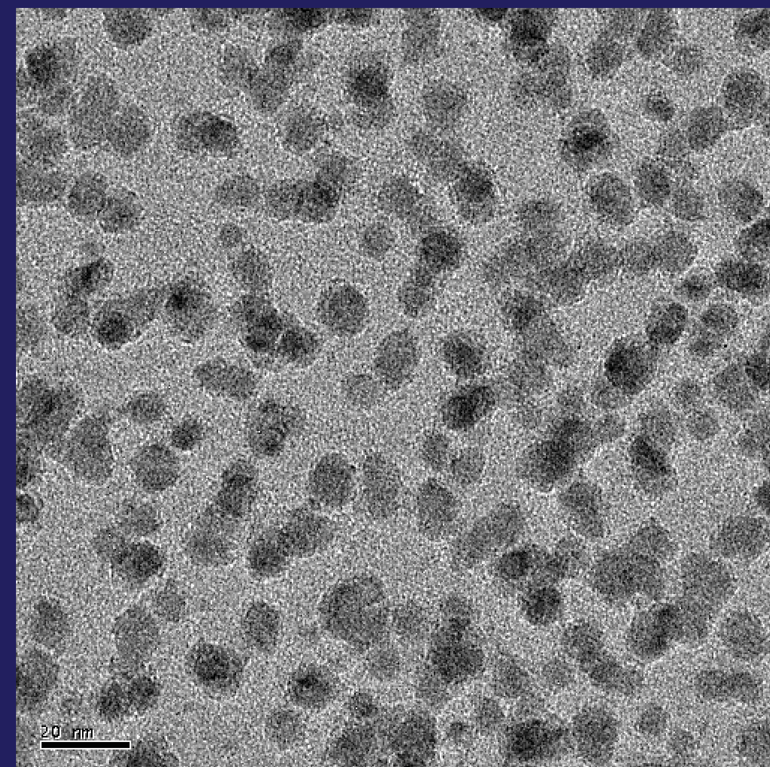
TEM of Nucleation of Nickel on SiO_2

Growth at 270 °C , 30 cycles

Thickness by RBS ~ 1.7 nm

Average grain diameter 5-10 nm



Scale bar = 20 nm

Most of the grains have similar sizes; no small grains

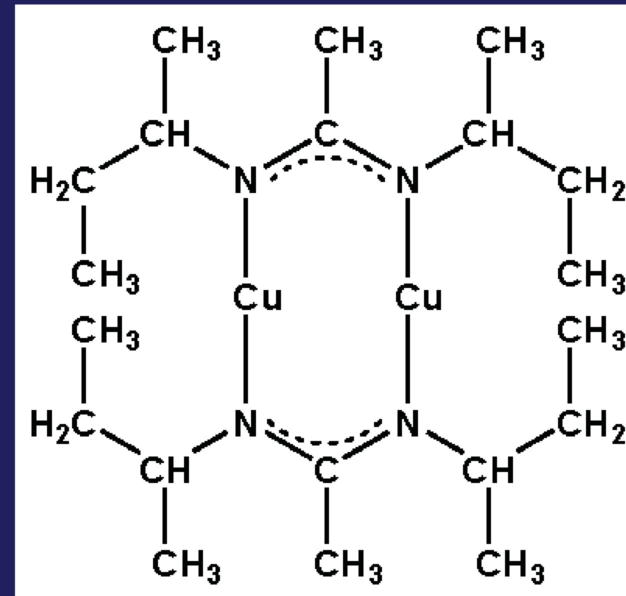
Most of the growth occurs directly on bare SiO_2, with Ni atoms then diffusing to the initial nuclei.

Precursors for ALD of Copper Films

Cu(I) N,N'-di-*sec*-butylacetamidinate
[Cu(sec-Bu$_2$-amd)]$_2$
Melting point: 77 °C
Vapor pressure of liquid: 95 °C/0.2 Torr

Reactive to molecular hydrogen, H_2

0.1 to 2 Angstrom per cycle



Substrate	Growth (A/cycle)
Cu	0.4 - 0.5
Co	0.4 - 0.5
Ru	0.1 - 0.2
SiO_2, Al_2O_3, HfO_2	1 - 2

