Choice of ALD Precursors for Microelectronics and Nanoelectronics

Roy G. Gordon
Harvard University Chemical Laboratories, Cambridge, MA 02138, USA
Gordon@chemistry.harvard.edu (617)495-4017

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

High-k dielectric on Si ($GdScO_3$)

High-k dielectric on Ge (HfO_xN_y)

High-k dielectric on GaAs ($Gd_xGa_{1-x}O_3$)

High-k dielectric on noble metals (Ta_2O_5)

Thermally stable metal gates (HfN, TaN)

Replacement metal gates (Ru, WN, $CoSi_2$, NiSi)

Source/drain contacts ($CoSi_2$, NiSi)

Pre-metal dielectric (carbon-doped silica)

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

Copper diffusion barriers (WN)

Copper adhesion layers (Ru, Co)

Copper seed layers (Cu)

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

Insulation for through-die interconnects (doped SiO_2)

Coaxial gated transistors on single-walled carbon nanotubes (any high-k/metal combination, following non-covalent functionalization with NO_2)

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

Choice of ALD Precursors for Microelectronics and Nanoelectronics

Roy G. Gordon
Harvard University
Cambridge, MA

Outline

High-k Dielectrics

- More Stable Precursors for Zirconium and Hafnium
- First Precursors for ALD of $GdScO_3$

Interconnects

- ALD / CVD Ruthenium Glue Layers
- ALD Copper Seed Layers
- Electroplating on Cu / Ru / WN

Why More Stable Hf and Zr Precursors?

High-k HfO_2 or ZrO_2 with very low electrical leakage is needed

Carbon impurity in films increases leakage

Thermal decomposition of organic precursors adds C to films

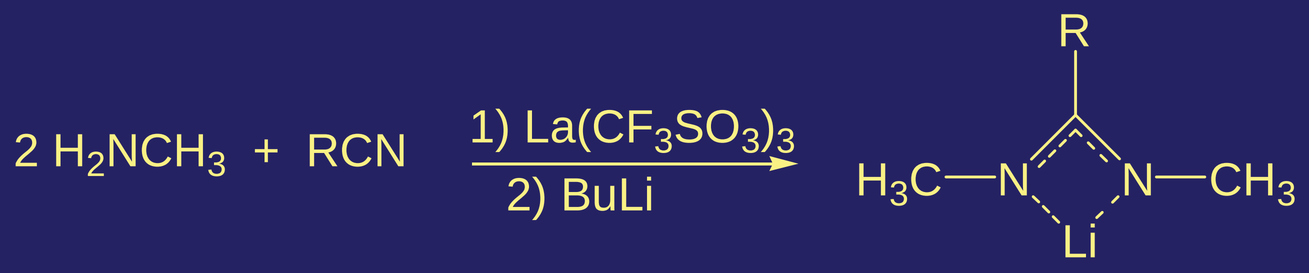
Thermal decomposition destroys uniformity and confomality

Deposition T ~ 400 ^{o}C needed for $HfAlO_x$ with ALD Al_2O_3

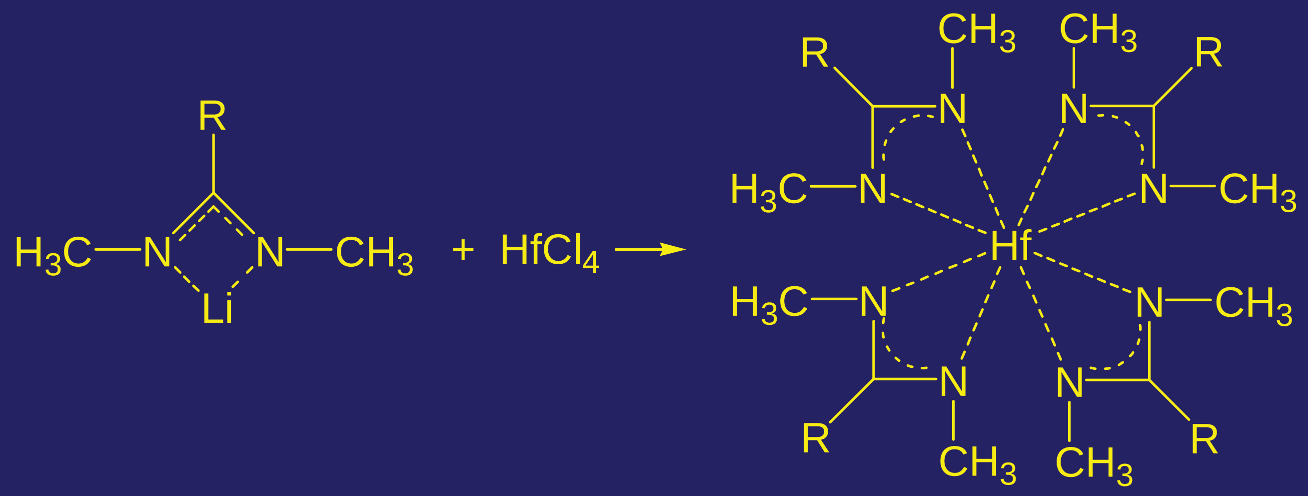
Known Hf precursors decompose too quickly
(except $HfCl_4$, which makes non-conformal films)

Synthesis of Hf Tetra-Amidinates

Couple methylamine with an alkylnitrile and deprotonate with butyllithium:

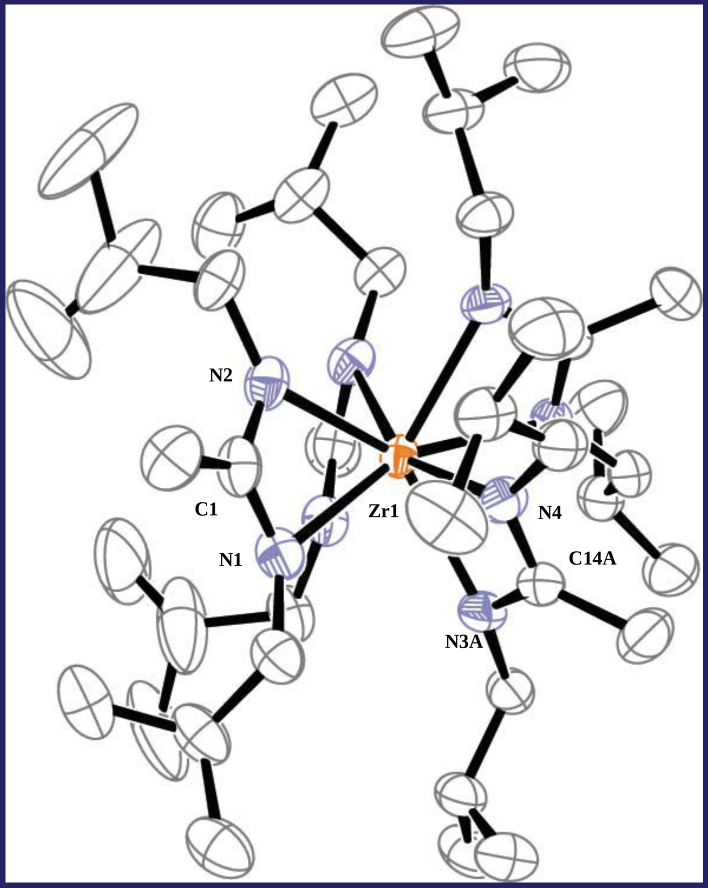


React the lithium salt with hafnium chloride:



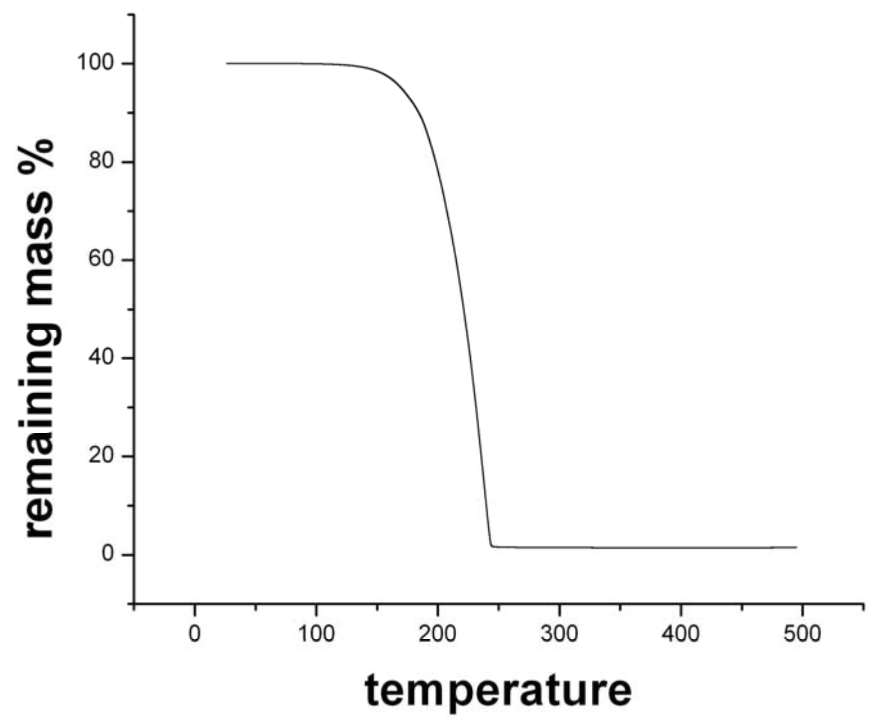
Structure of a Zr Tetra-Amidinate

X-ray structure of $Zr(isobutyl_2\text{-}amd)_4$



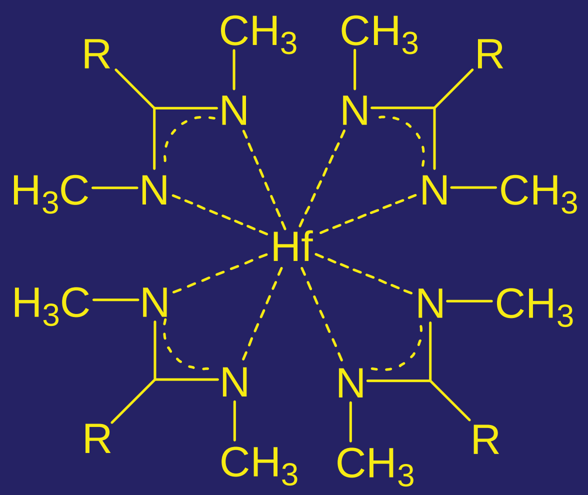
Properties of a Hf Amidinate

TG data for
$Hf(Me_2\text{-}amd)_4$



High thermal stability:
- No residue after TG
- No change of NMR after heating at 250 °C for 1 week

Melting Points of Hf Amidinates



R	Melting Point, ^oC	TG $T_{½}$ ^oC
CH_3	171	221
CH_2CH_3	80	251
$CH_2CH_2CH_3$	<20	246

⇒ R = CH_3 (methyl) is the most volatile;
soluble in hydrocarbons for use in direct liquid injection

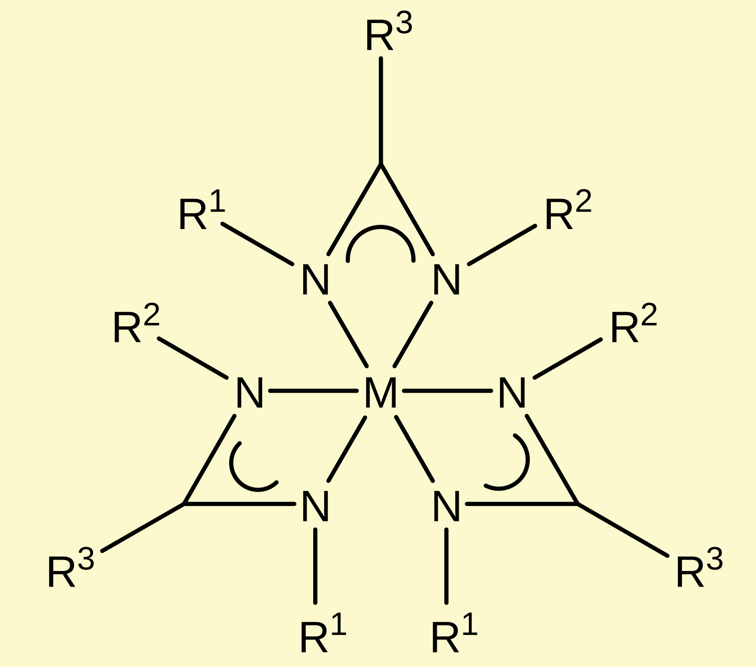
⇒ R = $CH_2CH_2CH_3$ (propyl) is a liquid Hf precursor

ALD experiments in progress

Advantages of $GdScO_3$ as high-κ dielectric

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

Amidinate Precursors for Gd and Sc



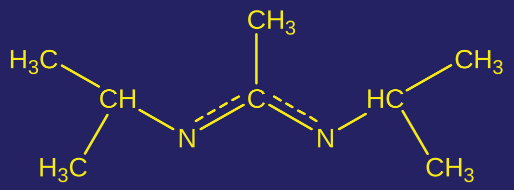
The R^n are typically alkyl groups: ethyl, isopropyl, etc.

The choices of R^n affect the reactivity, stability and volatility.

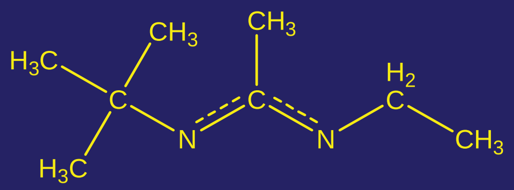
Some Amidinate Ligands

Increasing ligand bulk ↑

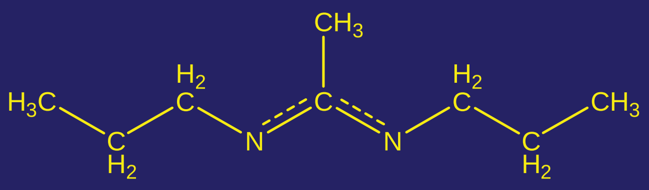
tert-butyl$_2$-acetamidinate



isopropyl$_2$-acetamidinate



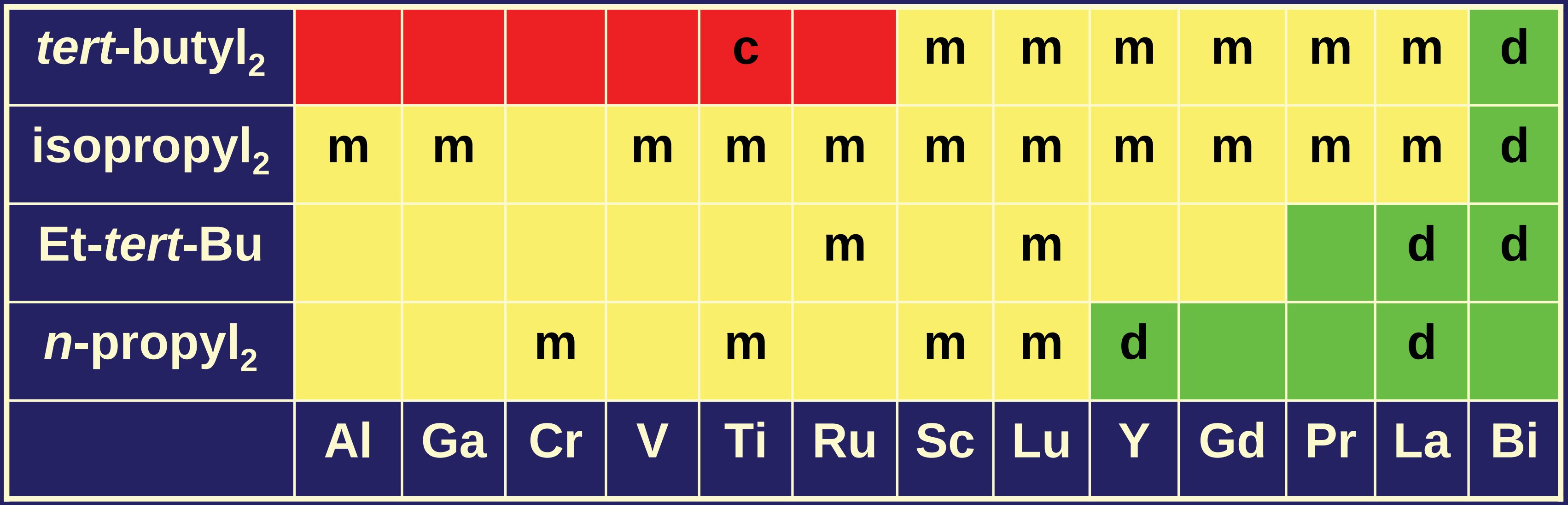
ethyl-*tert*-butyl-acetamidinate



n-propyl$_2$-acetamdinate

Structures of Metal(III) Amidinates

Increasing ligand bulk →



tert-butyl$_2$					c		m	m	m	m	m	m	d
isopropyl$_2$	m	m		m	m	m	m	m	m	m	m	m	d
Et-*tert*-Bu						m		m				d	d
n-propyl$_2$			m		m		m	m	d			d	
	Al	Ga	Cr	V	Ti	Ru	Sc	Lu	Y	Gd	Pr	La	Bi

