ALD Precursors and Reaction Mechanisms

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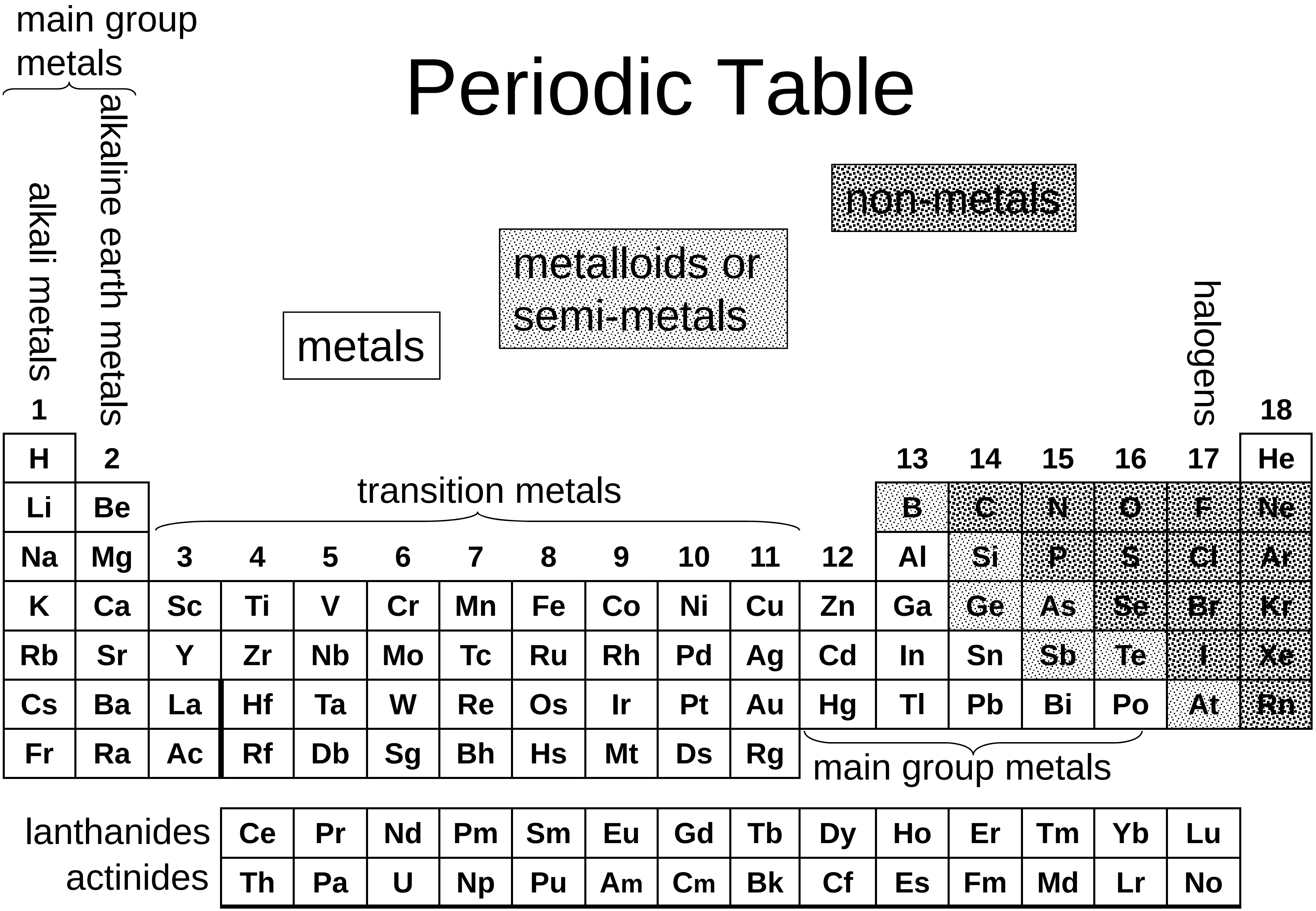
Outline

- 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

Periodic Table



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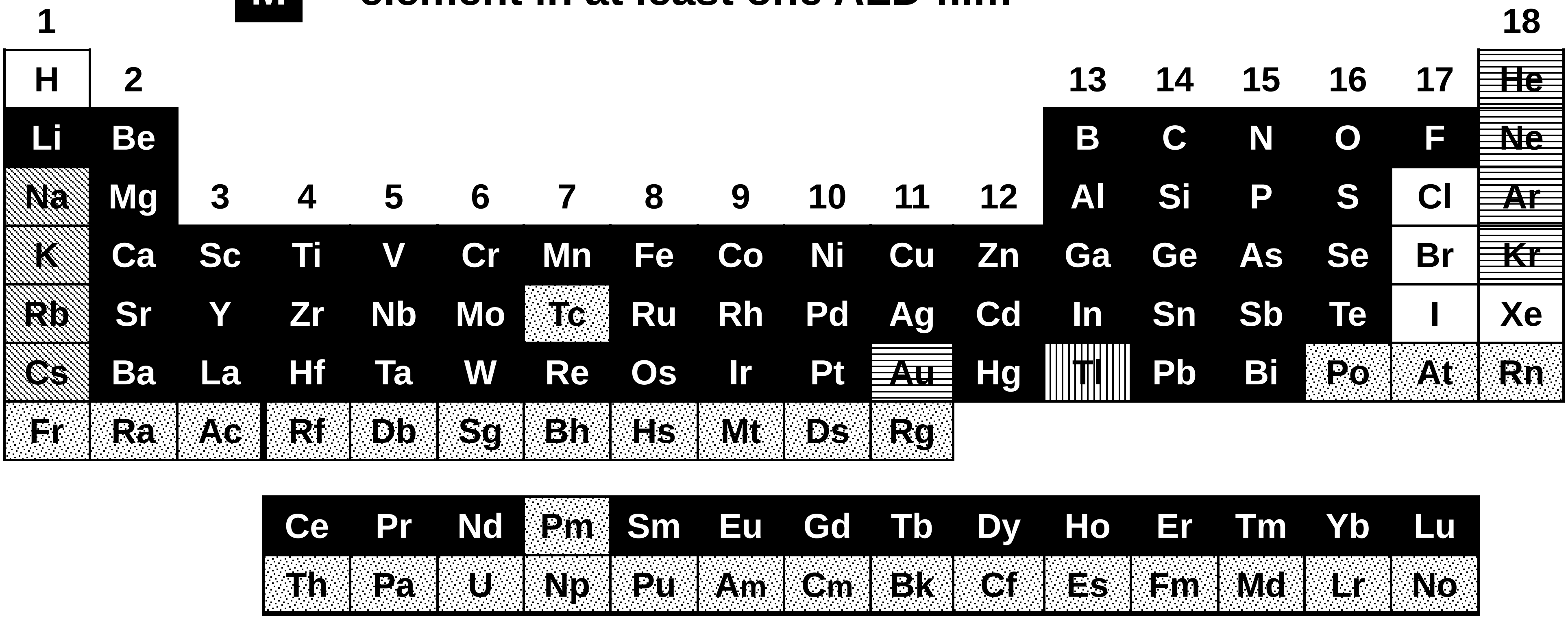
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

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

Elements in ALD Films

■ M = element in at least one ALD film



1																	18
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■ Li	■ Be											■ B	■ C	■ N	■ O	■ F	▤ Ne
▨ Na	■ Mg	3	4	5	6	7	8	9	10	11	12	■ 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	░ Rf	░ Db	░ Sg	░ Bh	░ Hs	░ Mt	░ Ds	░ Rg							

■ 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

Not used in ALD because the elements are

▨ = low-volatility compounds

░ = radioactive

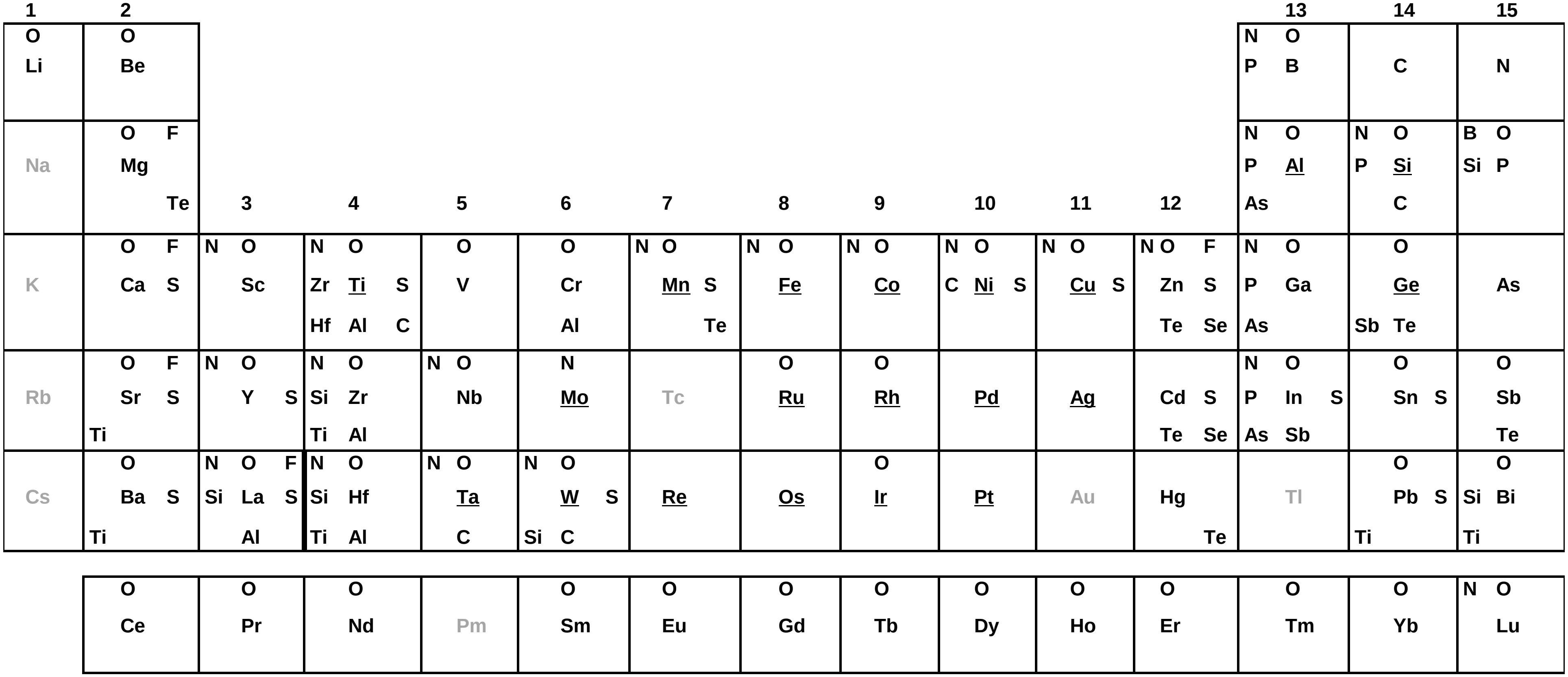
▥ = highly toxic

▤ = 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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Na	O F Mg Te											N O P Al As	N O P Si C	B O Si P
K	O F Ca S	N O Sc	N O Zr Ti S Hf Al C	O V	O Cr Al	N O Mn S Te	N O Fe	N O Co	N O C Ni S	N O Cu S	N O F Zn S Te Se	N O P Ga As	O Ge Sb Te	As
Rb	O F Sr S Ti	N O Y S	N O Si Zr Ti Al	N O Nb	N Mo	Tc	O Ru	O Rh	Pd	Ag	Cd S Te Se	N O P In S As Sb	O Sn S	O Sb Te
Cs	O Ba S Ti	N O F Si La S Al	N O Si Hf Ti Al	N O Ta C	N O W S Si C	Re	Os	O Ir	Pt	Au	Hg Te	Tl	O Pb S Ti	O Si Bi Ti
	O Ce	O Pr	O Nd	Pm	O Sm	O Eu	O Gd	O Tb	O Dy	O Ho	O Er	O Tm	O Yb	N O Lu

Updated table from R. Puurunen, *J. Appl. Phys.* 97, 121301 (2005)

ALD Materials by Type

Oxide dielectrics	**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_x, Gd_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3, $SrTiO_3$, $BaTiO_3$, $PbTiO_3$, $PbZrO_3$, Bi_xTi_yO, Bi_xSi_yO, $SrTa_2O_6$, $SrBi_2Ta_2O_9$, $YScO_3$, $LaAlO_3$, $NdAlO_3$, $GdScO_3$, $LaScO_3$, $LaLuO_3$, $LaYbO_3$, $Er_3Ga_5O_{13}$**
Oxide conductors or semiconductors	**In_2O_3, In_2O_3:Sn, In_2O_3:F, In_2O_3:Zr, SnO_2, SnO_2:Sb, Sb_2O_3, ZnO, ZnO:Al, ZnO:B, ZnO:Ga, RuO_2, RhO_2, IrO_2, Ga_2O_3, VO_2, V_2O_5, WO_3, W_2O_3, NiO, CuO_x, FeO_x, CrO_x, CoO_x, MnO_x**
Other ternary oxides	**$LaCoO_3$, $LaNiO_3$, $LaMnO_3$, $La_{1-x}Ca_xMnO_3$**
Nitride dielectrics or semiconductors	**BN, AlN, GaN, InN, Si_3N_4, Ta_3N_5, Cu_3N, Zr_3N_4, Hf_3N_4, LaN, LuN**
Metallic nitrides	**TiN, Ti-Si-N, Ti-Al-N, TaN, NbN, MoN, WN_x, WN_xC_y, Co_xN, Sn_xN**
II-VI semiconductors	**ZnS, ZnSe, ZnTe, CaS, SrS, BaS, CdS, CdTe, MnTe, HgTe**
II-VI based phosphors	**ZnS:M (M=Mn,Tb,Tm); CaS:M (M=Eu, Ce, Tb, Pb); SrS:M(M=Ce,Tb, Pb)**
III-V semiconductors	**GaAs, AlAs, AlP, InP, GaP, InAs**
Fluorides	**CaF_2, SrF_2, MgF_2, LaF_3, ZnF_2**
Elements	**Ru, Pt, Ir, Pd, Rh, Ag, Cu, Ni, Co, Fe, Mn, Ta, W, Mo, Ti, Al, Si, Ge**
Other semiconductors	**PbS, SnS, In_2S_3, Sb_2S_3, Cu_xS, $CuGaS_2$, WS_2, SiC, $Ge_2Sb_2Te_5$**
Others	**La_2S_3, Y_2O_2S, TiC_x, TiS_2, TaC_x, WC_x, $Ca_3(PO_4)_2$, $CaCO_3$, 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