Zhengwen Li, ALD 2005 (Tuesday, 1:45pm)
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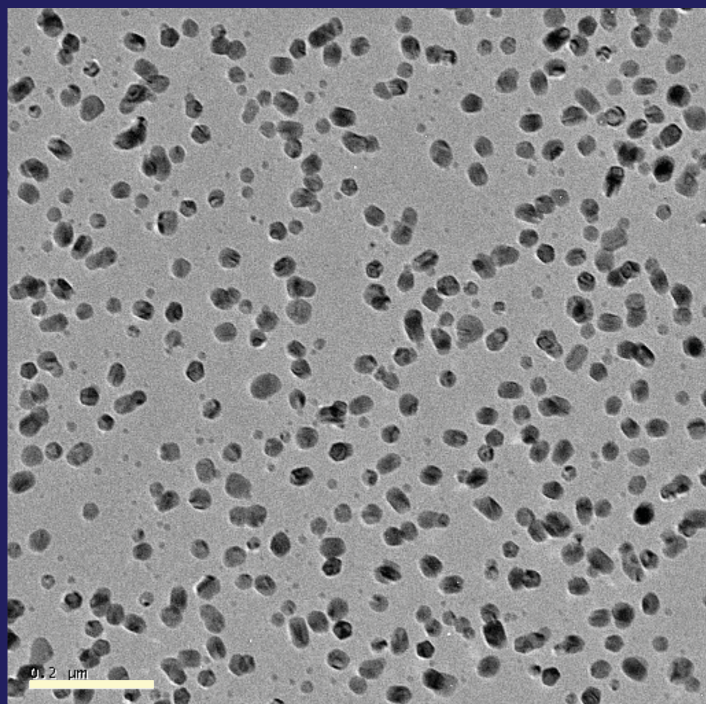
TEM Study of Cu Nucleation on SiO_2 and on Co

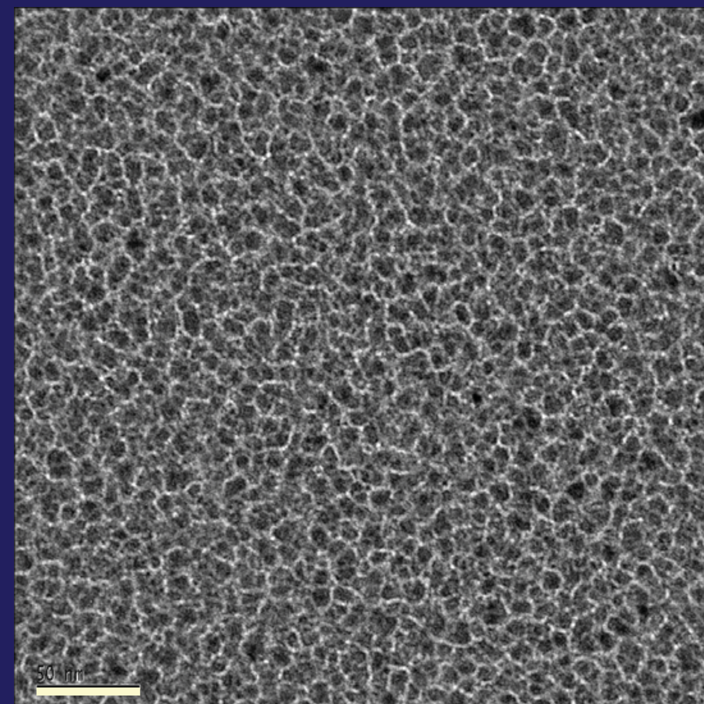
30 ALD cycles of Cu/H_2 on a SiO_2 substrate :



200 nm

6 nm Cu, few large nuclei not electrically connected

50 ALD cycles of Cu/H_2 on a Co/SiO_2 substrate:



50 nm

2 nm Cu, many small nuclei electrically connected

40 Ω/□ for 4 nm thick Cu seed layer

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ALD of metal nitrides from nitrogen-based ligands

Film	Precursor Type	Precur. Temp.	Depos. Temp.	Growth Rate	Metal dose	Ammonia Dose
		^oC	^oC	Å/cycle	$nmol/cm^2$	$nmol/cm^2$
AlN	alkylamide	95	200	0.8		
TiN	alkylamide	75	180	1.5		
Zr_3N_4	alkylamide	65	200	1.2	1.5	7
Hf_3N_4	alkylamide	55	220	1.2	1.5	7
Ta_3N_5	imide-amide	90	250	1.2	1	
WN	imide-amide	65	380	1.5		
Ni_xN	amidinate	55	250	0.2-0.5		
Cu_3N[1]	amidinate	105	170	0.2-0.5		