Increasing size of metal atom →

c = too crowded to make

m = monomer

d = dimer

=> Can’t make precursor if ligands are too bulky for a metal

=> Dimers are nearly as volatile as monomers

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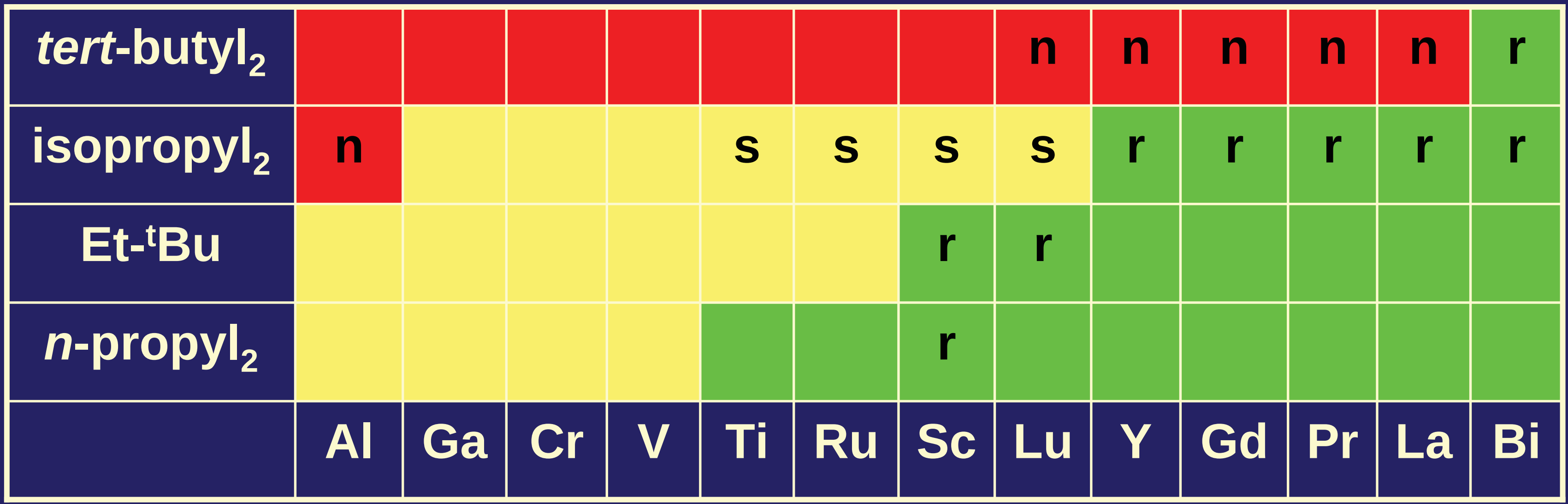
Reactivity of Metal(III) Amidinates with H_2O



Increasing ligand bulk ↑

tert-butyl$_2$	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥 n	🟥 n	🟥 n	🟥 n	🟥 n	🟩 r
isopropyl$_2$	🟥 n	🟨	🟨	🟨	🟨 s	🟨 s	🟨 s	🟨 s	🟩 r	🟩 r	🟩 r	🟩 r	🟩 r
Et-^{t}Bu	🟨	🟨	🟨	🟨	🟨	🟨	🟩 r	🟩 r	🟩	🟩	🟩	🟩	🟩
n-propyl$_2$	🟨	🟨	🟨	🟨	🟩	🟩	🟩 r	🟩	🟩	🟩	🟩	🟩	🟩
	Al	Ga	Cr	V	Ti	Ru	Sc	Lu	Y	Gd	Pr	La	Bi

Increasing size of metal atom →

🟥 n = no reaction

🟨 s = slow reaction

🟩 r = rapid reaction

=> Too bulky ligands slow or stop reactions

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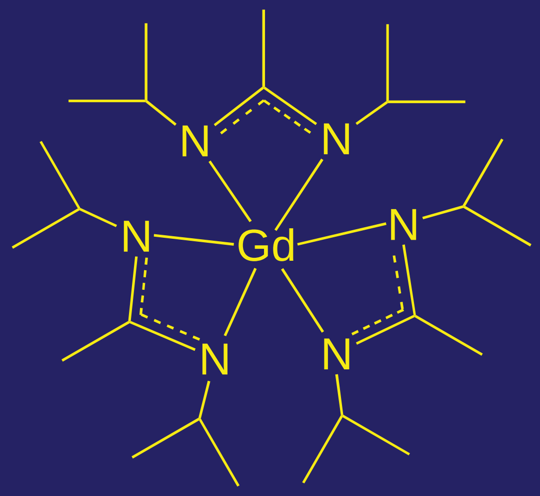
Precursors for $GdScO_3$ ALD

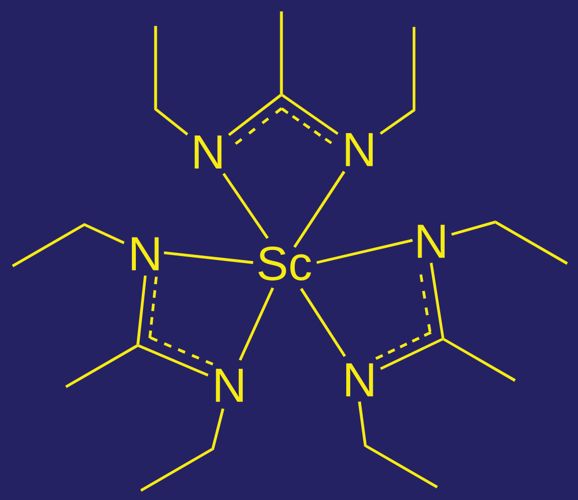


Tris-diisopropylacetamidinato
Gadolinium (III)

$Gd(N_2C_8H_{17})_3$ $Gd({}^iPr\text{-}amd)_3$

Bubbler Temp. : 140 ºC

Thermally Stable to 320 ºC



Tris-diethylacetamidinato
Scandium (III)

$Sc(N_2C_6H_{13})_3$ $Sc(Et\text{-}amd)_3$

Bubbler Temp. : 140 ºC

Thermally Stable to 350 ºC

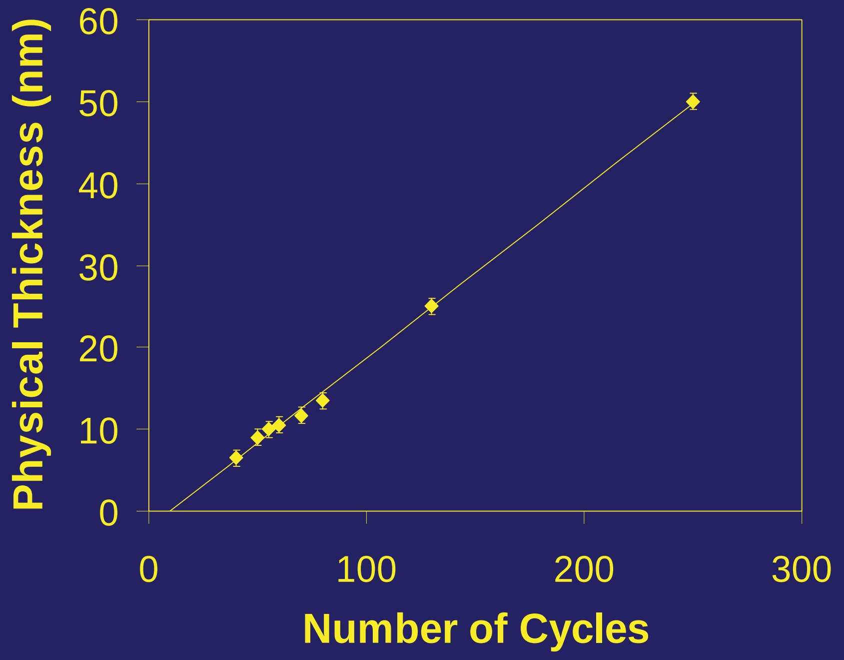
Both precursors nucleate well on hydrogenated Si surfaces and show high reactivity with H_2O.

No need for chemical oxide interlayer to initiate growth

ALD of $GdScO_3$ films

1cycle :	Sc	Purge	H_2O	Purge	Gd	Purge	H_2O	Purge
	6s	15s	4s	40s	6s	15s	4s	40s

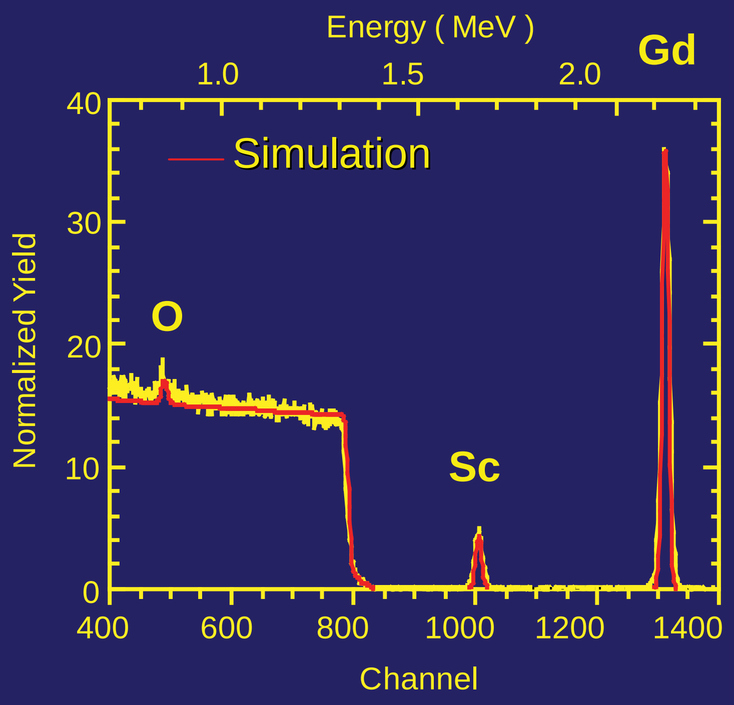
- Flow-through type tube reactor
- Substrate temperature 310 °C



- Linear growth rate ~ 2.0 Å/cycle
- Slight inhibition (~10 cycles) on HF-last Si