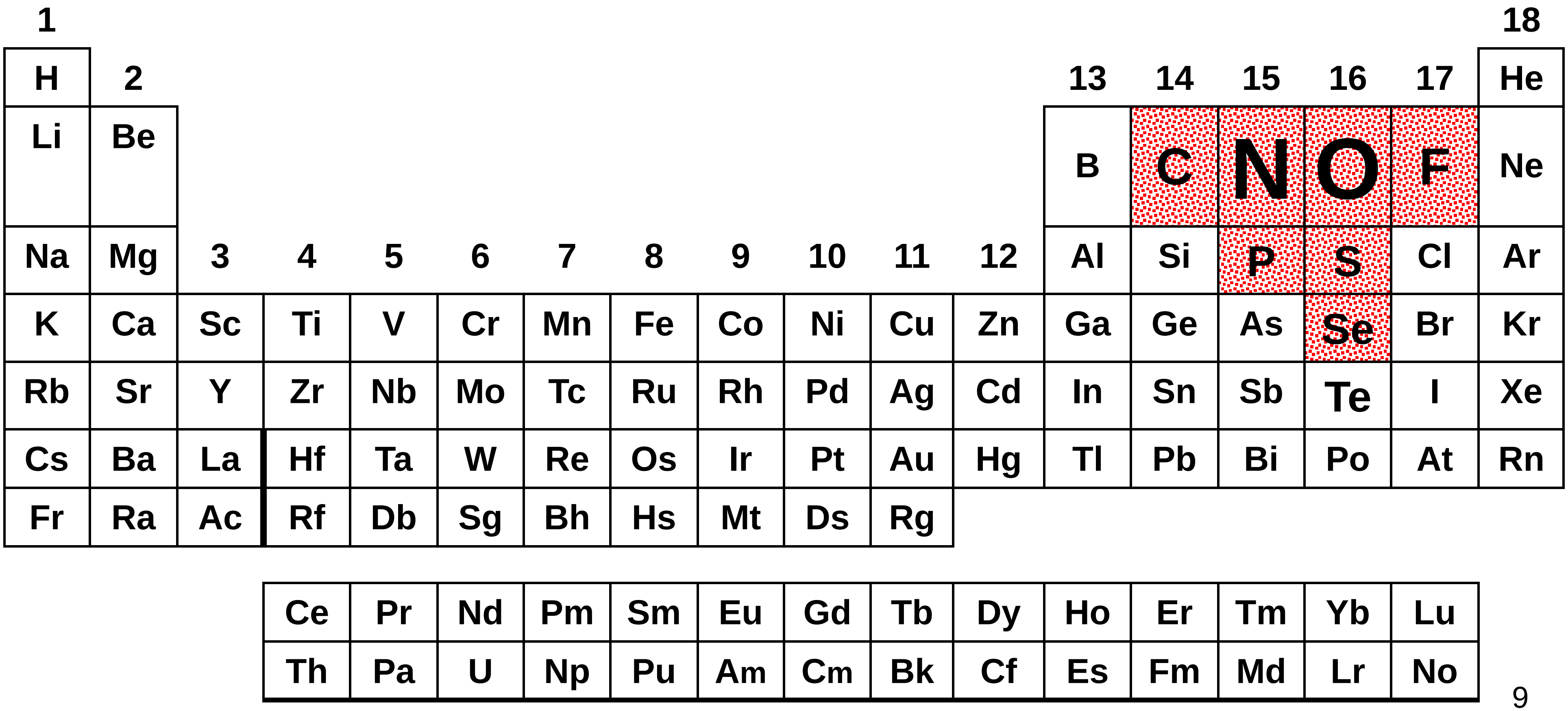
Non-Metals Important in ALD Films

C = Carbon

N = Nitrogen
P = Phosphorus

O = Oxygen
S = Sulfur
Se = Selenium

F = Fluorine



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			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	Lr	No	

ALD Precursors for Oxygen

Water vapor, H_2O

Hydrogen peroxide, H_2O_2, sometimes more reactive than H_2O (always accompanied by water)

Alcohols, ROH, such as methanol CH_3OH or ethanol C_2H_5OH

Di-oxygen, O_2, the common form of oxygen in the air

Ozone, O_3, a more reactive form of oxygen, made in a plasma, can flow through tubing; (always accompanied by O_2)

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 O_2

Nitrogen dioxide**,** NO_2 (always accompanied by its dimer N_2O_4)

ALD Precursors for Nitrogen

Ammonia, NH_3

Hydrazine, N_2H_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

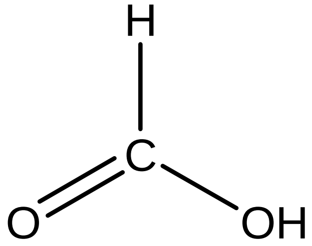
Plasma-activated N_2 is more reactive than N_2

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

ALD Precursors for Carbon

Acetylene gas $H-C\equiv C-H$

Formic acid vapor



Carbon contained in a metal compound

ALD Precursors for Fluorine

Hydrogen fluoride gas, HF

Fluorine contained in a metal compound such as 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, $(Et_3Si)_2Te$

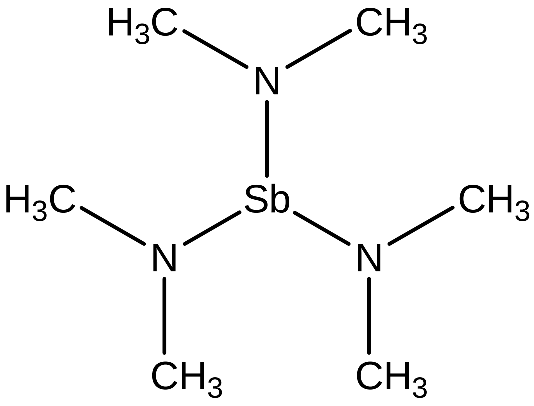
ALD Precursors for Phosphorus, Arsenic and Antimony

phosphine gas, PH_3 (very poisonous)

arsine gas, AsH_3 (very poisonous)

antimony trichloride, $SbCl_3$

tris(dimethylamido)antimony

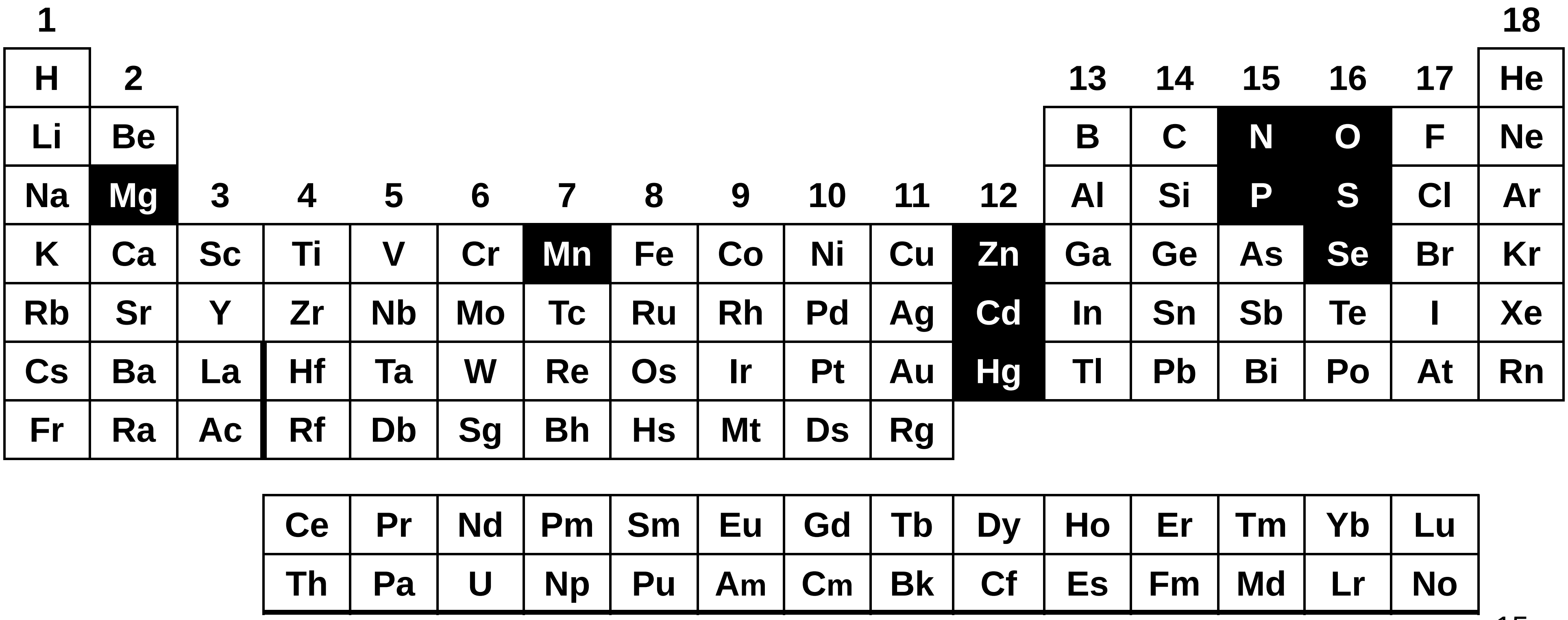


Elemental ALD Precursors

Examples:
Non-metals O_2, P_4, S_2 or S_8
Metals: Mg, Mn, Zn

Advantage: high purity

Disadvantage: low volatility (metals)



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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
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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

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 $\geq$1 units of positive charge

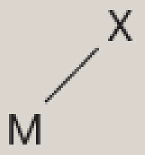
**Metals with 1 unit of positive charge M^+ may be written M(I),
and are said to be in oxidation state +1.**

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

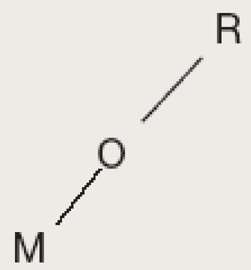
**Most ligands used in ALD can be considered to have electrical charge -1.
A few ligands, e.g. oxides (O^{2-}) and imides $(NC_xH_{2x+1})^{2-}$, have charge -2.**

The total charges of the metal and ligands in a precursor must add to zero.

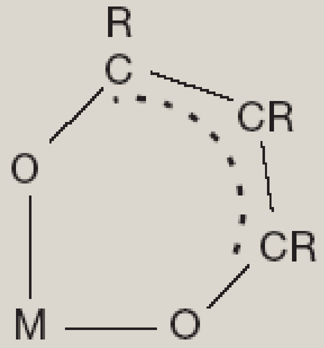
Types of Metal Precursors for ALD



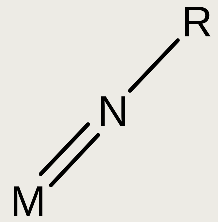
Halides, where X = F, Cl, Br, I



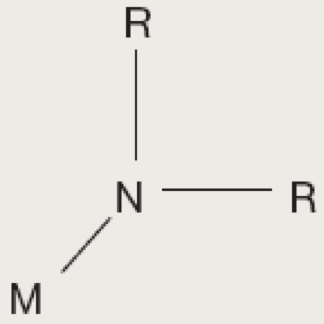
Alkoxides



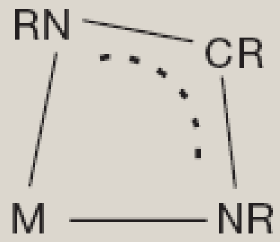
β-diketonates



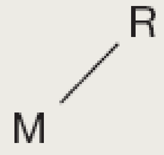
Alkylimides



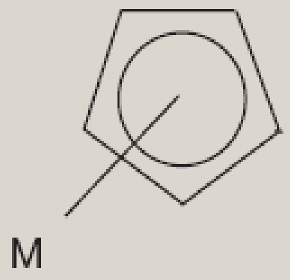
Alkylamides



Amidinates



Alkyls



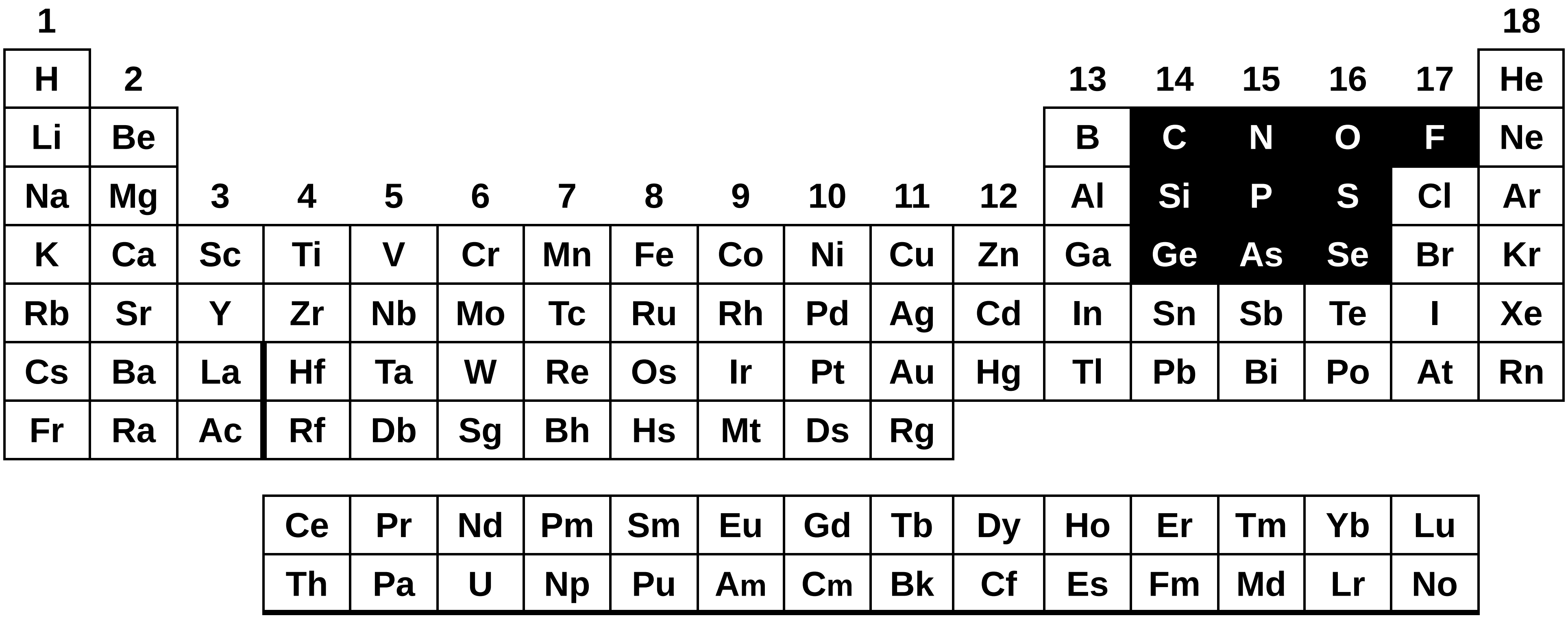
Cyclopentadienyls

R = alkyl group = C_nH_{2n+1}

Elements with Hydride ALD Precursors

Hydrides are compounds of an element X and hydrogen

XH_n n = 1, 2, 3 or 4



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Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
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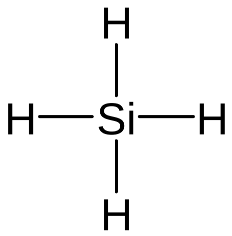
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	Lr	No