[1]Zhengwen Li, ALD 2005 (Tuesday 1:45pm)

ALD of Hafnium Nitrides, Hf_3N_4 and HfN

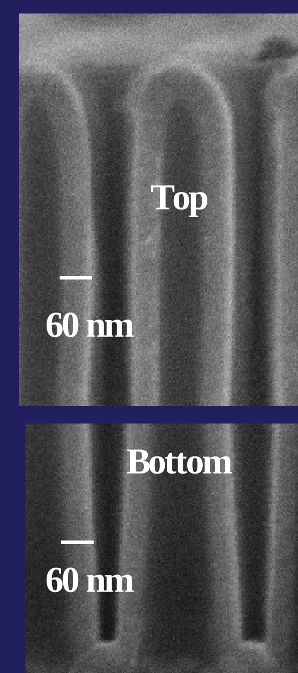
Hf_3N_4, insulator, refractive index ~2.5, dielectric constant ~30

HfN, metal, bulk resistivity ~ 39 μΩ-cm, melting pt. ~ 3300 °C

ALD of Hf_3N_4 on substrates at 150 °C to 250 °C by reaction:

tetrakis(dimethylamido)hafnium, $Hf(NMe_2)_4 + NH_3 \Rightarrow Hf_3N_4$

Smooth, amorphous, highly conformal Hf_3N_4 in holes with aspect ratio > 40:1.



Jill S. Becker, Esther Kim and Roy G. Gordon, ***Chem. Mater.*** **(2004), 16, 3497.**

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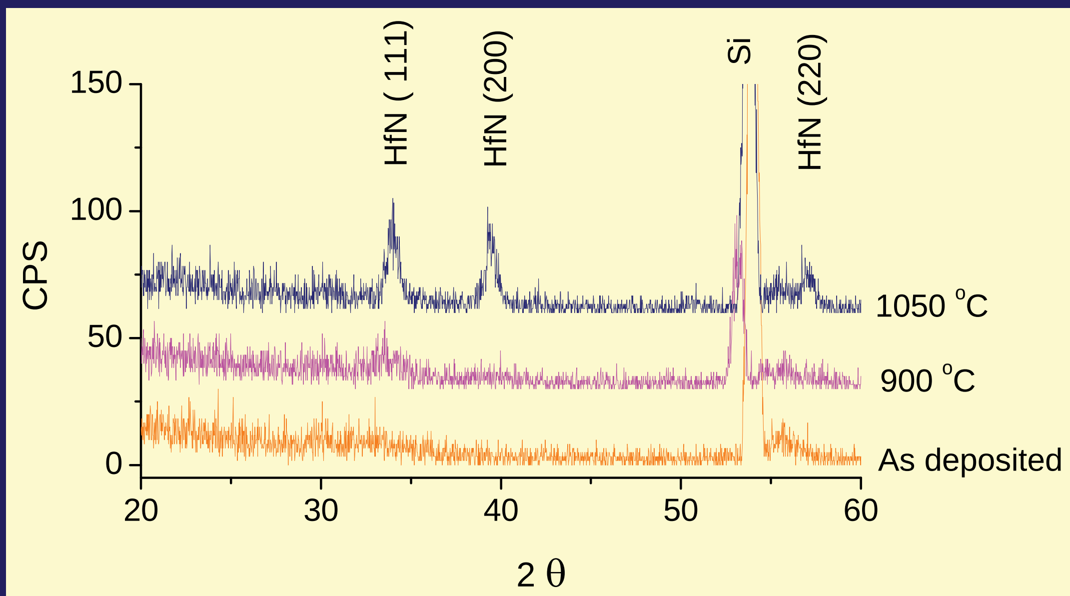
Conversion of Insulating Hf_3N_4 to Metallic HfN

Rapid thermal annealing (~ 1 minute at 1000 ^oC) dissociates some nitrogen from Hf_3N_4 to form metallic HfN.



Amorphous Hf_3N_4 forms crystalline HfN

HfN resistivity is ~ 156 μΩ-cm > bulk resistivity ~ 39 μΩ-cm

This HfN is a candidate for a conformal, refractory gate metal.