Structural Properties of $GdScO_3$ Films

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



- Stoichiometry of a 25nm thick film by RBS: $Gd_1\,Sc_{1.07}\,O_3$ with 1:1 dosing of Gd and Sc

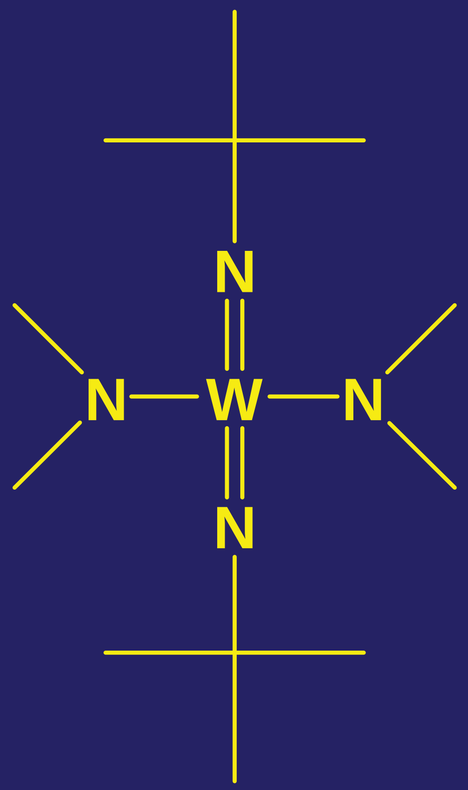
Advantages of WN as a Gate Metal

- Excellent diffusion barrier for oxygen and metal atoms
- Can be etched easily
- Good thermal stability
- Good adhesion to oxides as well as metals

ALD of Tungsten Nitride, WN

- Precursor :

Bis(*tert*-butylimido)bis-
(dimethylamido)tungsten(VI)



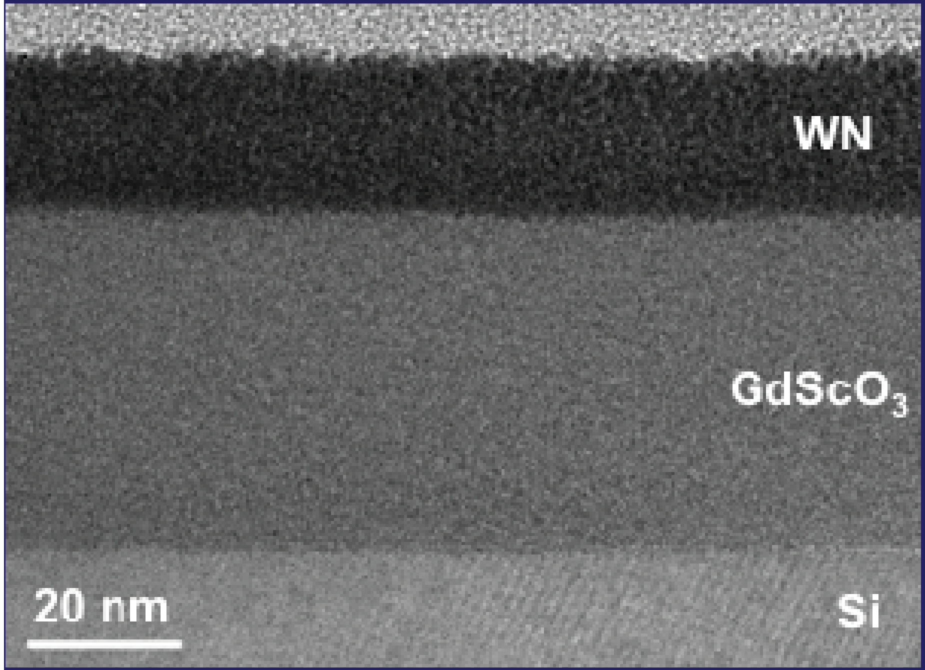
Vapor pressure ~ 37 mTorr at 30 ^{o}C

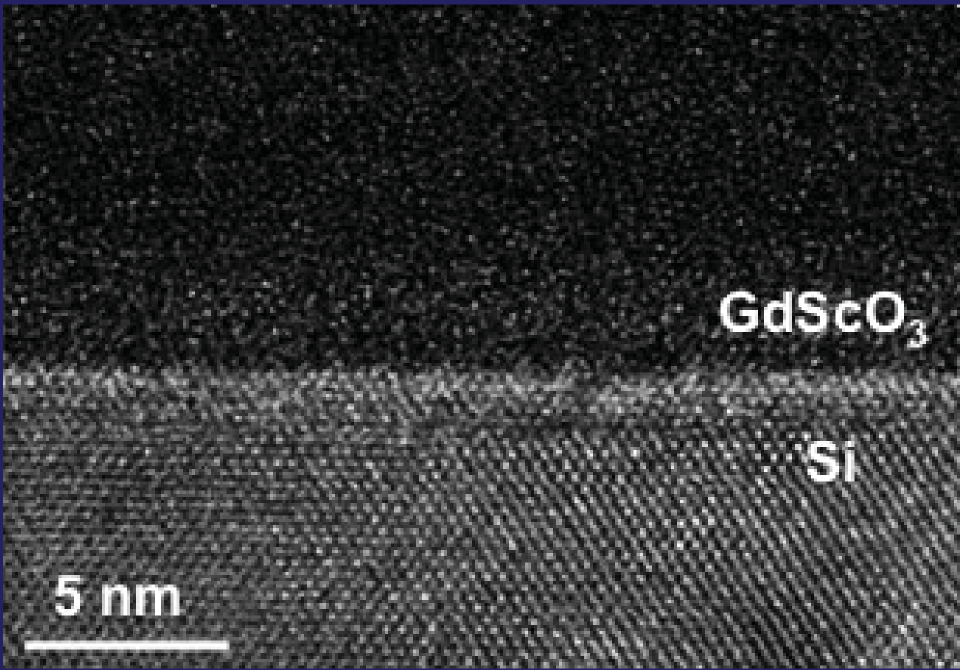
Liquid at room temperature

- NH_3 gas is used as a co-reactant
- Growth Rate at 385 ^{o}C ~ 2.0 Å / cycle
- Resistivity of W after anneal > 750 ^{o}C ~ 10^{-4} Ω-cm

J. S. Becker and R. G. Gordon, Appl. Phys. Lett. 82, 2239 (2003)

HRXTEM of a WN / $GdScO_3$ / Si Stack

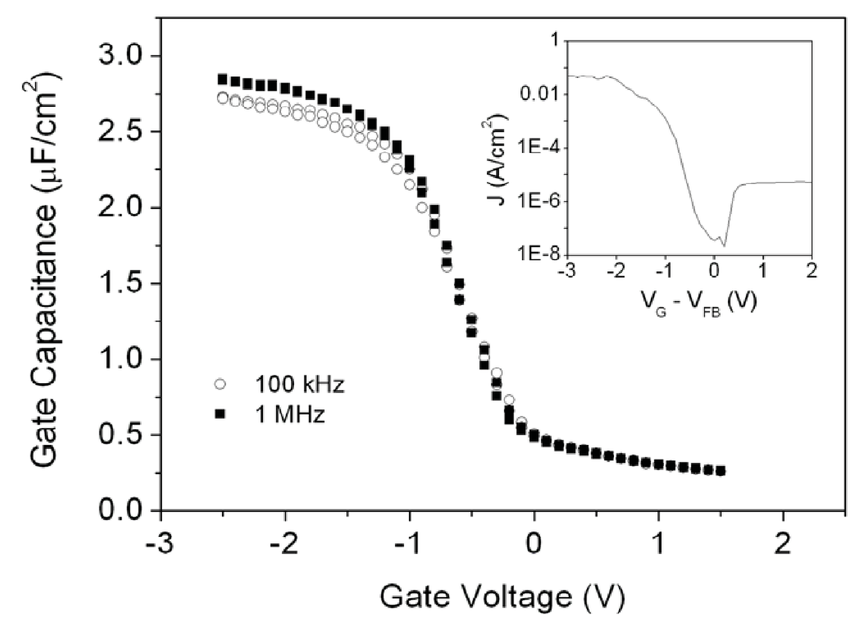


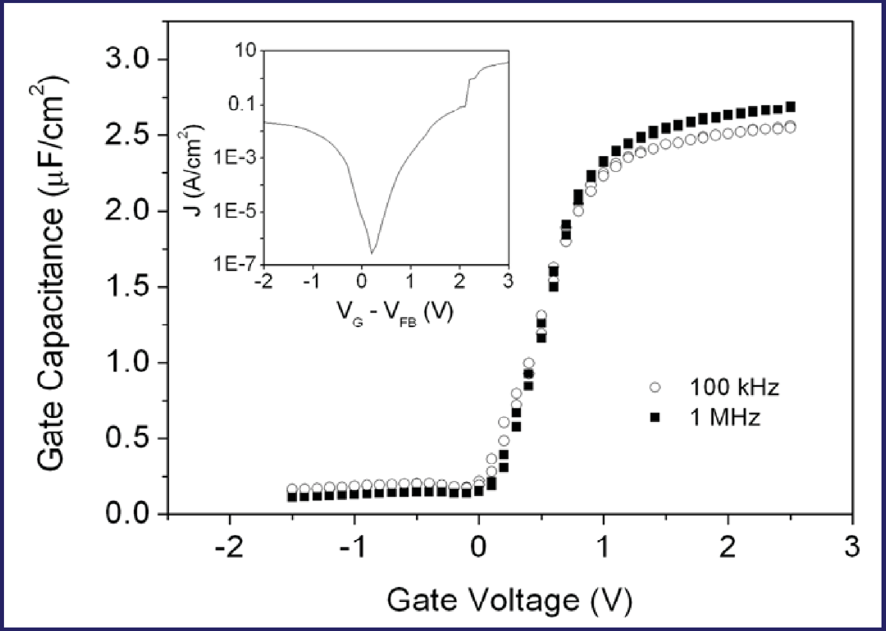


- Films are very uniform over a wide area.
- $GdScO_3$ is amorphous as deposited.
- Interfaces are sharp and smooth.