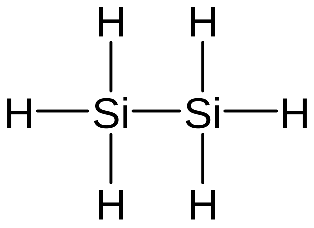
Examples of Hydride Precursors

SiH_4 = silane



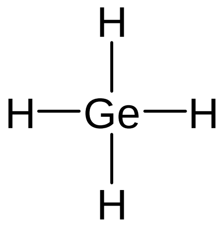
$H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{Si}}}}-H$

Si_2H_6 = disilane,
more reactive than silane



$H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{Si}}}}-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{Si}}}}-H$

GeH_4 = germane



$H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{Ge}}}}-H$

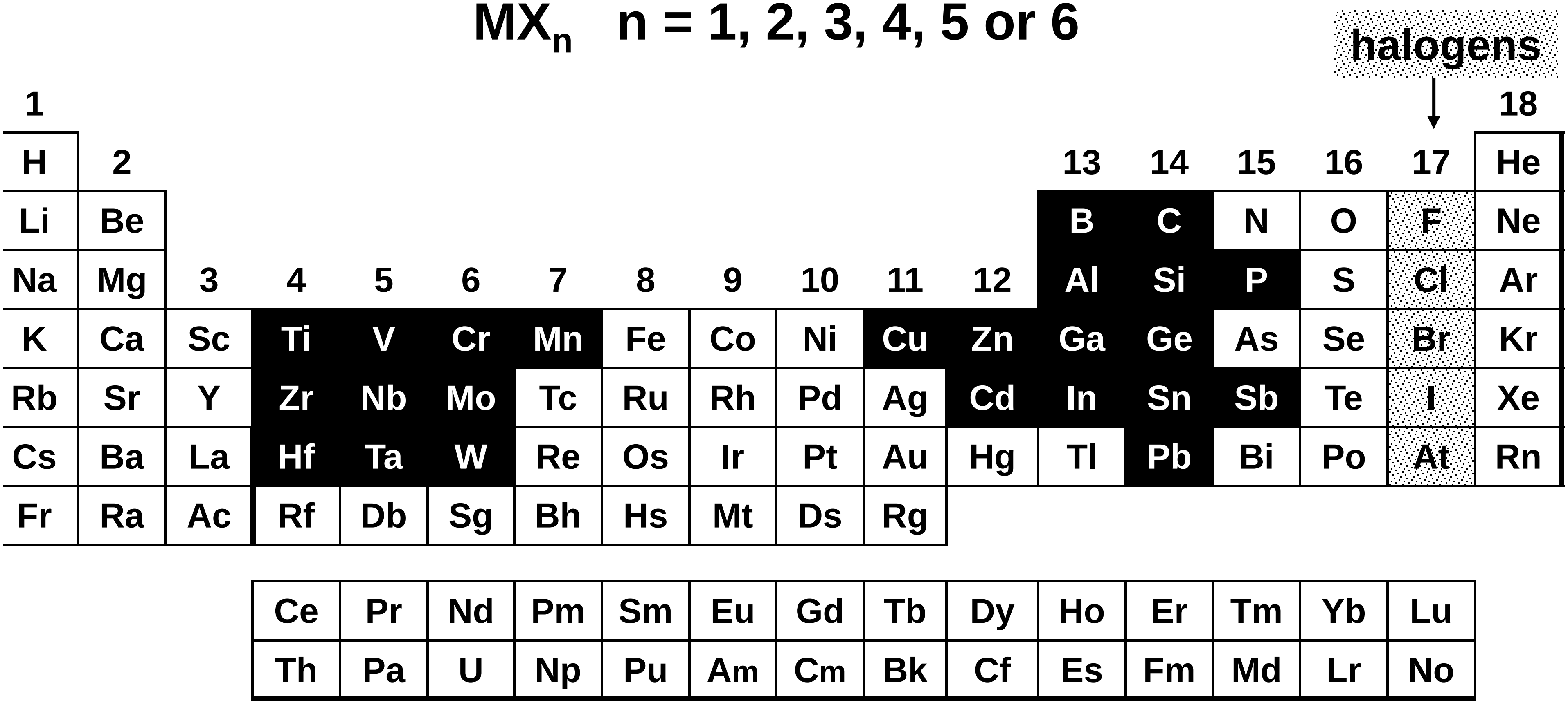
Advantage:
very volatile

Disadvantage:
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 n = 1, 2, 3, 4, 5 or 6



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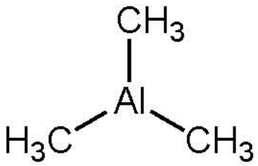
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	Lr	No

Advantages:
thermally stable
usually inexpensive

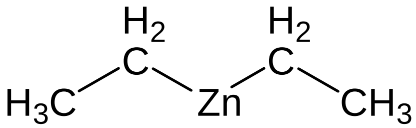
Disadvantages:
halogen impurities in films
corrosive byproducts
low volatility for some elements

Metal Alkyl ALD Precursors

$(CH_3)_3Al$ = trimethylaluminum



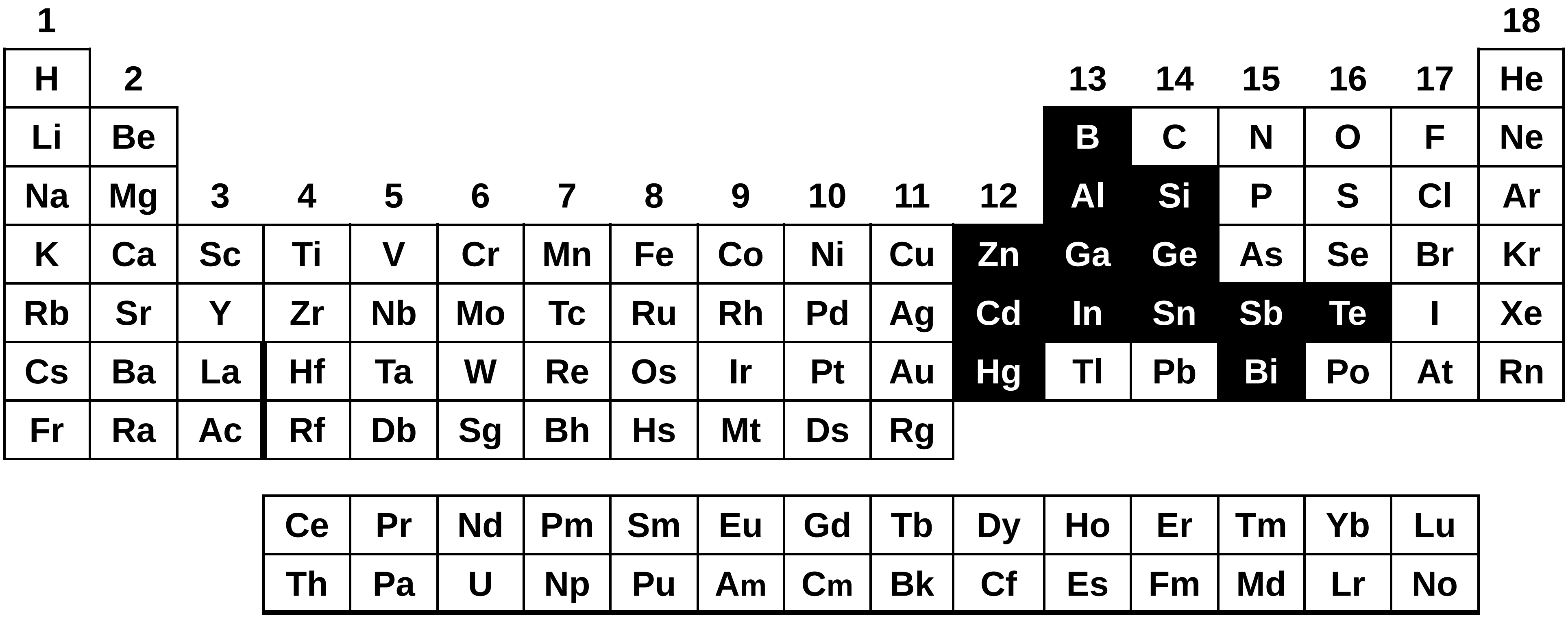
$(CH_3CH_2)_2Zn$ = diethylzinc



Advantage: volatile, highly reactive in ALD

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

Elements with Alkyl ALD Precursors



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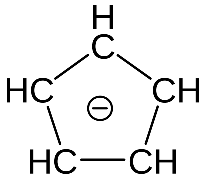
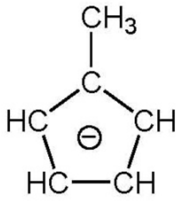
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	**Cd**	**In**	**Sn**	**Sb**	**Te**	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	**Hg**	Tl	Pb	**Bi**	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	Lr	No	

Cyclopentadienyl Ligands

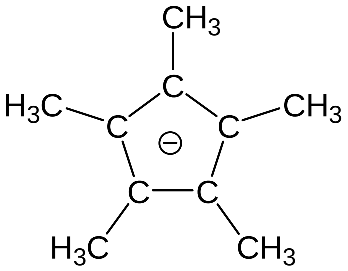
Cp = cyclopentadienyl



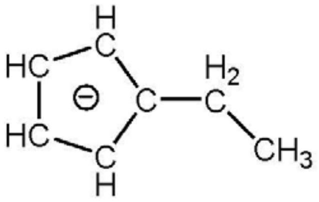
MeCp = methylcyclopentadienyl



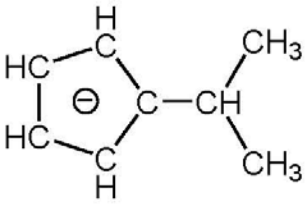
Me$_5$Cp = Cp* = pentamethylcyclopentadienyl



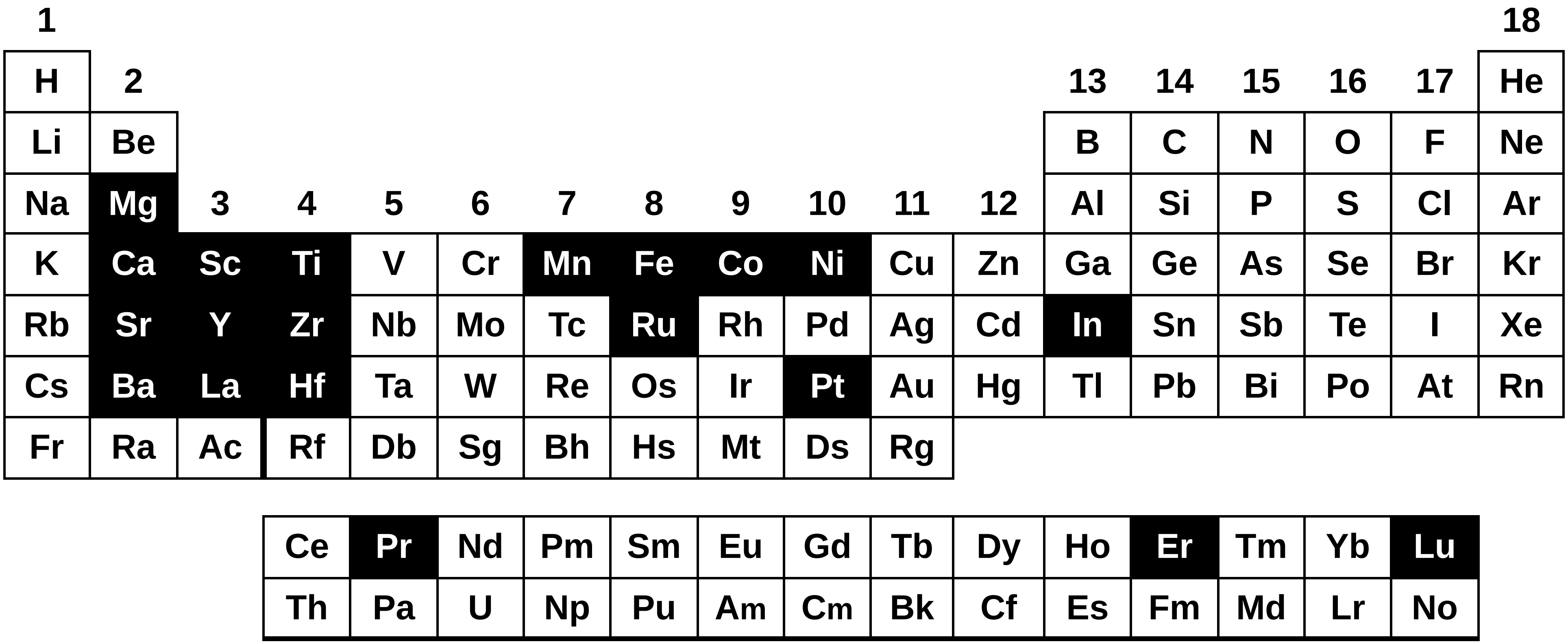
EtCp = ethylcyclopentadienyl



^{i}PrCp = isopropylcyclopentadienyl



Cyclopentadienyl ALD Precursors



1																	18
H	2											13	14	15	16	17	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12	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	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							
			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	

Advantage:

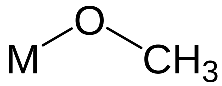
thermally stable

Disadvantages:

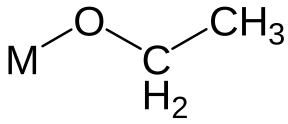
some have low reactivity (Ni, Ru)
some are solids (Ni, Sr, Mg, In, La)
some have low volatility (La, Sr)