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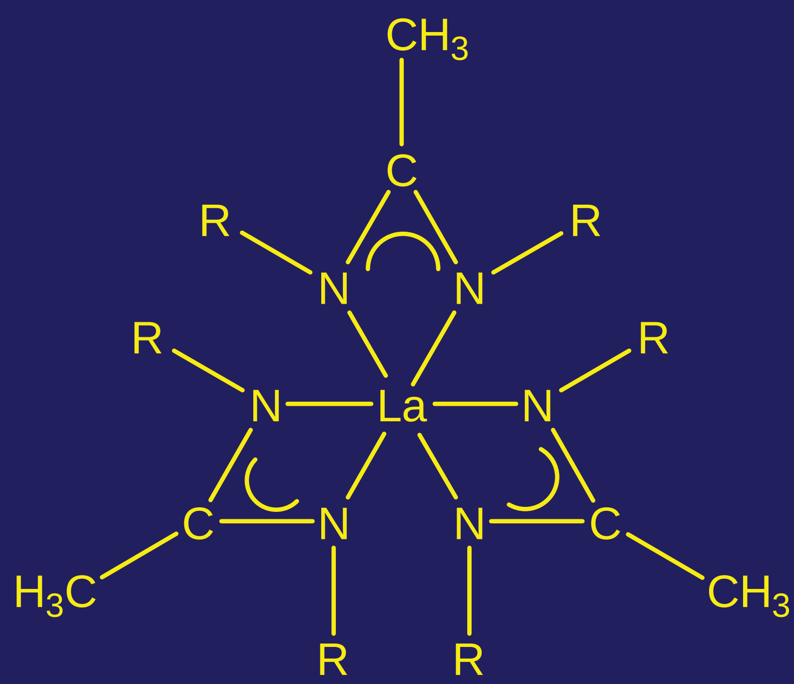
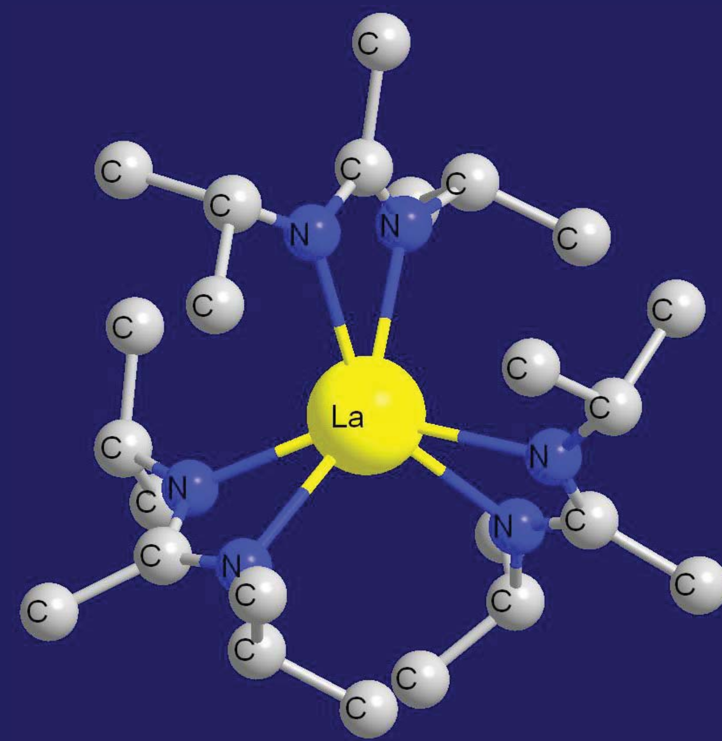
New Lanthanide Precursors



R = isopropyl



Most volatile La compound known (~0.1 Torr/130 ^oC)

High thermal stability (~300 ^oC in ALD reactor)

Initiates growth on HF-last silicon, EOT ~ 1nm, < mA leakage

Similar precursors prepared for other lanthanide metals, including Pr, Gd, Lu, Y and Sc