Electrical Properties of a Low EOT Film

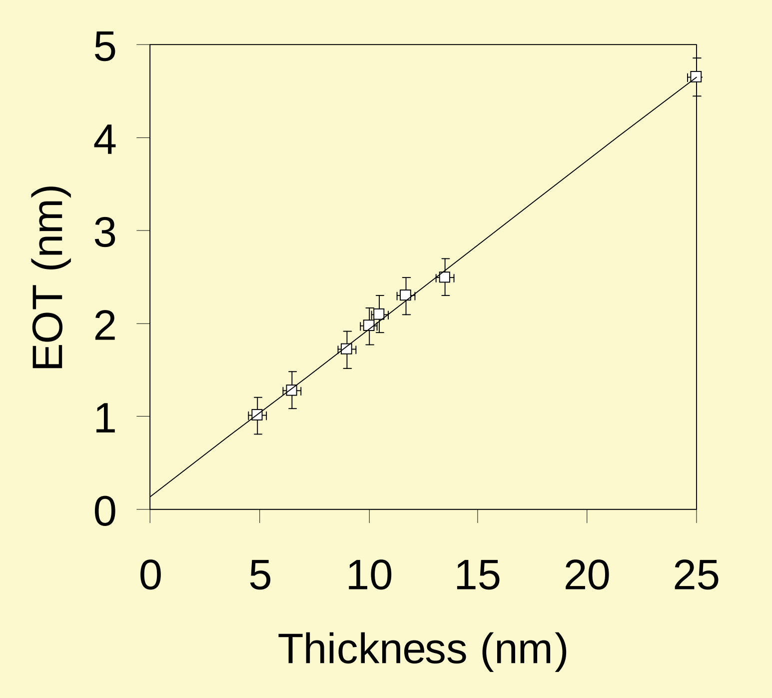
WN / $GdScO_3$ / Si (100) Capacitors





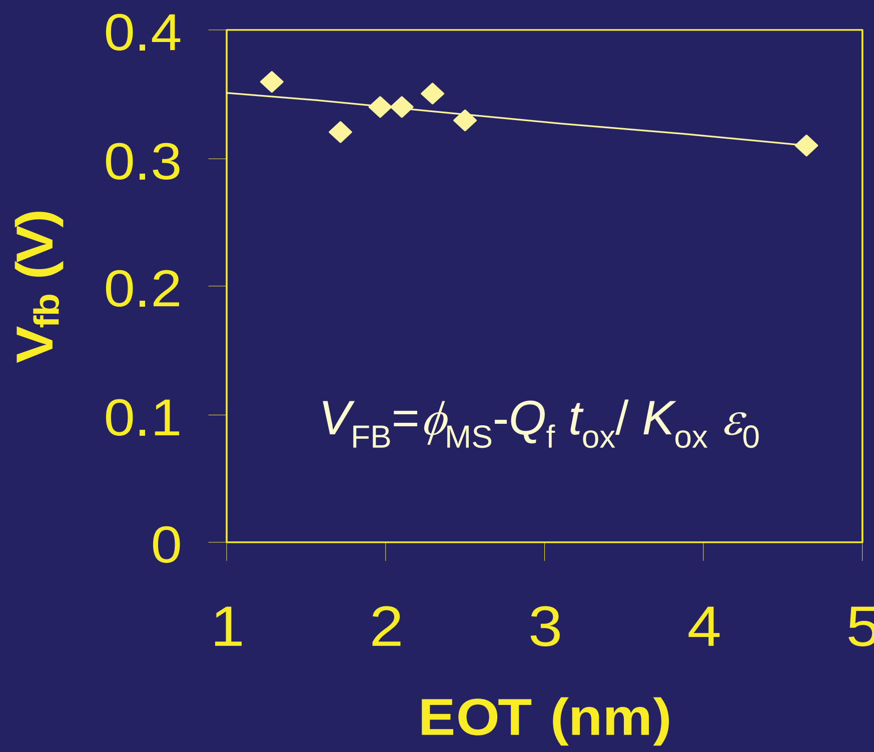
- EOT ~ 1 nm
- Flatband Voltage ~ +0.35 V
- Hysteresis $\Delta V < 60$ mV
- Leakage Current density at 1V ~ 10^{-3} A/cm²

Equivalent Oxide Thickness vs. Physical Thickness



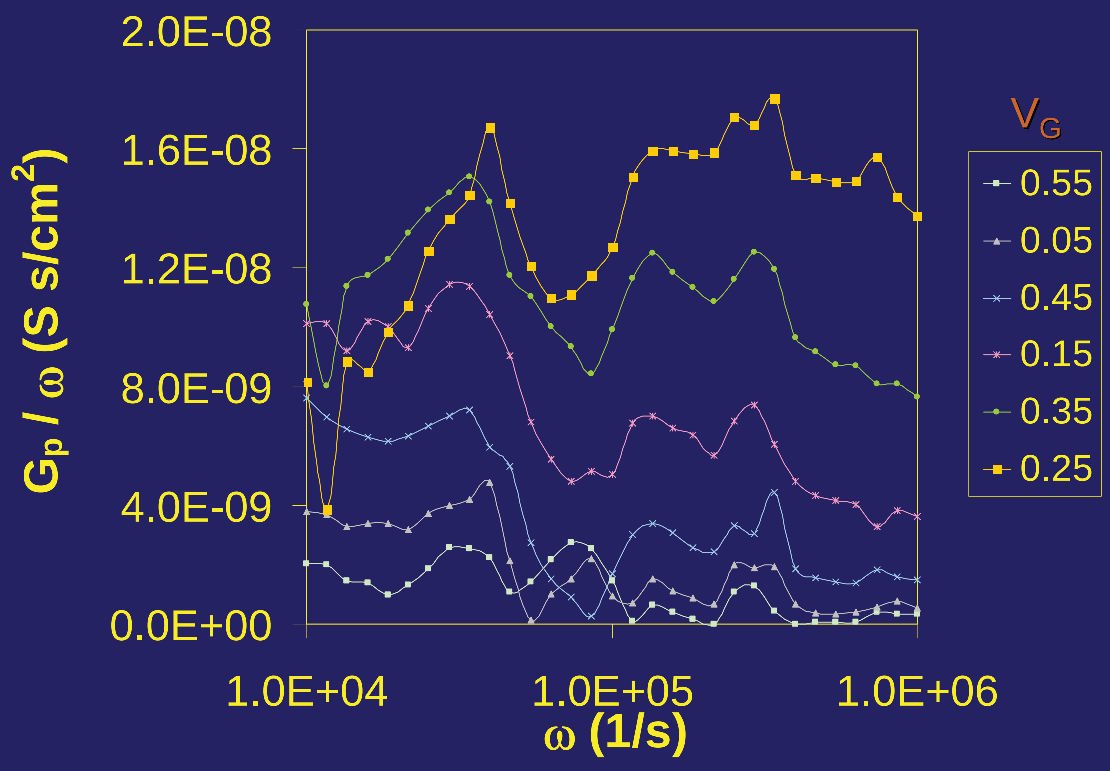
$\kappa \sim 21.5$, interfacial layer ~ 1.5 Å

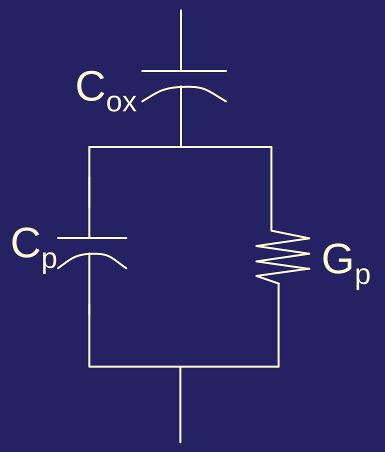
Fixed Charge Density and Work Function of WN



- Fixed Charge Density ~ 2.4 x 10^{11} cm^{-2}
- Work Function of WN ~ 4.6 eV (midgap metal)