Alkoxide Ligands

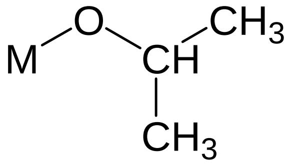
OMe = methoxy



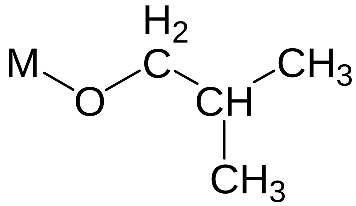
OEt = ethoxy



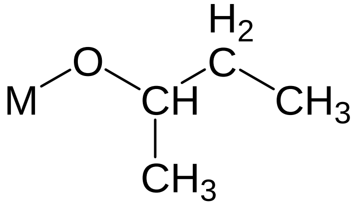
O^{i}Pr = isopropoxy



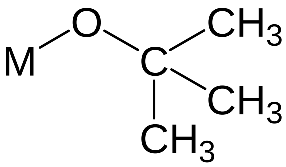
O^{i}Bu = isobutoxy



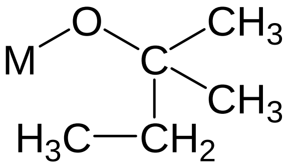
O^{s}Bu = *sec*-butoxy



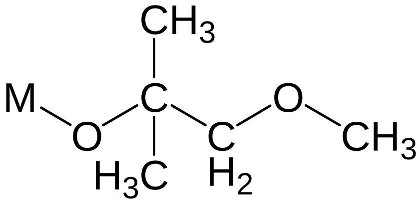
O^{t}Bu = *tert*-butoxy



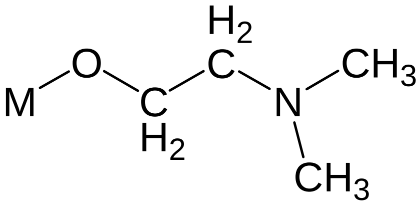
O^{t}Pe = *tert*-pentoxy



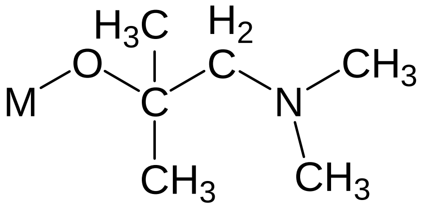
mmp = 1-methoxy-
2-methyl-2-propoxy



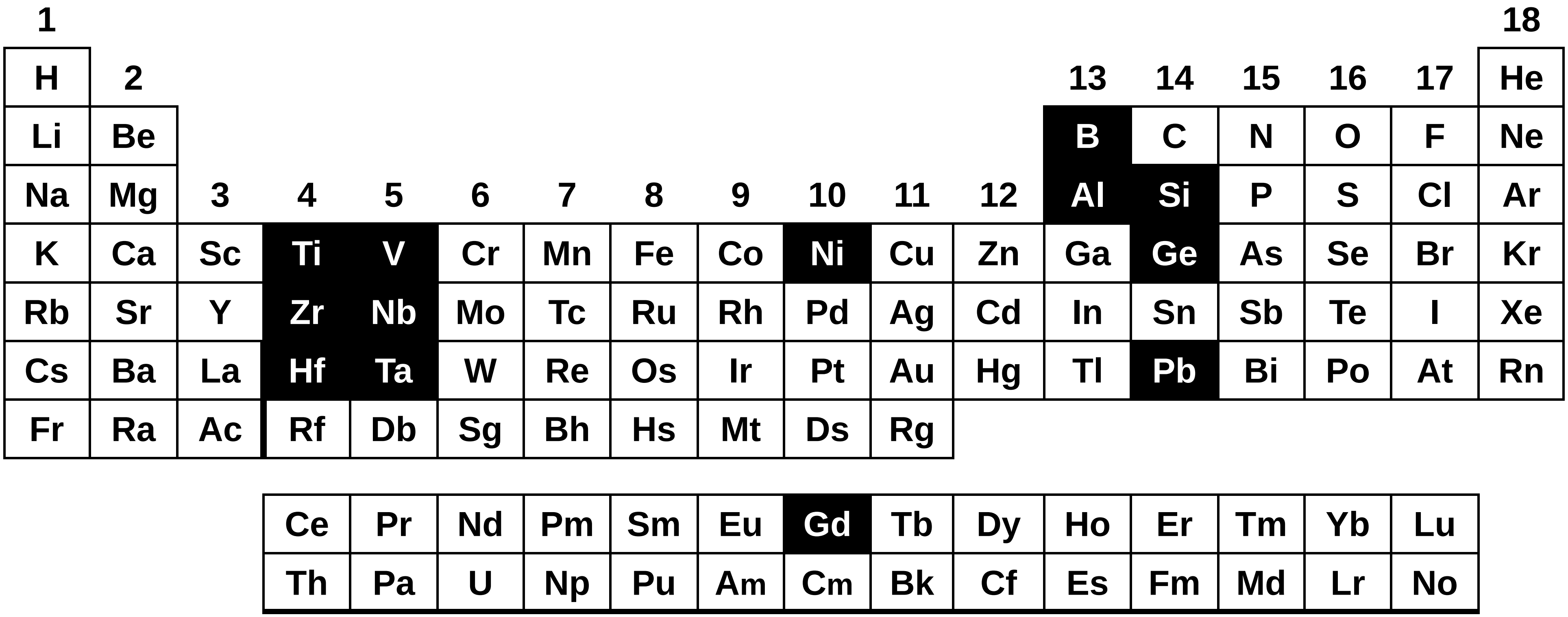
dmae = dimethylamino-
ethoxy



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



Elements with Alkoxide ALD Precursors



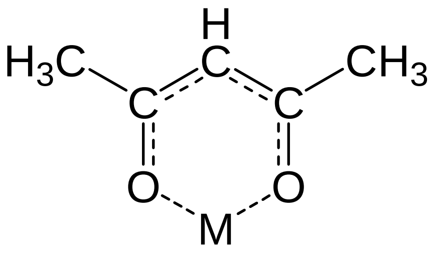
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											**B**	C	N	O	F	Ne
Na	Mg											**Al**	**Si**	P	S	Cl	Ar
K	Ca	Sc	**Ti**	**V**	Cr	Mn	Fe	Co	**Ni**	Cu	Zn	Ga	**Ge**	As	Se	Br	Kr
Rb	Sr	Y	**Zr**	**Nb**	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	**Hf**	**Ta**	W	Re	Os	Ir	Pt	Au	Hg	Tl	**Pb**	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

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

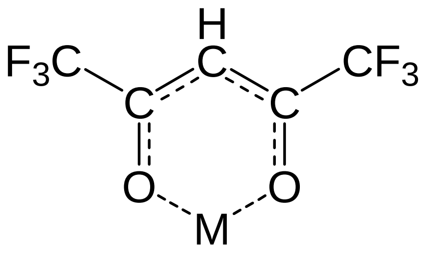
Advantages:
reactive to water vapor => oxides

Disadvantages:
limited thermal stability
not suitable for making nitrides
not suitable for making pure metals

Beta-diketonate Compounds

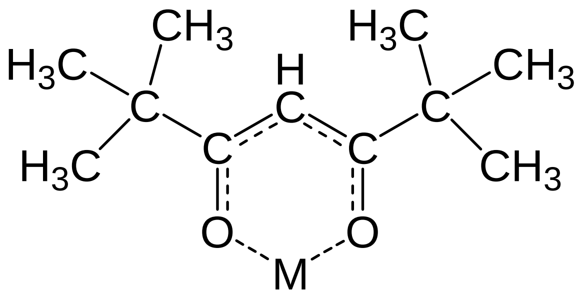


pentane-2,4-dionate, or
acetylacetonate (acac)



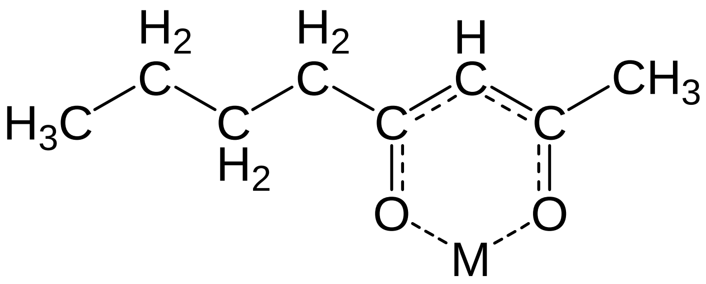
1,1,1,5,5,5-hexafluoro-
acetylacetonate (hfac)

(more volatile)



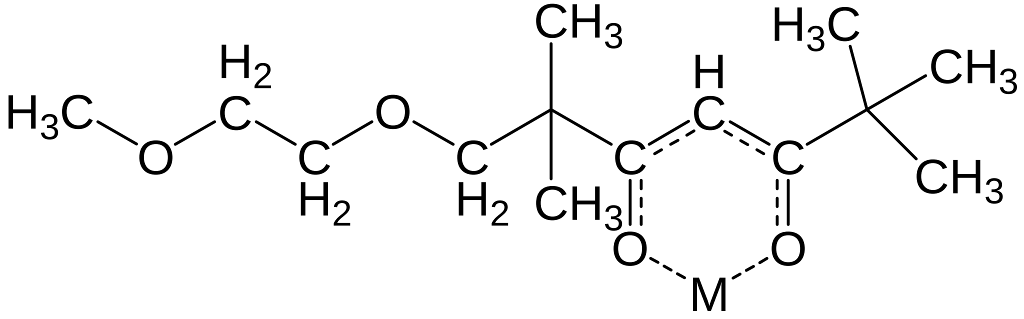
2,2,6,6-tetramethyl-
heptane-3,5-dionate
(thd or tmhd)

(more bulky)



octane-2,4-dionate (od)

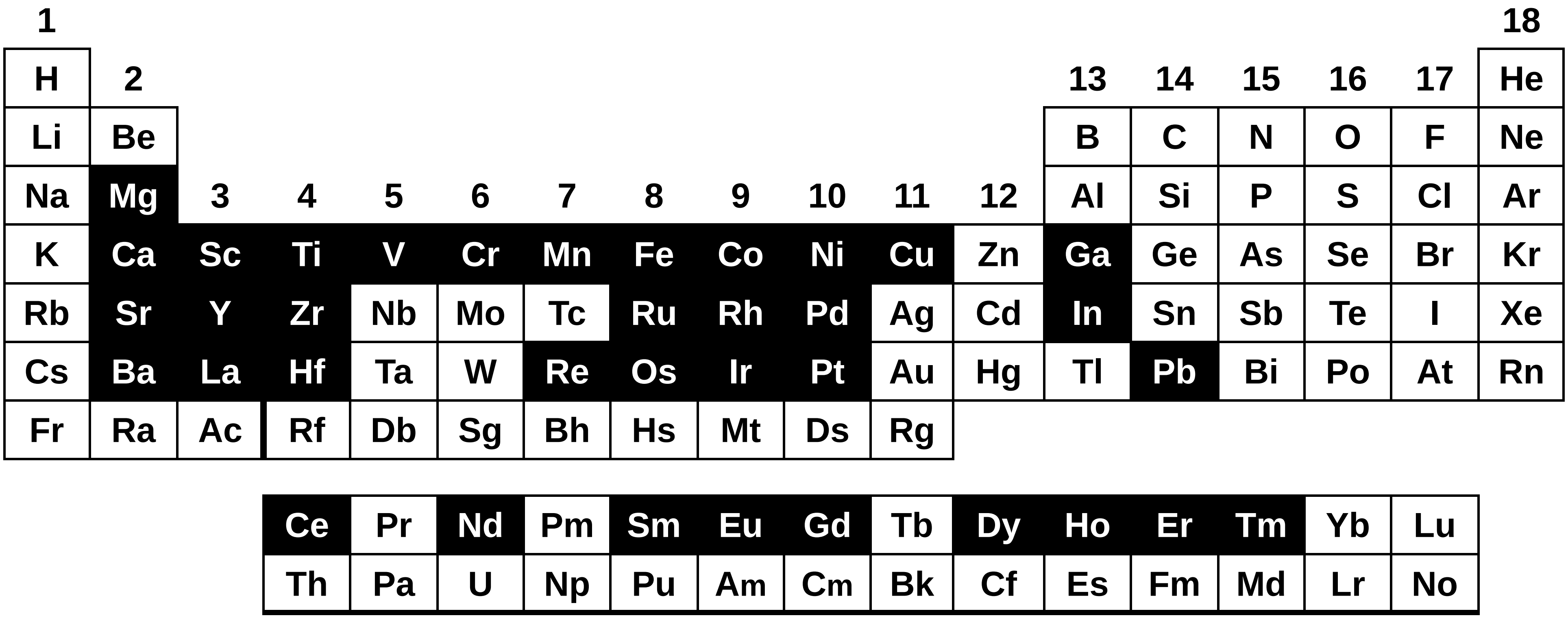
(lower melting point)



1-(2-methoxyethoxy)-2,2,6,6-tetramethyl-
heptane-3,5-dionate (methd)

(very bulky)

Beta-diketonate ALD Precursors



1																	18
H	2											13	14	15	16	17	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12	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	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							
			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	

Advantage:

thermally stable

Disadvantages:

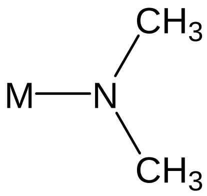
low reactivity

not suitable for making nitrides

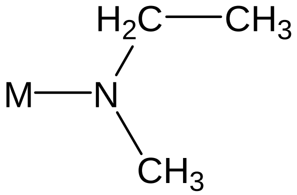
not suitable for making pure metals

Amide Ligands

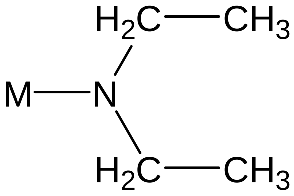
NMe_2 = dimethylamino = dimethylamido



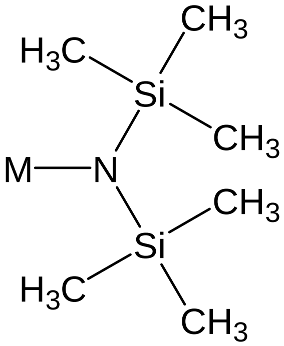
NEtMe = ethylmethylamino = ethylmethylamido