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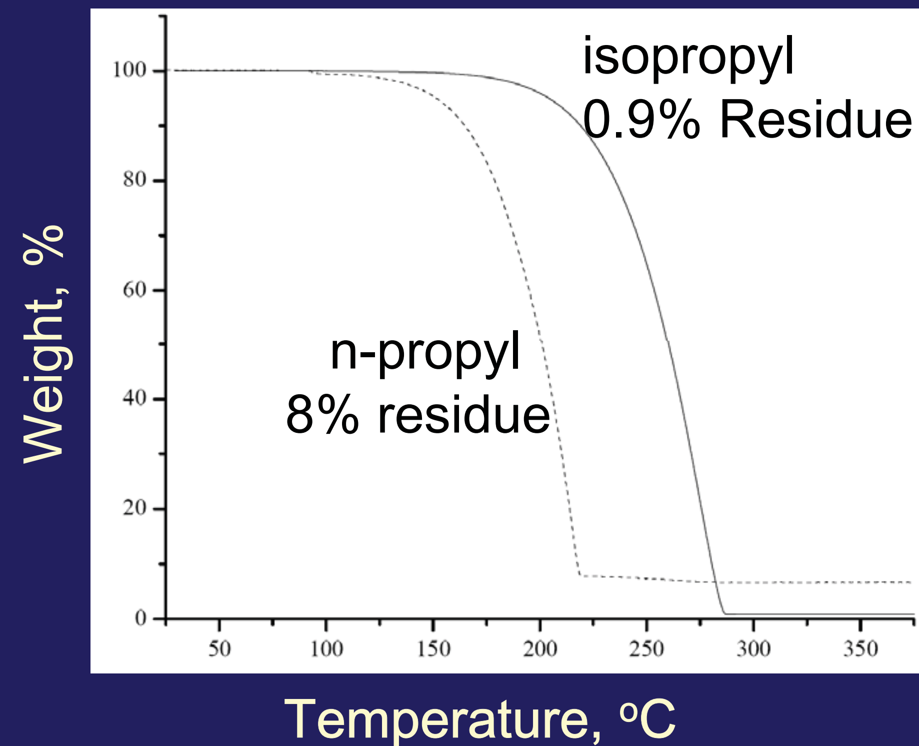
TG of Yttrium Amidinates