Interface Trap Density
by Conductance Method



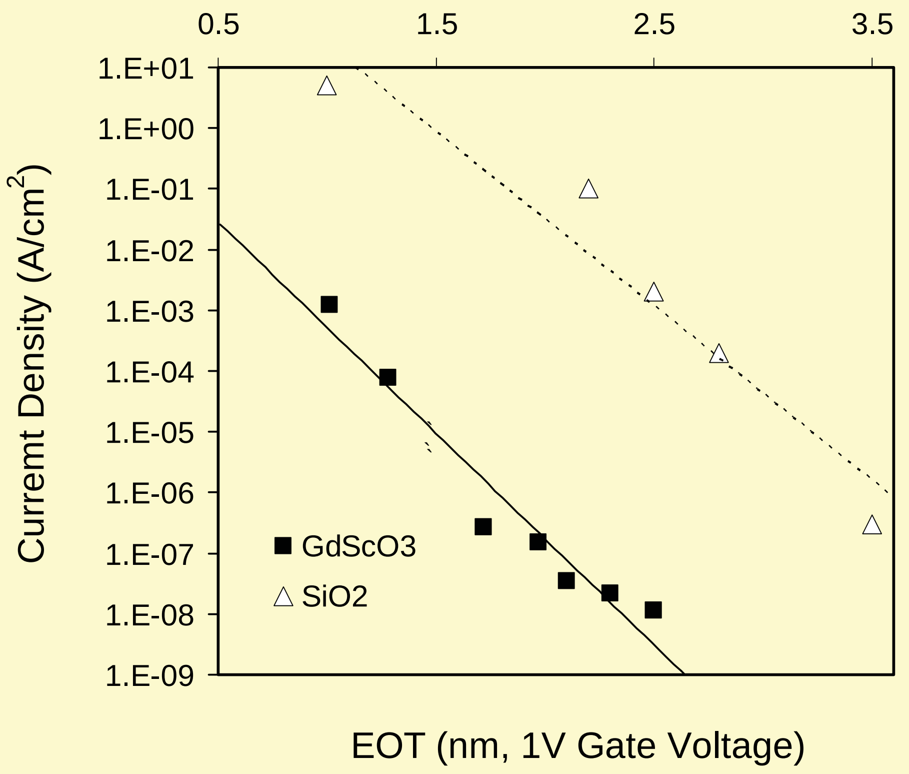


Equivalent circuit
for the Gate Capacitor

$$D_{it} \approx \frac{2.5}{q}\left(\frac{G_p}{\omega}\right)_{\max}$$

- Interface Trap Density ~ 2.8 x 10^{11} cm^{-2} eV^{-1}

Leakage Current vs. EOT



- leakage current ~ 10^{-3} A cm^{-2} at EOT = 1 nm
- leakage current ~ 10^{-7} A cm^{-2} at EOT = 2 nm
- ~ 10^4 times lower than SiO_2

Summary of $GdScO_3$

- Ultrathin amorphous $GdScO_3$ films were deposited on HF-last Si substrates by ALD using Gd and Sc amidinate precursors.
- ALD WN / $GdScO_3$ gate stacks show promising electrical properties for future MOSFET and DRAM applications
  - **High κ (k~ 21.5) and Low EOT (~ 1 nm)**
  - **Low leakage current (< 10^{-3} A/cm^2 at 1V for EOT ~ 1 nm)**
  - **Reasonably low fixed charge and interface trap density**

Outline of Cu / Ru / WN for Interconnects

Ru(amidinate) precursor
    structure
    deposition conditions

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

Copper seed layers
    conformal and complete coverage
    low resistance
    electrochemical deposition of Cu
    survive CMP of Cu

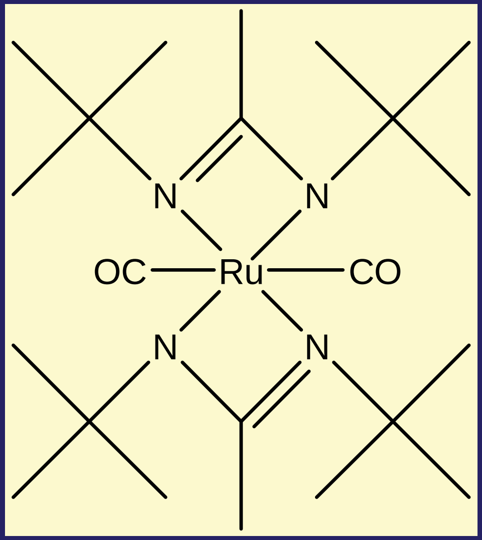
Motivation for using Ruthenium or Cobalt instead of Tantalum as an adhesion layer

Tantalum has low adhesion to CVD or ALD copper

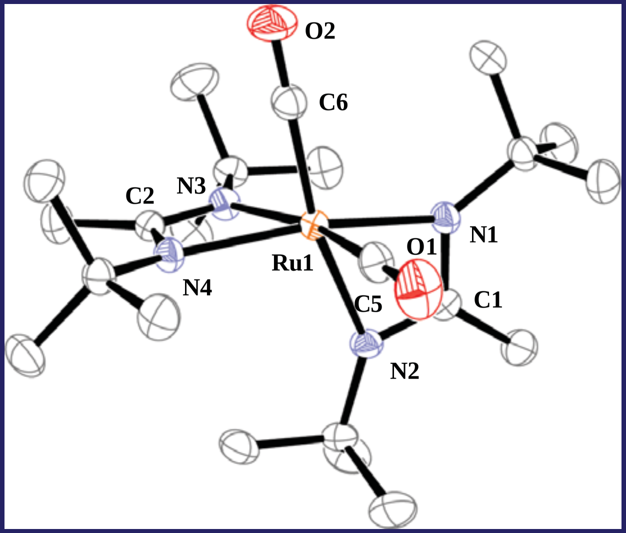
Ta, Ru and Co all have these required properties:

- Low solubility in copper
- Strong interfacial adhesion to copper
  Ta >6 J m^{-2}
  Ru ~4 J m^{-2}
  Co >30 J m^{-2}
- Low electrical resistivity
  Ta 13.4 $\mu\Omega$-cm
  Ru 7.4 $\mu\Omega$-cm
  Co 5.8 $\mu\Omega$-cm

Ru Precursor Ru(^{t}Bu-amd)$_2$(CO)$_2$



Chemical formula



Molecular structure by x-ray crystallography

- vapor pressure >0.05 Torr at 130 ºC
- low evaporation residue 0.14% by TG
- air and moisture stable

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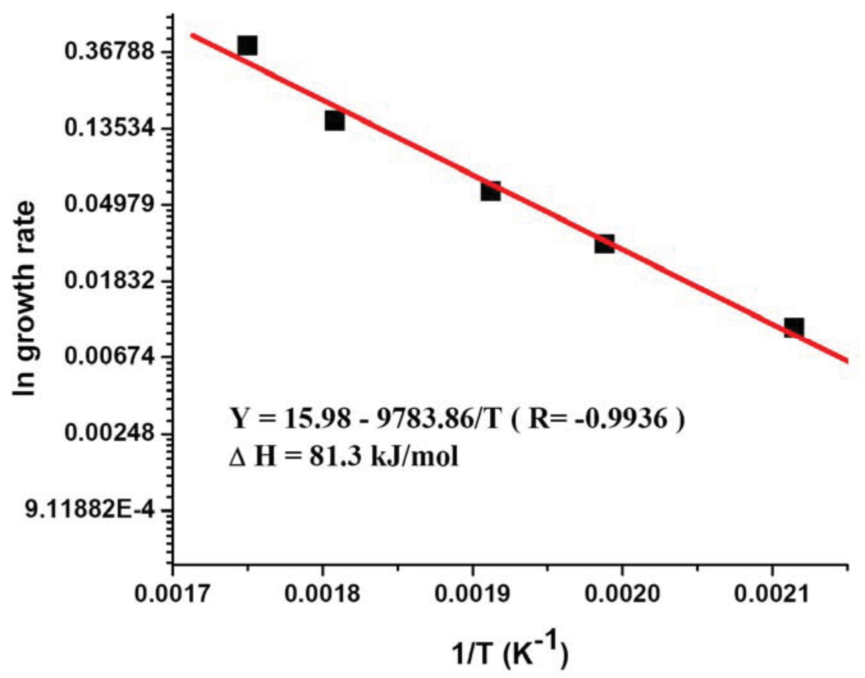
ALD/CVD of Ru

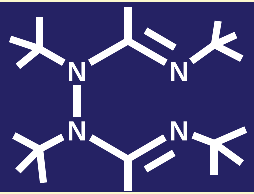
Conditions:

- Bubbler: 130 ºC
- Substrate: 200 - 300 ºC
- co-reactant: NH_3
- Pressure: 1 ~ 2 Torr
- ~1.5 Angstrom/cycle at 300 ºC
- No saturation of growth/cycle