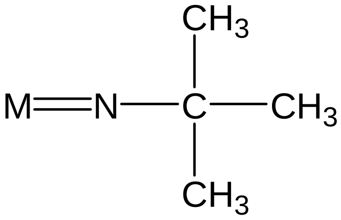
NEt_2 = diethylamino = diethylamido



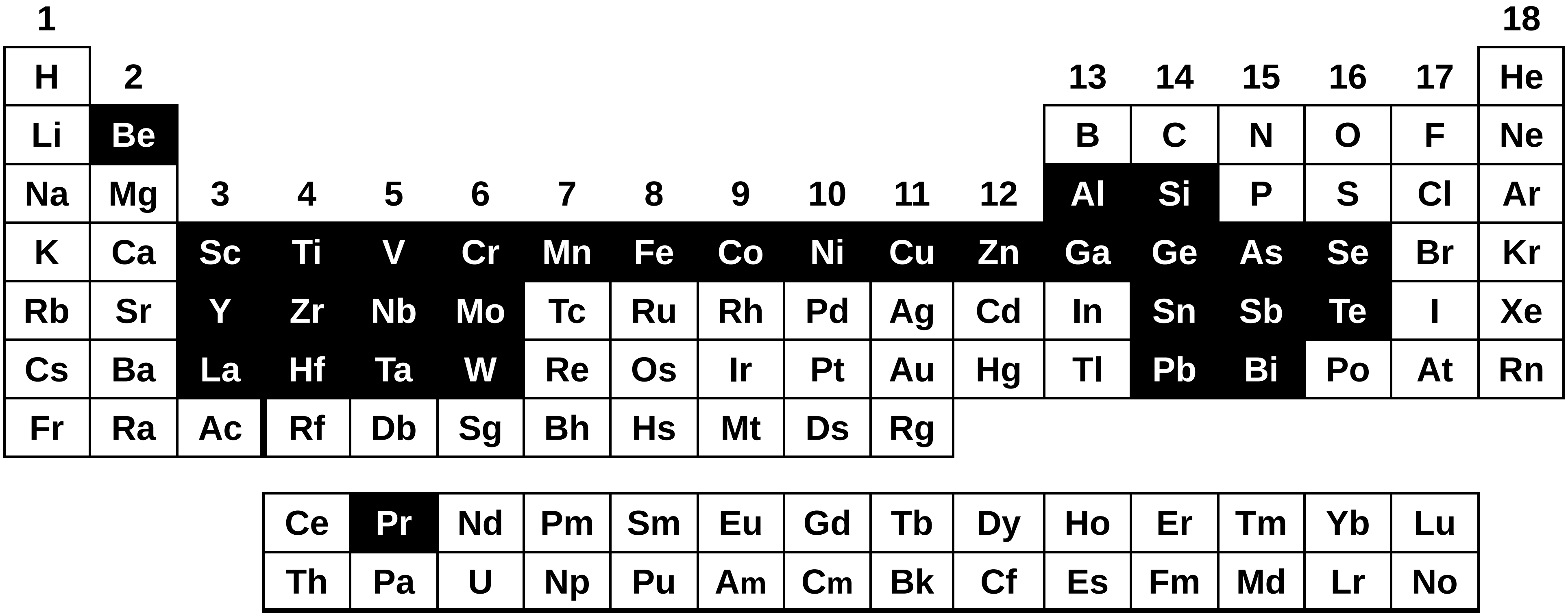
$N(SiMe_3)_2$ = bis(trimethylsilyl)amido = bis(trimethylsilyl)amino



N^tBu = tert-butylimino = tert-butylimido



Amide and Imide Precursors for ALD



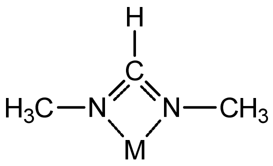
1																	18
H	2											13	14	15	16	17	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

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

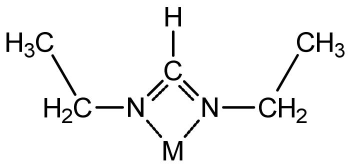
Advantages:
highly reactive
suitable for oxides and nitrides

Disadvantages:
limited thermal stability
silicon impurity from silylamides

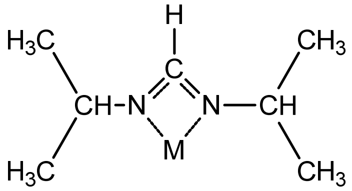
Some Amidinate Ligands



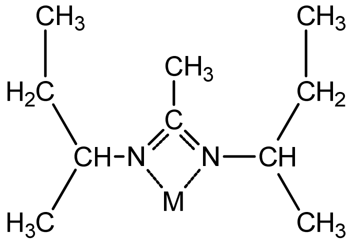
N,N’-dimethyl-formamidinate (Me_2fmd)



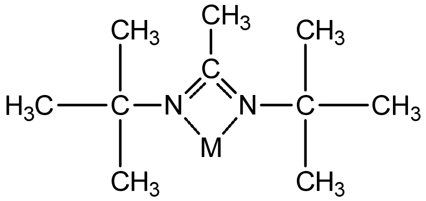
N,N’-diethyl-formamidinate (Et_2fmd)



N,N’-diisopropyl-formamidinate ($^iPr_2$fmd)

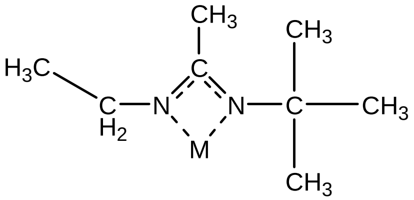


N,N’-di-*sec*-butyl-acetamidinate ($^sBu_2$amd)

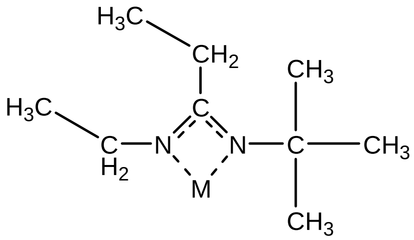


N,N’-dimethyl-acetamidinate ($^tBu_2$amd)

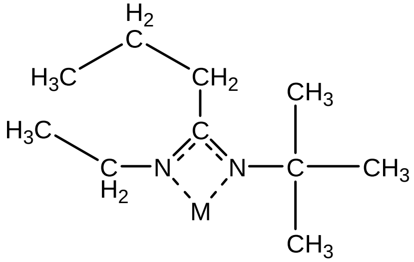
Increasing steric bulk →



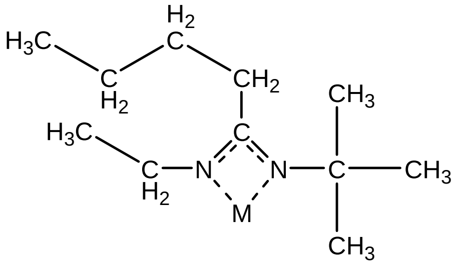
N’-*tert*-butyl-N-ethyl-acetamidinate (^{t}BuEt-amd)



N’-*tert*-butyl-N-ethyl-propionamidinate (^{t}BuEt-pmd)



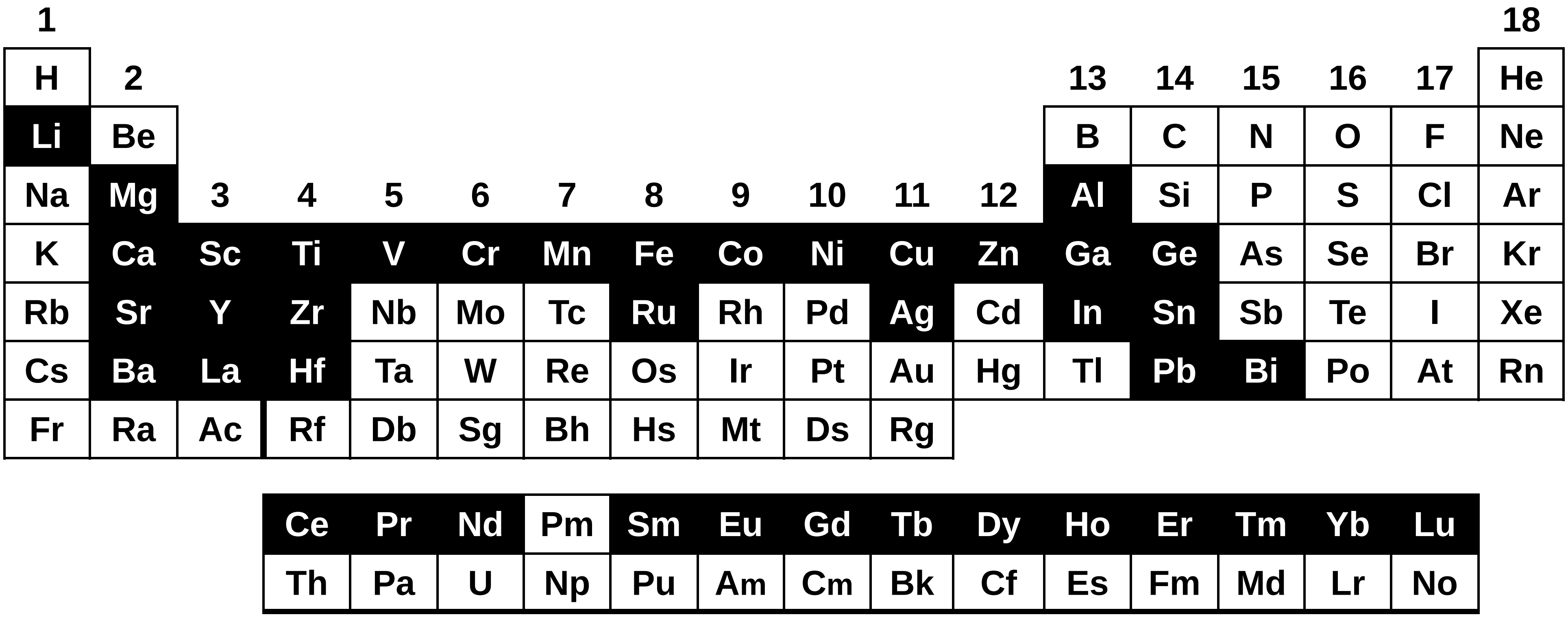
N’-*tert*-butyl-N-ethyl-butyramidinate (^{t}BuEt-bmd)



N-ethyl-N’-*tert*-butyl-pentylamidinate (^{t}BuEt-pemd)

Increasing flexibility leads to decreasing melting points and liquids →

Amidinate ALD Precursors



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
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	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

■ 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

Advantages:

high reactivity to water => oxides
high reactivity to ammonia => nitrides
high reactivity to H_2S => sulfides
reactive to hydrogen gas H_2 => metals

Disadvantage:

some are solids, not liquids

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

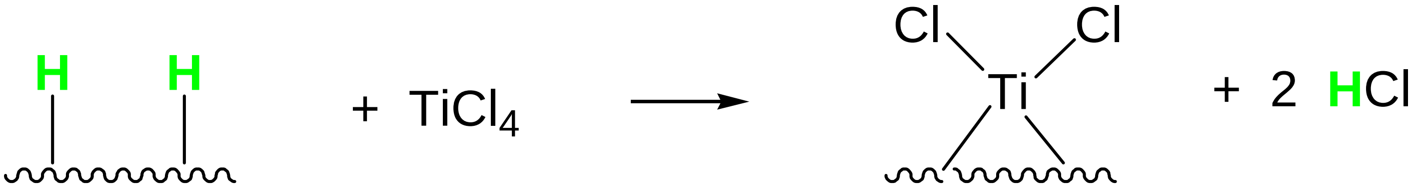
metals	**H-reduction reactions => transition metals (Ti, Mn, Fe, Co, Ni, Cu)**
	oxygen O-transfer reactions => noble metals (Pt, Ru, Ir)
	fluoride to silicon reactions => tungsten or molybdenum
oxides	**water H-transfer reactions => metal oxides**
	ozone O-transfer reactions => metal oxides
	silanol H-transfer reactions => metal silicates
nitrides	**ammonia H-transfer reactions => metal nitrides**
chalcogenides	**chloride to trialkylsilyl reactions => selenides or tellurides**
organics	**ethanolamine H-transfer reactions => organic groups**

Metals by Reduction with H Atoms

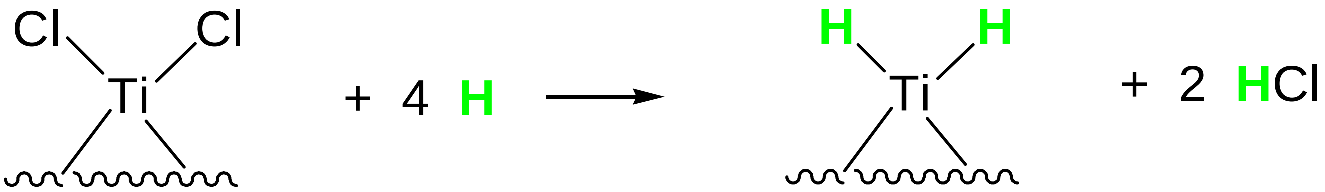
Titanium from titanium tetrachloride and hydrogen atoms in a plasma

$$TiCl_4 + 4\,H \Rightarrow Ti + 4\,HCl$$

Hydrogen atoms on surface transfer to chlorides on precursor:

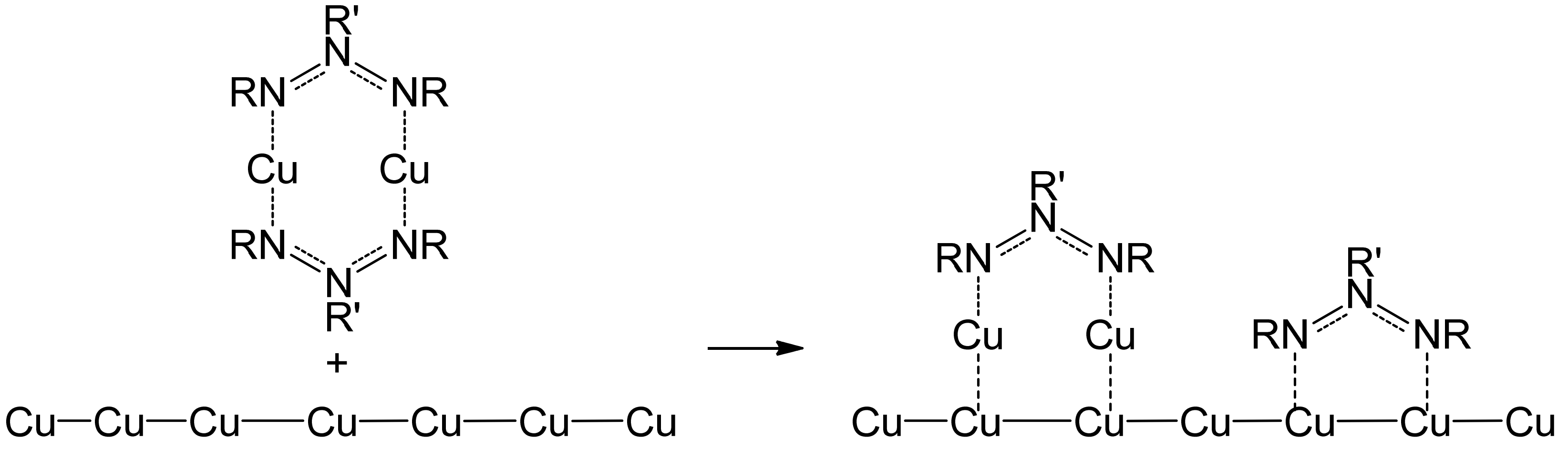


Hydrogen atoms from plasma remove chlorine as hydrogen chloride gas:

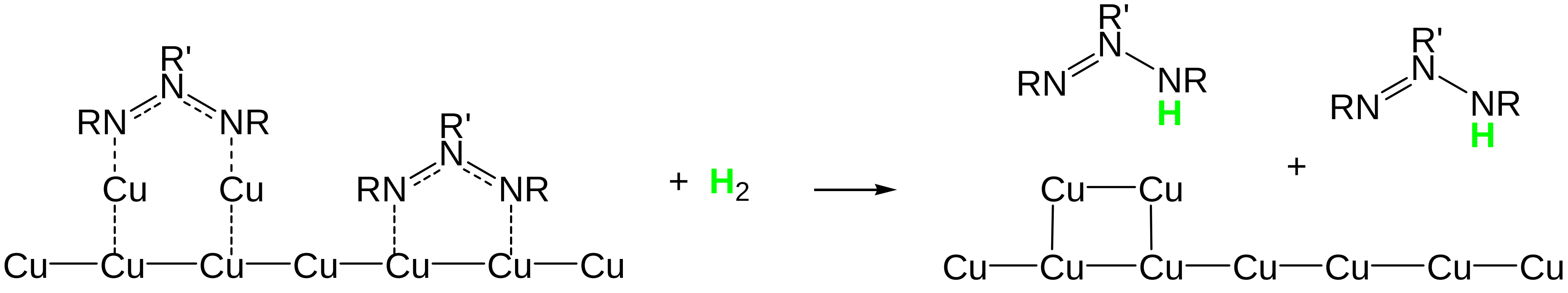


Metals by Reduction with H_2 Molecules

Dissociative chemisorption of copper amidinate on a copper surface:

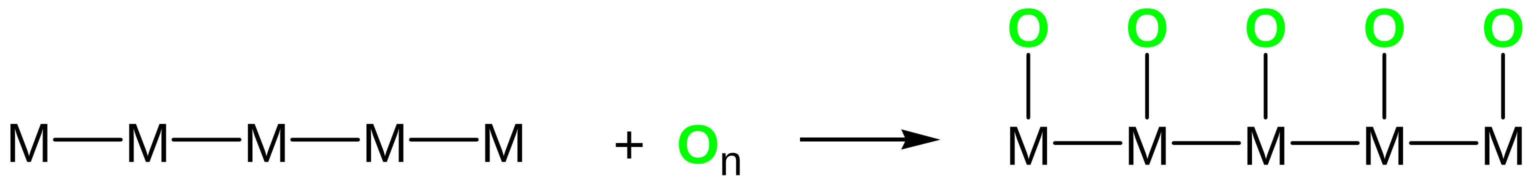


Hydrogen transfer to amidinate ligands to make copper & amidine vapor:



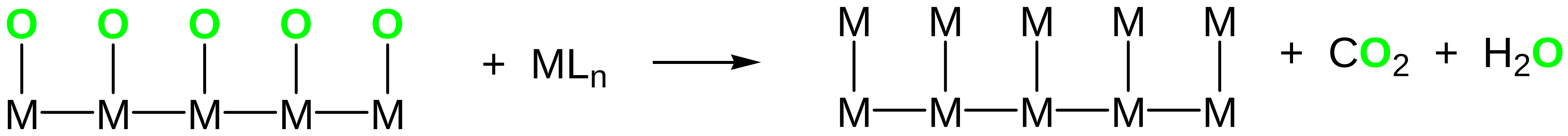
Noble Metals by Oxidation Reactions

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



$$\mathrm{M{-}M{-}M{-}M{-}M} + \mathrm{O}_n \longrightarrow \underset{\mathrm{M}}{\overset{\mathrm{O}}{|}}{-}\underset{\mathrm{M}}{\overset{\mathrm{O}}{|}}{-}\underset{\mathrm{M}}{\overset{\mathrm{O}}{|}}{-}\underset{\mathrm{M}}{\overset{\mathrm{O}}{|}}{-}\underset{\mathrm{M}}{\overset{\mathrm{O}}{|}}$$

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



$$\underset{\mathrm{M}}{\overset{\mathrm{O}}{|}}{-}\underset{\mathrm{M}}{\overset{\mathrm{O}}{|}}{-}\underset{\mathrm{M}}{\overset{\mathrm{O}}{|}}{-}\underset{\mathrm{M}}{\overset{\mathrm{O}}{|}}{-}\underset{\mathrm{M}}{\overset{\mathrm{O}}{|}} + \mathrm{ML}_n \longrightarrow \underset{\mathrm{M}}{\overset{\mathrm{M}}{|}}{-}\underset{\mathrm{M}}{\overset{\mathrm{M}}{|}}{-}\underset{\mathrm{M}}{\overset{\mathrm{M}}{|}}{-}\underset{\mathrm{M}}{\overset{\mathrm{M}}{|}}{-}\underset{\mathrm{M}}{\overset{\mathrm{M}}{|}} + \mathrm{CO}_2 + \mathrm{H}_2\mathrm{O}$$

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:

surface-$WSiF_2H + WFF_5 \Rightarrow$ surface-$WWF_5 + SiFF_2H$

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

surface-$WWF_2F_3 + Si_2H_6 \Rightarrow$ surface-$WWSiF_2H + SiF_3H + 2\ H_2$

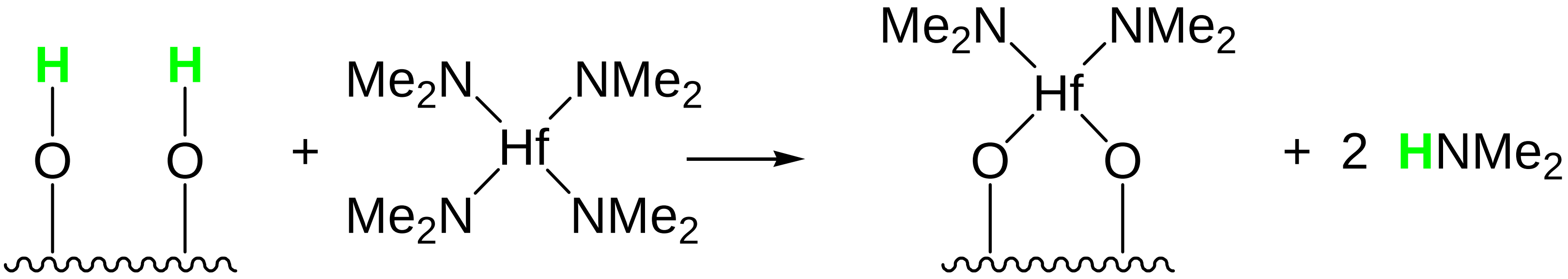
A very complex reaction, breaking 1 Si-Si, 5 W-F and 4 Si-H bonds while forming a new W-Si bond, 5 new Si-F bonds and 2 new H-H bonds

Oxides by Hydroxyl Exchange & Hydrolysis

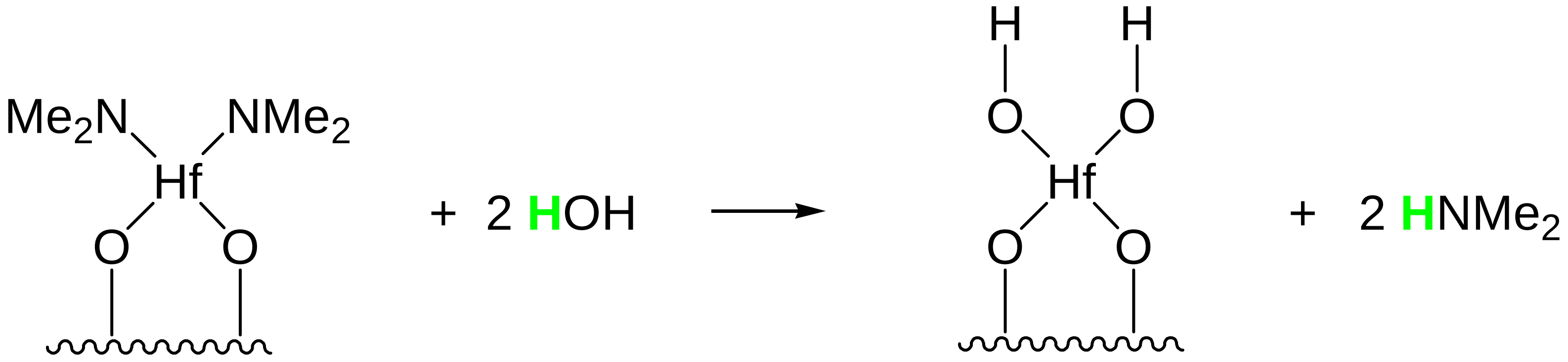
Tetrakis(dimethylamido)hafnium reacts with water to make hafnium dioxide

$Hf(NMe_2)_4$ + 2 H_2O => HfO_2 + 4 $HNMe_2$

Chemisorption by hydrogen transfer to ligands to form dimethylamine gas:



Transfer of hydrogen from water to surface-bound dimethylamide ligands:

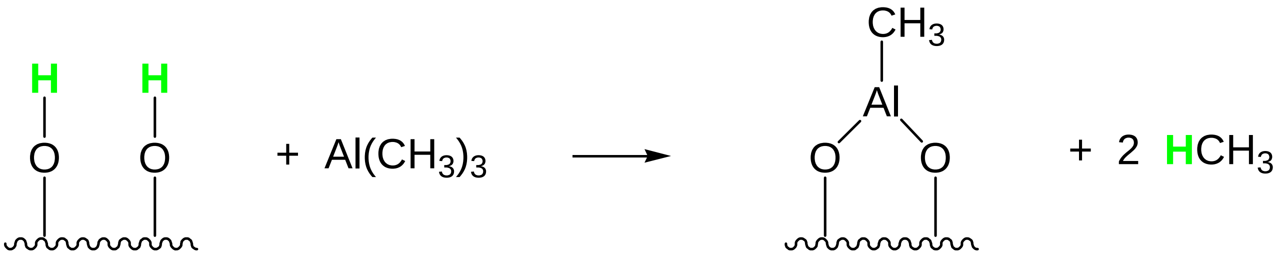


Oxides by Oxidation with Ozone

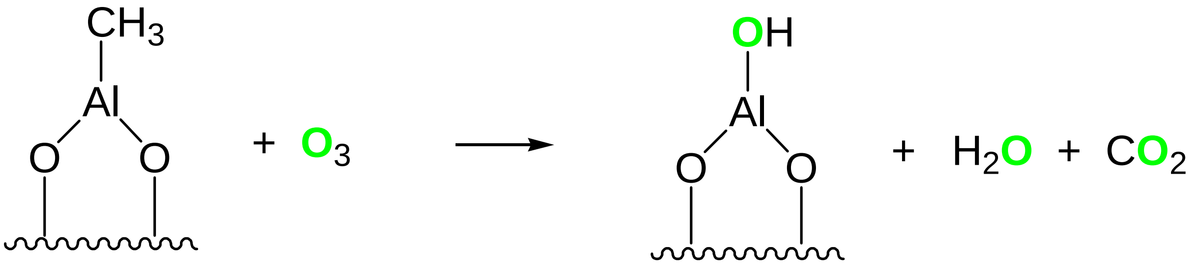
Trimethylaluminum reacts with ozone to make aluminum oxide:

$$(CH_3)_3Al + O_3 \Rightarrow Al_2O_3 + CH_4 + H_2O + CO_2$$

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



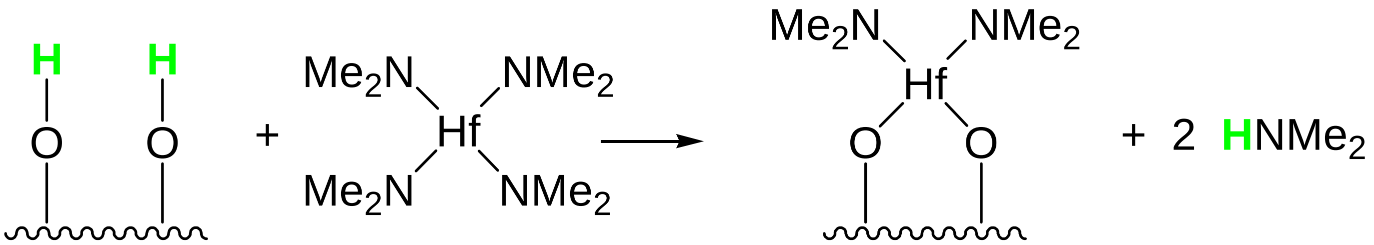
Oxygen atom transfer to surface ligand to form water and carbon dioxide:



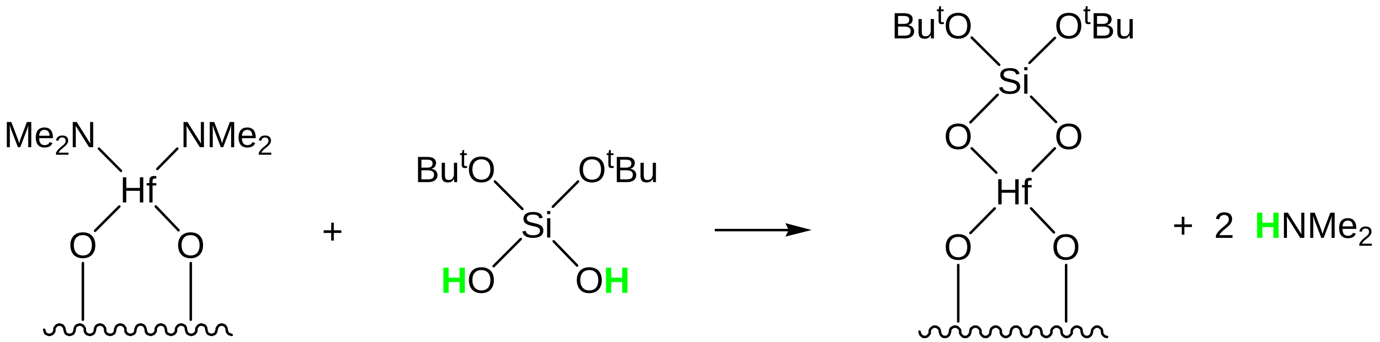
Water may not be detected because it reacts with other surface CH_3 groups