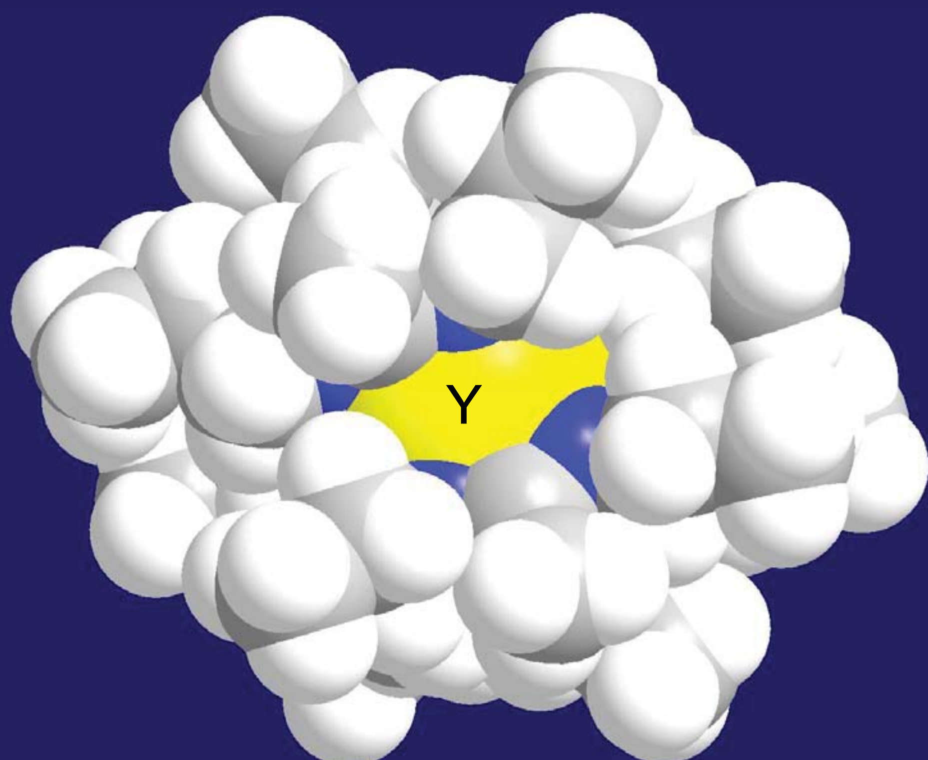


solid isopropyl is more stable, leaves low residue

n-propyl vaporizes more rapidly, because it is a liquid > 90 °C

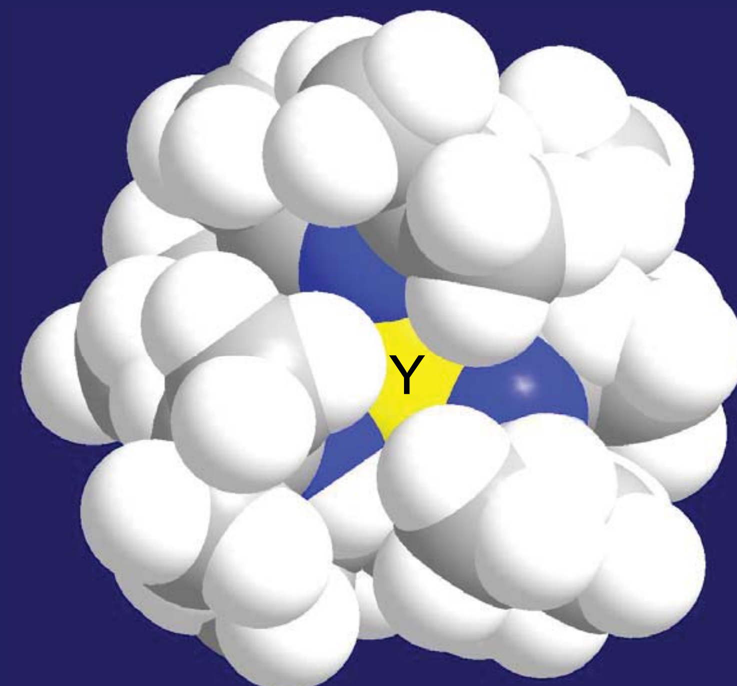
Models for Yttrium Amidinates

n-propyl amidinate ligands
are not crowded



Y open to decomposition

isopropyl amidinate ligands
are crowded



Y protected from
decomposition

ALD of metal(III) oxides from amidinate precursors

Film	Prec. Temp.	Depos. Temp.	Growth Rate	Metal Dose	H_2O Dose	Metal Exposure	H_2O Exposure
	°C	°C	Å/cycle	$nmol/cm^2$	$nmol/cm^2$	Torr-sec	Torr-sec
V_2O_3	120	250	0.5	7		0.18	
Sc_2O_3*	150	300	0.3	14	20	0.35	0.5
Lu_2O_3	140	300			20		0.5
Y_2O_3	140	300	0.8	6	46	0.15	1
Gd_2O_3	140	300	1.0		20		0.5
Pr_2O_3#	140	300	1.0	2	83	0.05	2
La_2O_3#	140	290	0.9	2	83	0.05	2
Bi_2O_3	90	220					

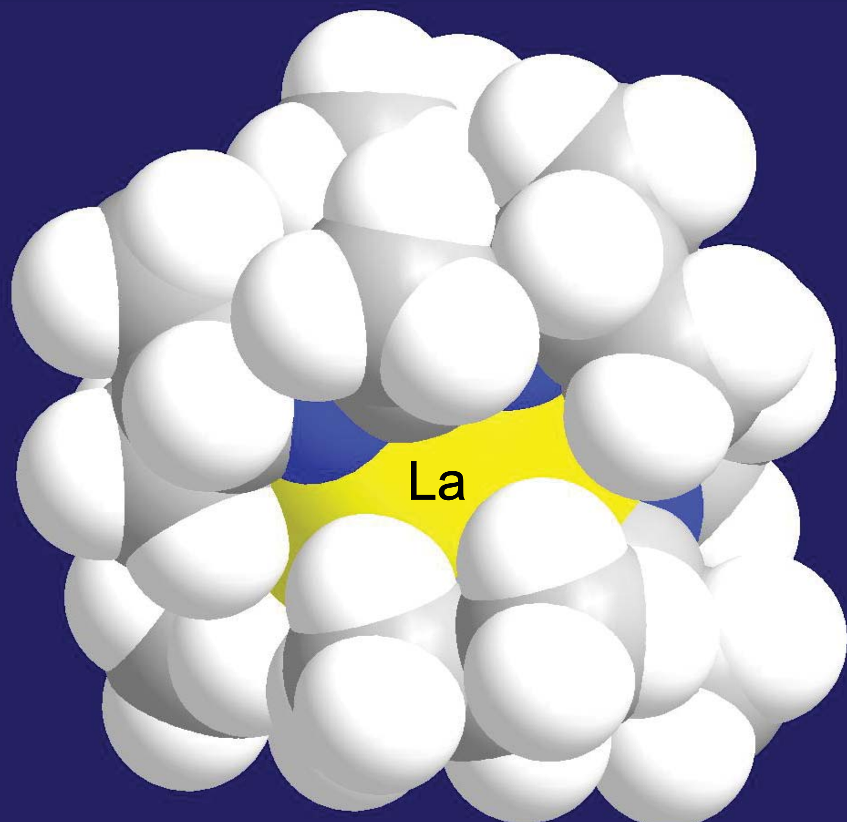
Smaller metals (V, Sc, near top of table) have lower growth per cycle, but require higher metal exposure to reach saturation (kinetic limitation).