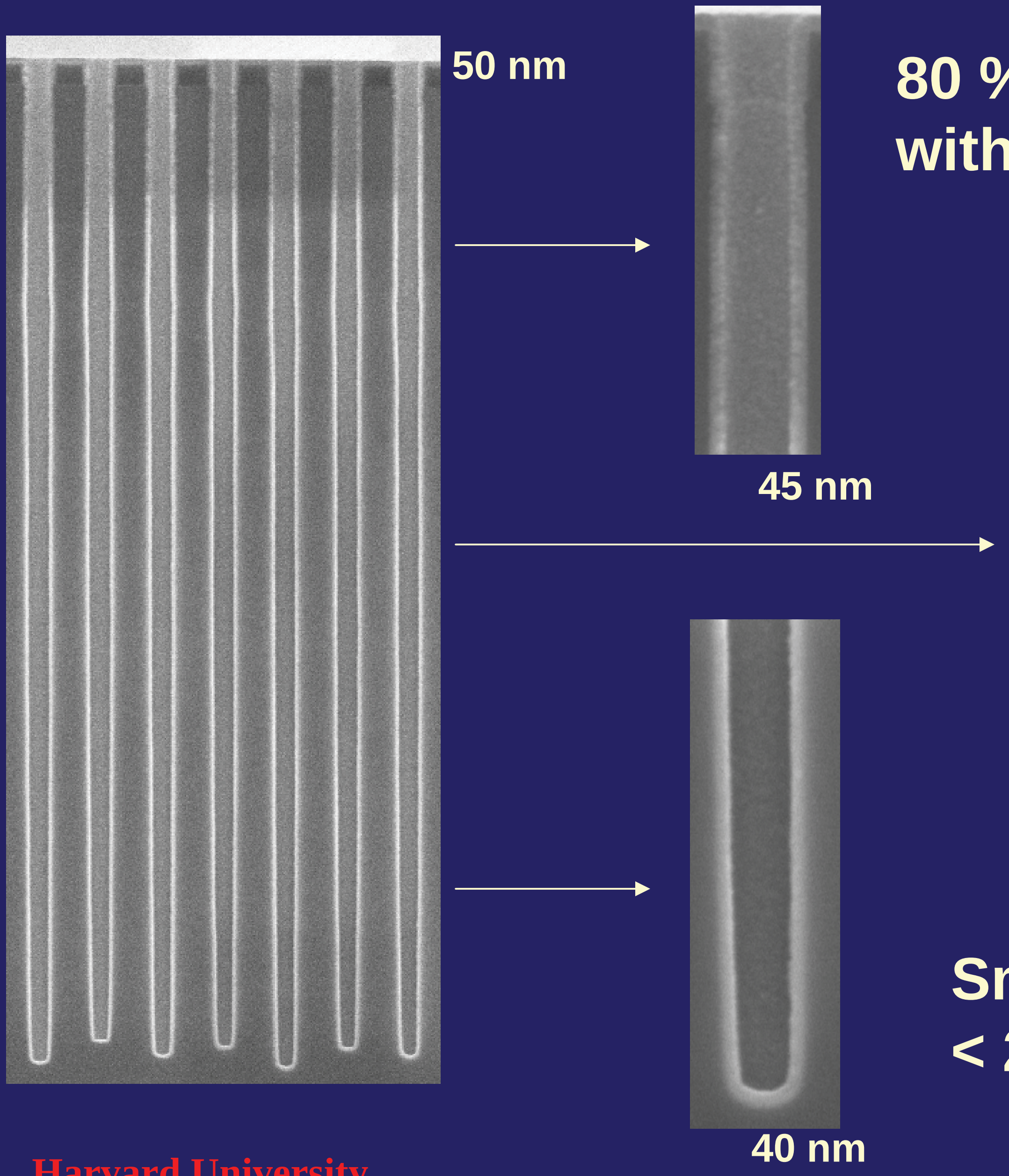
=> Mostly surface controlled CVD, only partly ALD

$Ru(^{t}Bu\text{-amd})_2(CO)_2 \longrightarrow Ru +$

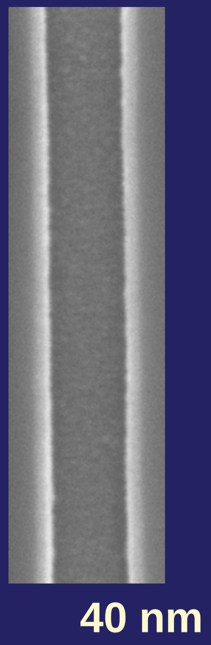


$+ 2 CO$

High Conformality of ALD/CVD Ru/WN/SiO_2



80 % conformal in trench
with 40:1 aspect ratio



Smooth films: by AFM
< 2 % rms roughness

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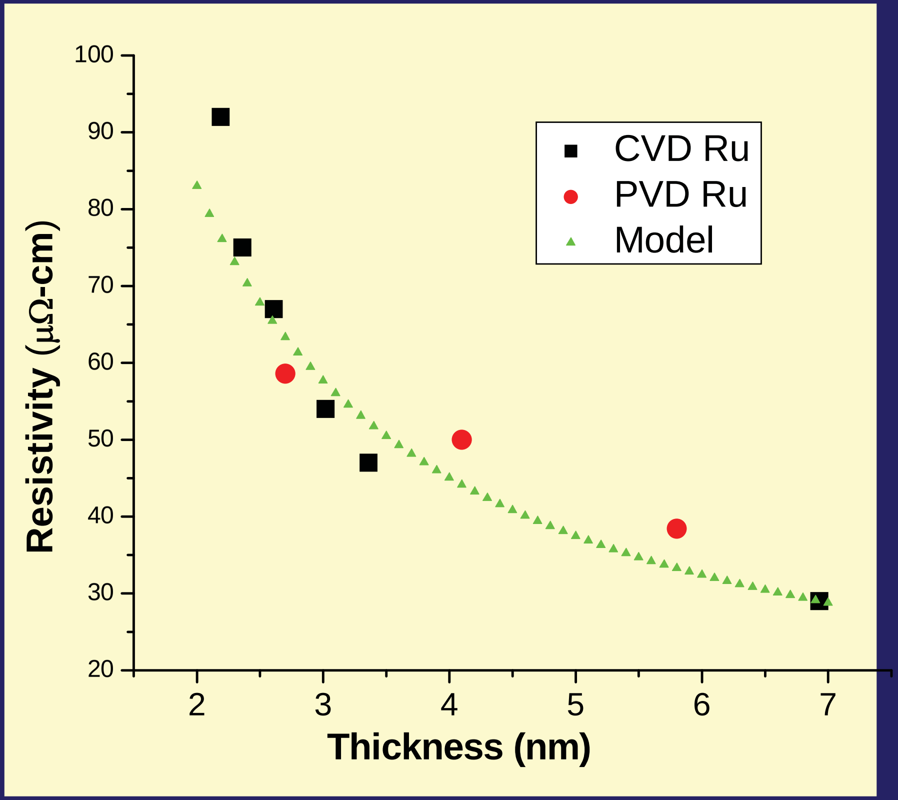
Electrical Conductivity of CVD Ru / SiO_2

Conductivity matches pure Ru films sputtered onto Ta



Grain Boundary Scattering Model

ρ/ρ_0 = 1+1.5{R/(1-R)} (λ / g) ▲▲▲▲▲▲

where the average grain size g is estimated as the film thickness

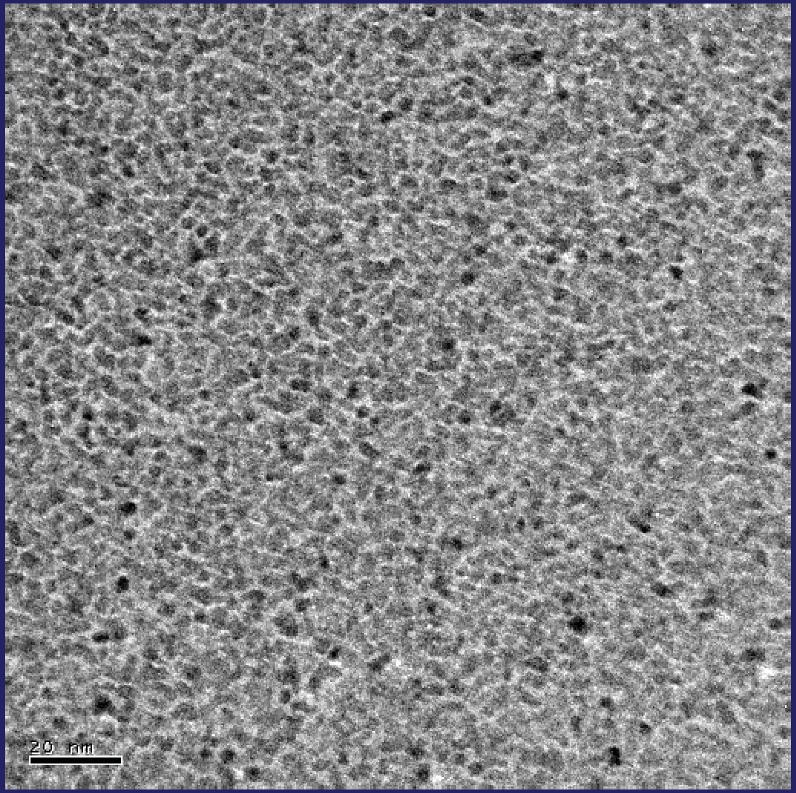
scattering coefficient for electrons at grain boundaries R = 0.58