Metal Silicates from Silanol

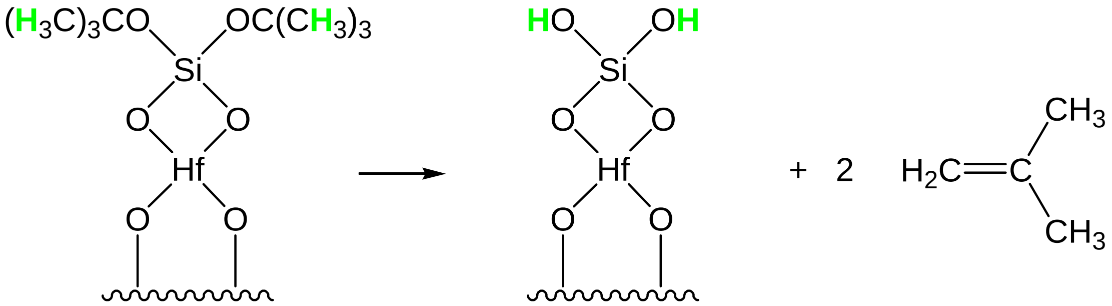
Hydrogen atom transfer from surface hydroxyls to dimethylamide ligands:



Hydrogen atom transfer from silanol to surface-bound dimethylamides:



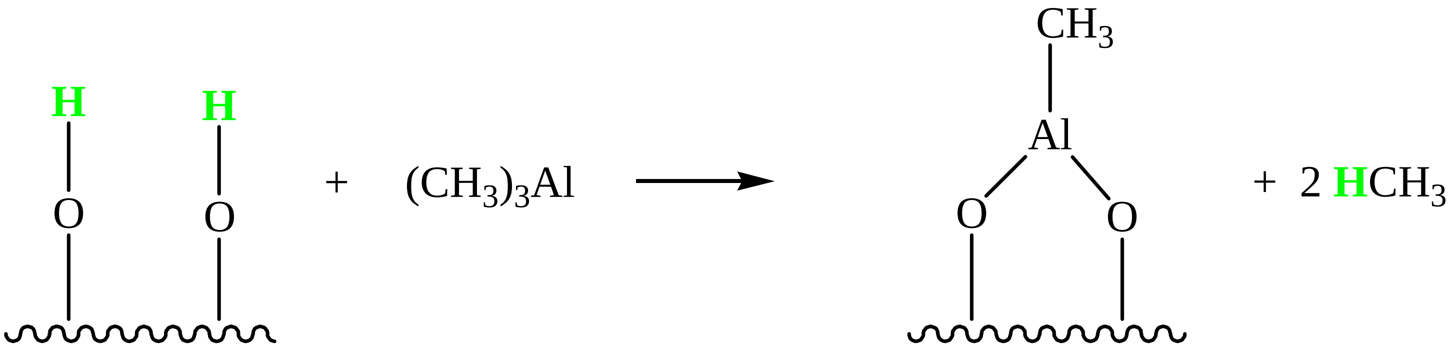
Regeneration of surface hydroxyls by hydrogen from tertiary butyl groups:



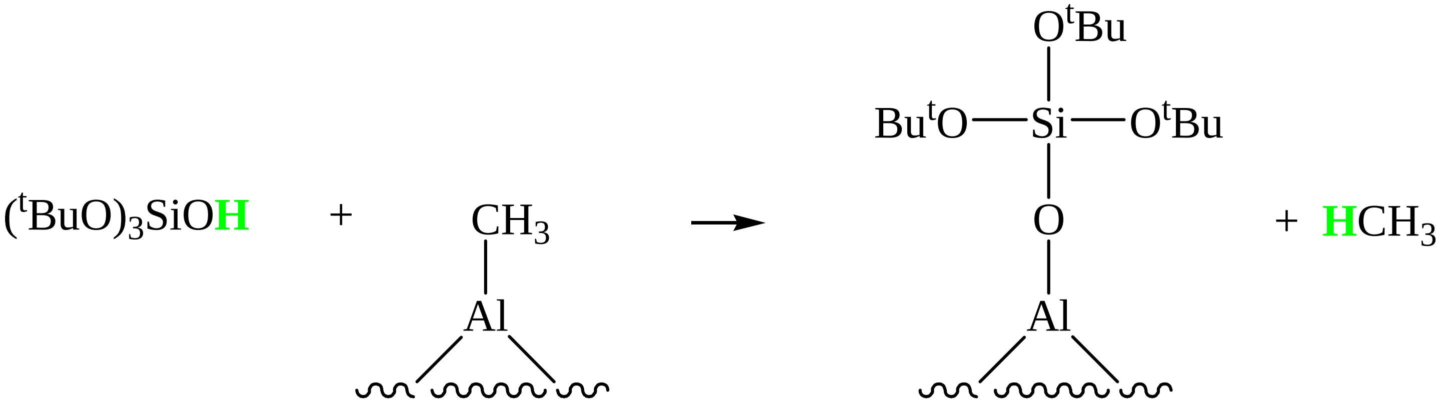
Al-doped SiO_2 from $AlMe_3$ and $(^tBuO)_3SiOH$

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

Hydrogen atom transfer from surface hydroxyl to methyl ligands:

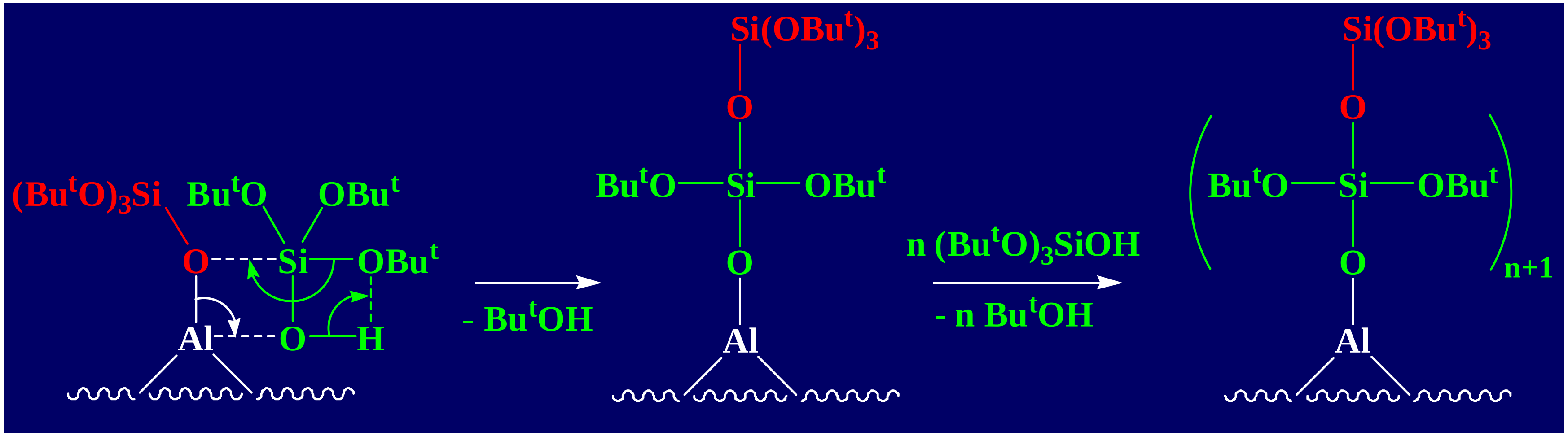


Hydrogen atom transfer from silanols to methyl ligands:



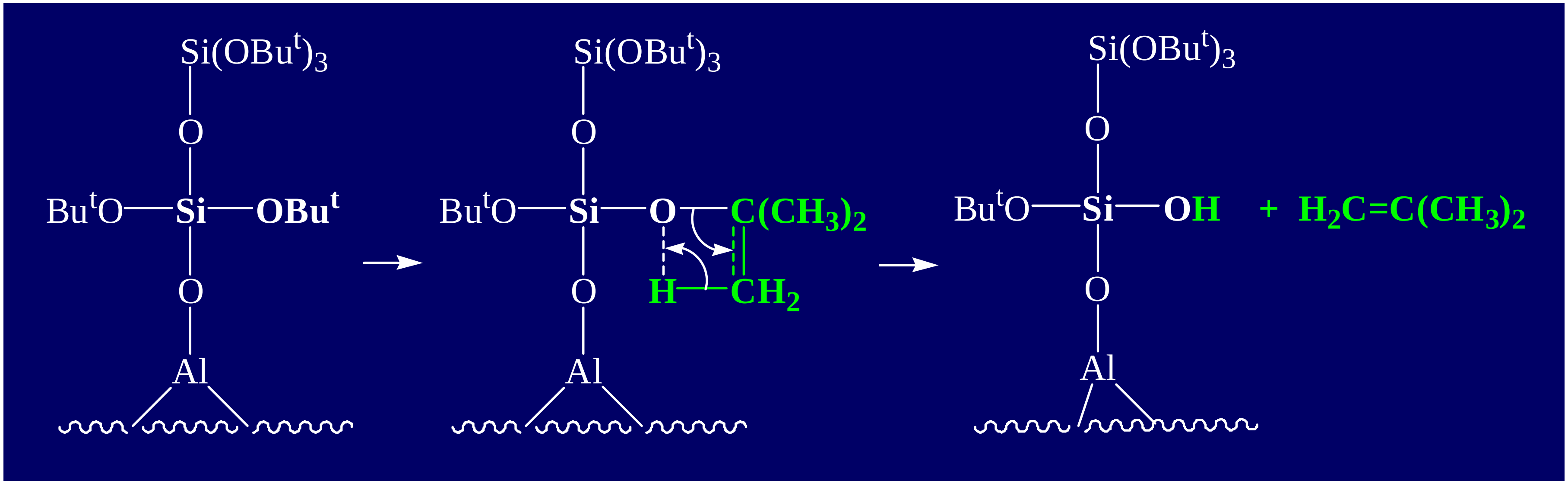
Al-doped SiO_2 from $AlMe_3$ and $(^tBuO)_3SiOH$

Repeated insertions of $(^tBuO)_3SiOH$ into an Al-O bond produces a siloxane polymer tethered to the surface:



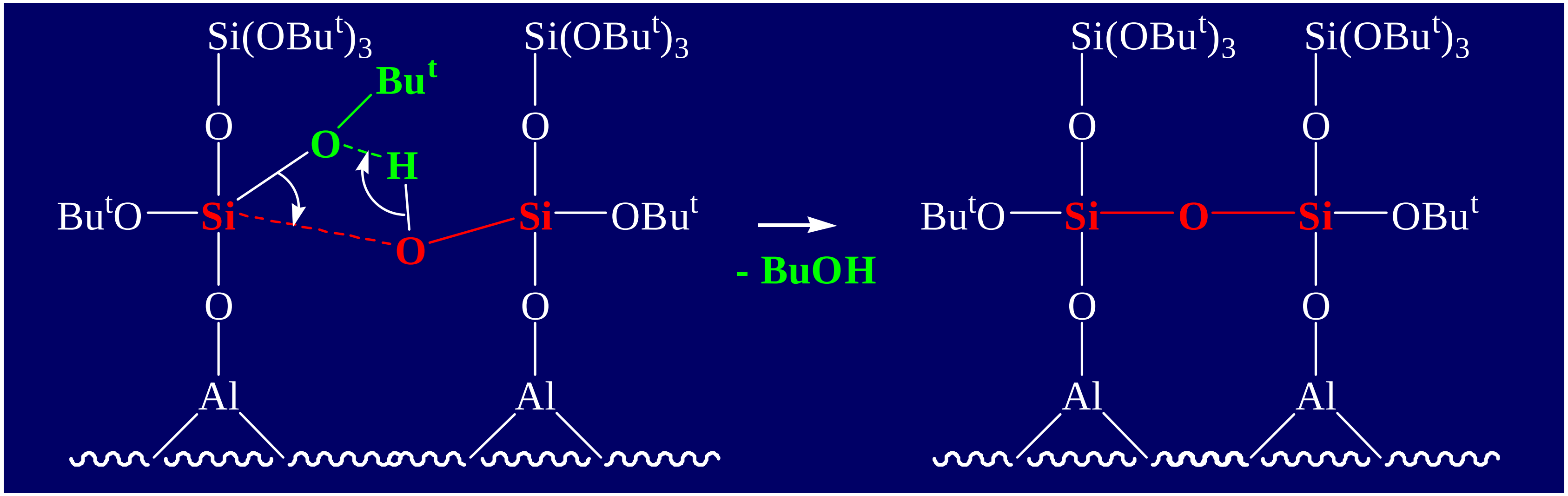
Al-doped SiO_2 from $AlMe_3$ and $(^tBuO)_3SiOH$

Elimination of isobutene by β-hydrogen transfer:



Al-doped SiO_2 from $AlMe_3$ and $(^tBuO)_3SiOH$

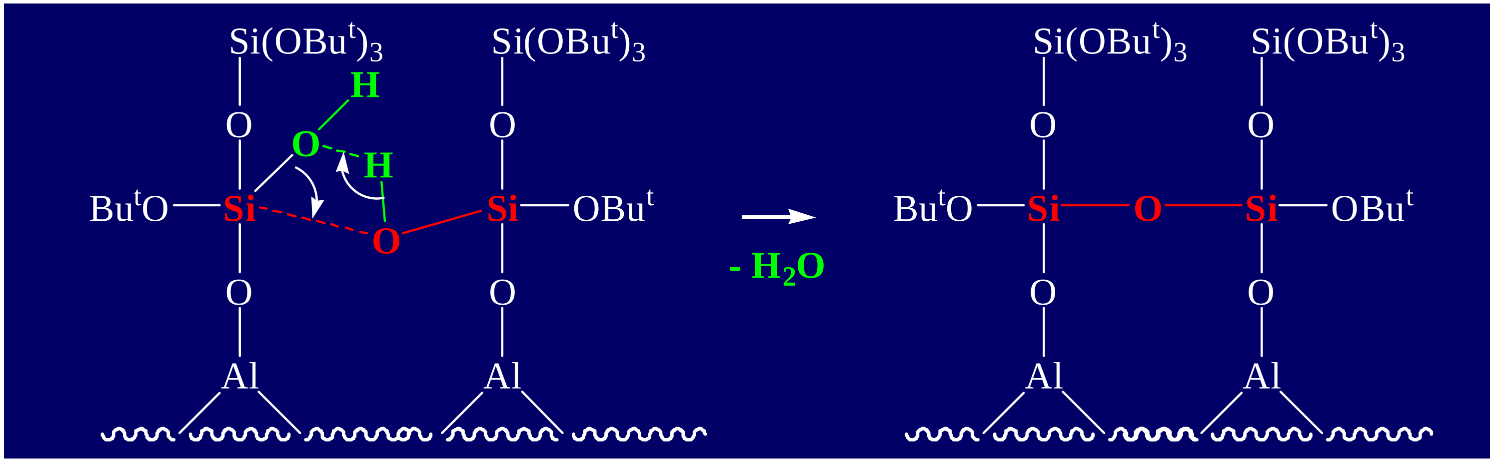
Siloxane polymer chains cross-link by elimination of *tert*-butanol:



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 $(^tBuO)_3SiOH$

Elimination of water also cross-links polymer chains:



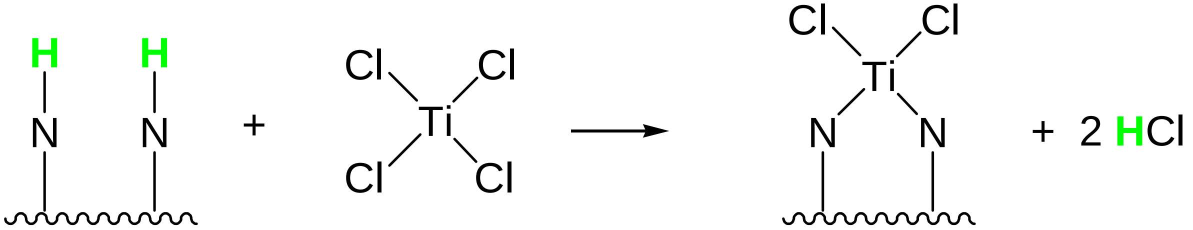
Complete crosslinking produces a solid silica layer that is impervious to diffusion of more silanol up to the aluminum catalyst, so reaction stops.