*Philippe de Rouffignac, ALD 2005 (Wednesday B 8:45 am)

#Kyoung-ha Kim, ALD 2005 (Wednesday B 8:15 am)

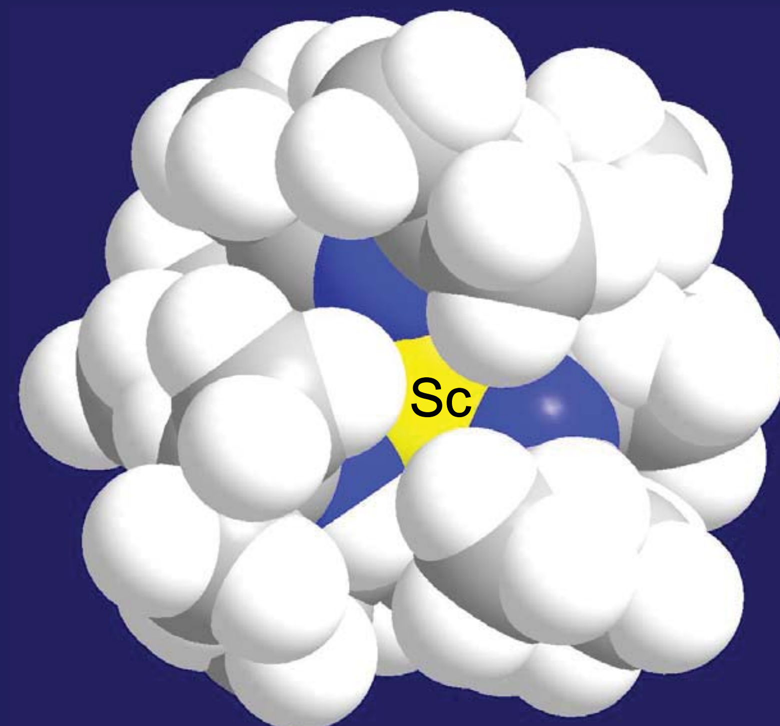
Models for Lanthanum and Scandium Amidinates