Nitrides by Chloride Exchange and Reduction

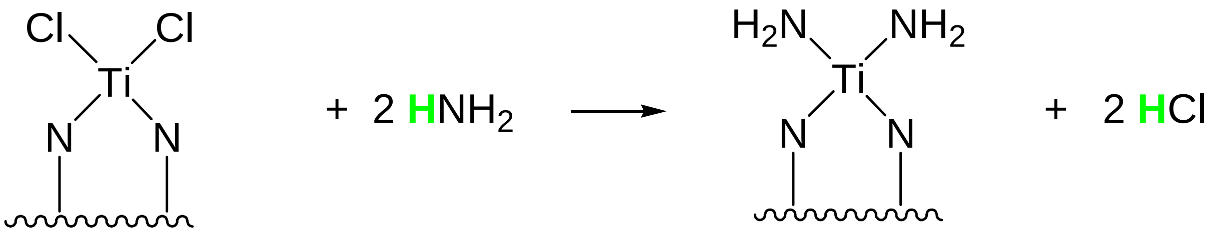
Titanium(IV) tetrachloride plus ammonia makes titanium(III) nitride:

$TiCl_4$ + NH_3 => TiN

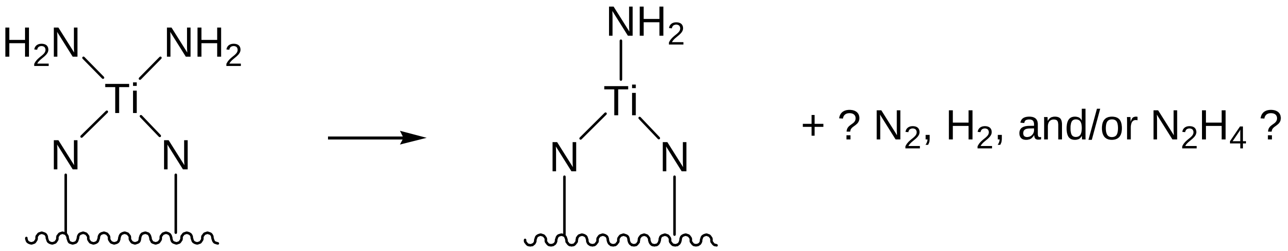
Hydrogen atom transfer from surface amides to chlorides on precursor:



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

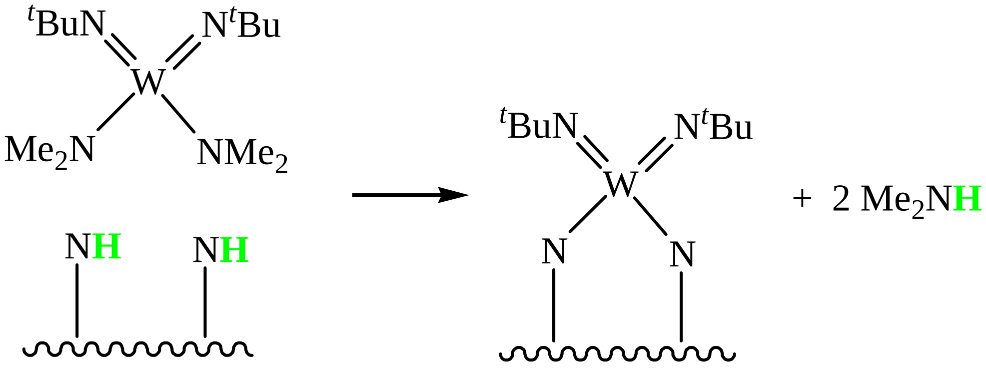


Titanium in oxidation state +4 is reduced to +3 by elimination reactions:

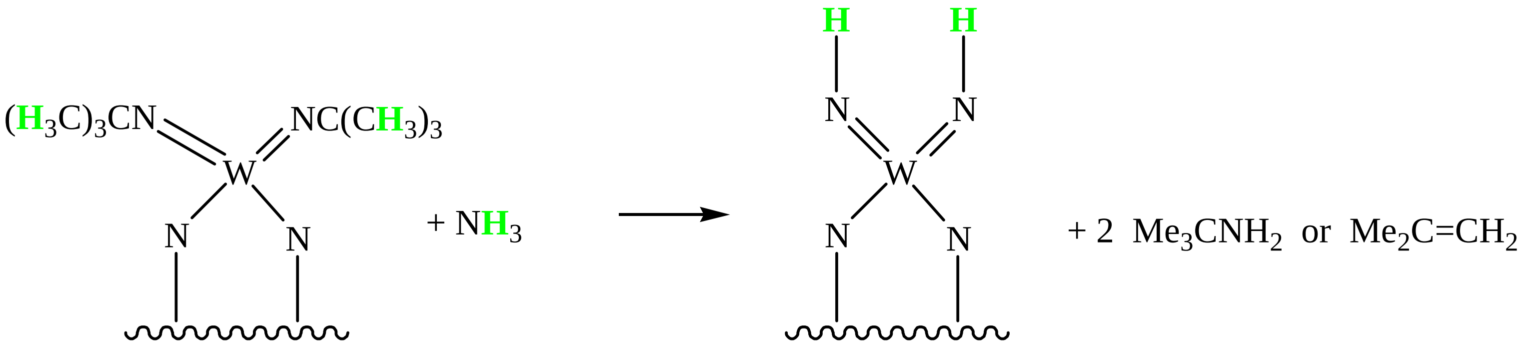


Tungsten Nitride by Exchange and Catalysis

Hydrogen transfer from surface imides to dimethylamides on precursor:



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

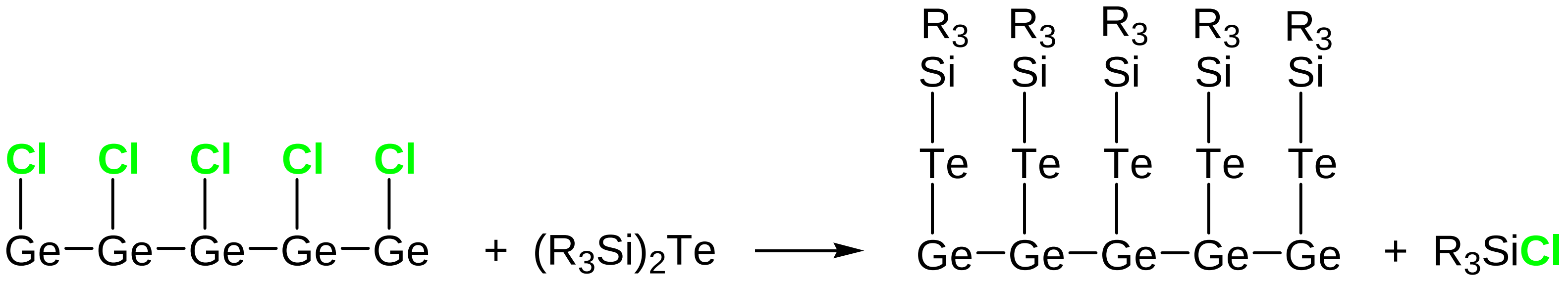


Reductive elimination of nitrogen to reduce W(VI) to W(III)

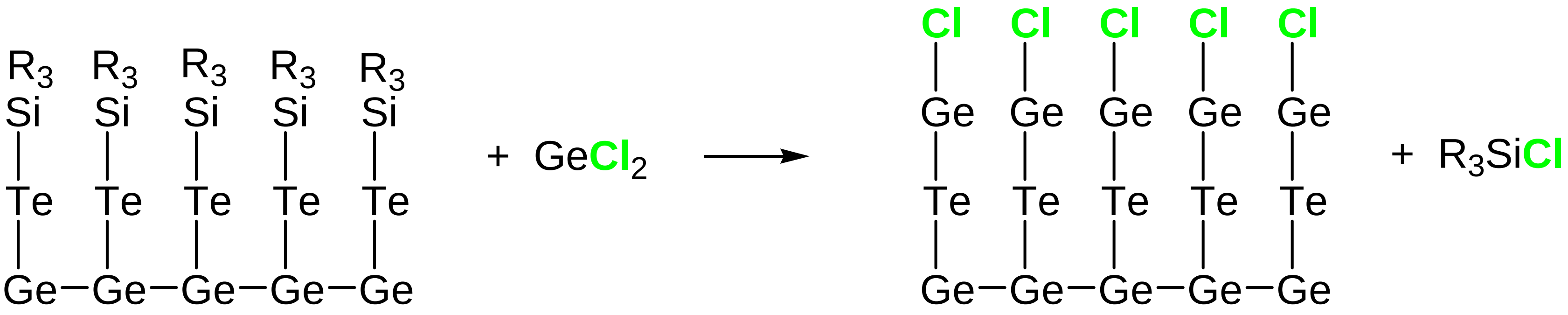
$$\mathbf{WN_2 \;\Rightarrow\; WN + \tfrac{1}{2}\,N_2}$$

Tellurides by Chloride Exchange Reactions

Chlorine atoms on surface move to trialkylsilyl groups on tellurium:



Chlorine atoms on germanium remove surface trialkylsilyl groups:



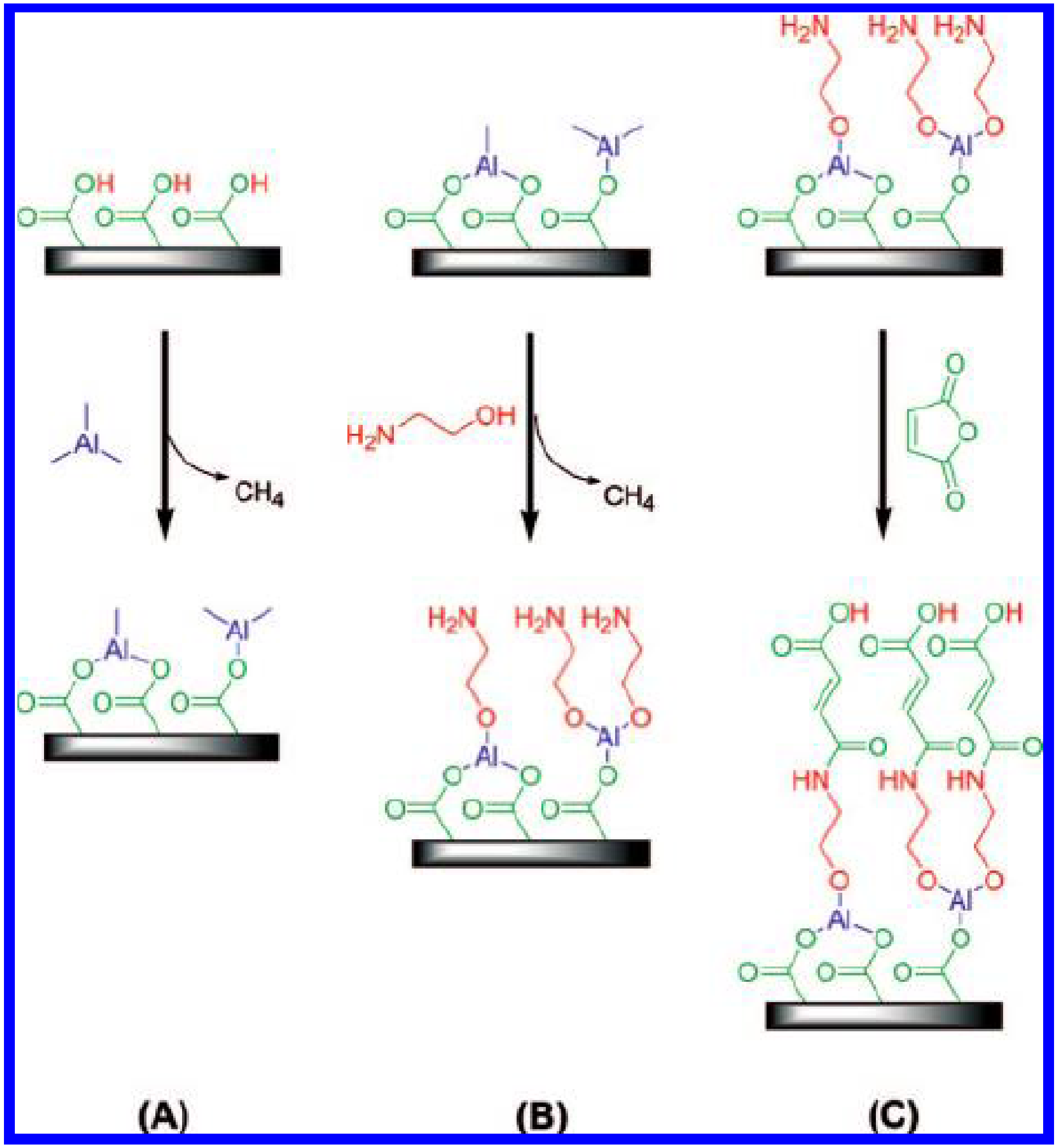
Adding Organic Components to ALD Films

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**

Recent Reviews of ALD Chemistry and Applications

R. Puurunen, *J. Appl. Phys.* 97, 121301 (2005)

J. Paivasaari et al., *Topics in Appl. Phys.* 106, 15 (2007)

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

S. M. George, *Chem. Rev.* 110, 111 (2010)

S. D. Elliott, *Langmuir* 26, 9179 (2010)

W. M. M. Kessels et al., *J. Vac. Sci. Technol*. A 29, 050801 (2011)

G. N. Parsons et al., *J. Vac. Sci. Technol*. A 30, 010803 (2012)

Acknowledgements

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

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

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