La ion is large, so 3 amidinate ligands are not crowded



La precursor reacts quickly with surface OH

Sc ion is small, so 3 amidinate ligands are crowded



Sc precursor reacts slowly with surface OH

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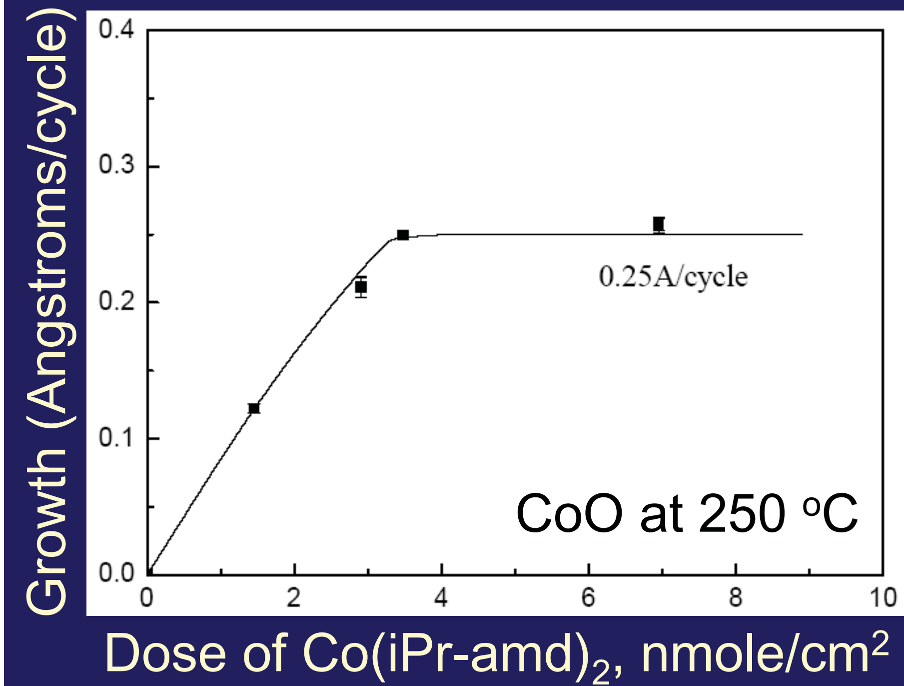
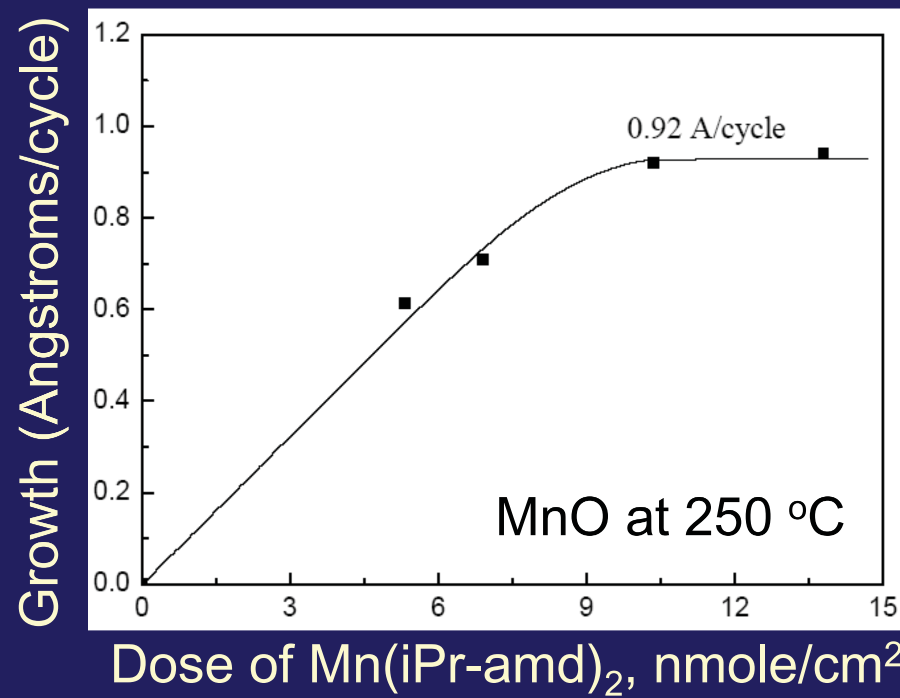
Saturation Curves for CoO and MnO from Amidinates





Shows self-limiting ALD reactivity with water vapor

ALD of metal(II) oxides from amidinates

Film	Prec. Temp.	Depos. Temp.	Growth Rate	Metal Dose	H_2O Dose	Metal Exposure	H_2O Exposure
	°C	°C	Å/cycle	nmol/cm²	nmol/cm²	Torr-sec	Torr-sec
FeO	75	250	0.2	2		0.04	
CoO	65	250	0.4	3.5	83	0.08	2
NiO	95						
CuO	95	250	0.5	5	83	0.1	2
MgO	65	250	0.8	8	83	0.16	2
MnO	105	250	0.9	10	83	0.2	2

Smaller metals (Fe, Co,near top of table) have lower growth per cycle,
& require lower metal doses to reach saturation (effect of stoichiometry?)

Summary

With suitable choices of alkyl groups on the ligands, precursors with metal-nitrogen bonds can have

- Sufficient volatility (> 0.1 Torr)
- Sufficient thermal stability
- High, self-limited reactivity with substrates
- High, self-limited reactivity with the surface prepared by the other precursor
- Precursors and byproducts that don’t etch or adsorb on the film or the substrate

These precursors are available for ALD of many metals, metal nitrides and metal oxides

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TEM: Damon Farmer

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