bulk scattering length λ = 10 nm

bulk resistivity ρ_0 = 7.1 μΩ-cm

2 nm ALD/CVD Ru completely covers WN

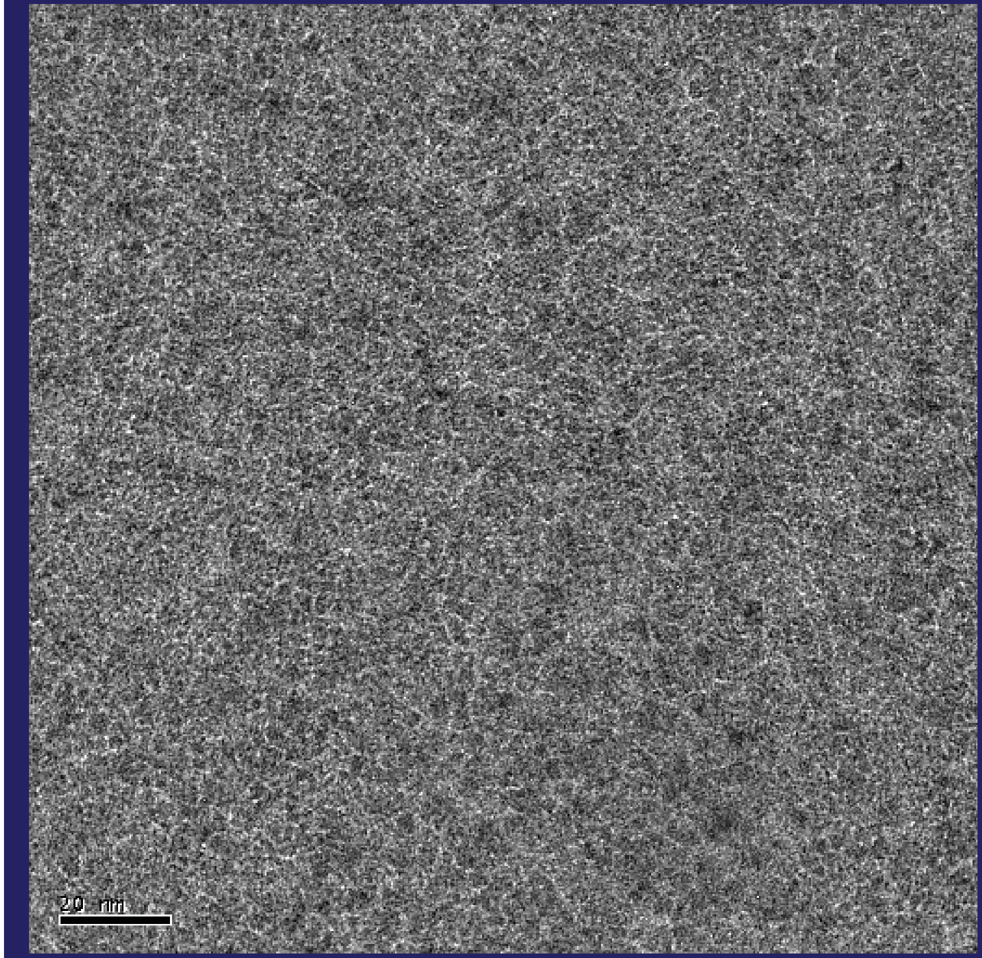
- no pinholes seen by vertical TEM:



- an etch solution H_2O_2/NH_4OH, which normally dissolves a WN film within one minute, does not etch the WN under a 2 nm Ru film even after one hour.

- Ru films are strongly adherent to freshly-deposited WN adhesion energy ~ 4 J/m^2 by 4-point bend test.

Nucleation of Cu(3nm) on Ru(2nm) / WN(3nm) / Si_3N_4



Vertical TEM shows complete coverage

Chemical test for completeness of coverage by copper:

Ru catalyzes H_2O_2 decomposition rapidly forming bubbles of oxygen

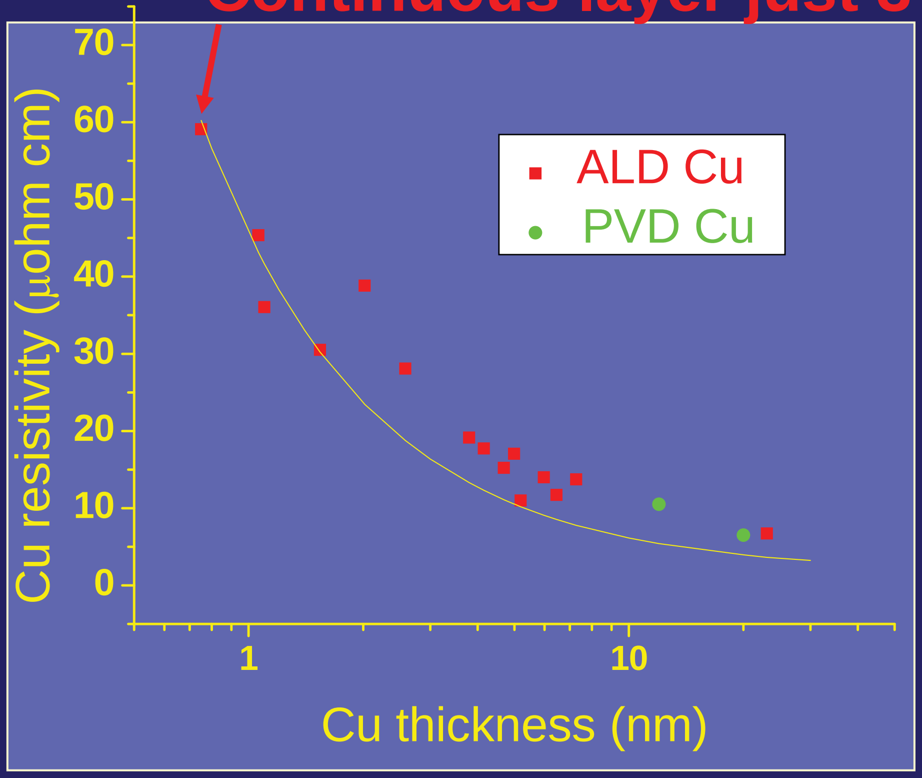
Cu bubbles very slowly

Cu / Ru also bubbles very slowly

Zhengwen Li and Roy G. Gordon, *Chem. Vap. Deposition* **2006**, *12*, 435–441

Electrical Resistance of ALD Cu on Ru

Continuous layer just 3 Cu atoms thick!



Grain Boundary Scattering Model

$\rho/\rho_0 = 1+1.5\{R/(1-R)\} (\lambda / g)$ ——

where the average grain size g is estimated as the film thickness

scattering coefficient for electrons at grain boundaries R = 0.3

bulk scattering length λ = 39 nm

bulk resistivity $\rho_0 = 1.7\ \mu\Omega$-cm

ALD Cu resistivity matches pure sputtered Cu films[a]

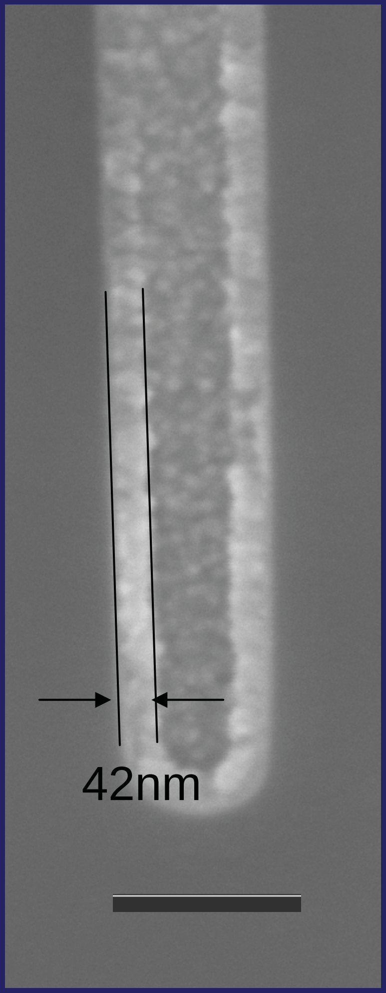
(a) Rossnagel, S.; Kuan, T.; *J. Vac. Sci. Tech. B* **22**, 240 (2004)

Conformality and Sheet Resistance of Cu / Ru / WN

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

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

Suitable for electroplating



Cross Section of Electroplated Cu/Ru/WN/SiO_2

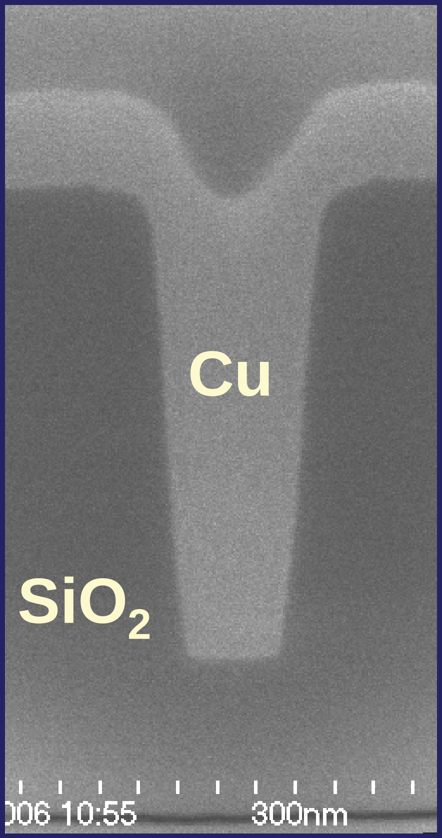
Electroplated by Tom P. Moffat

CMP by Christian Witt

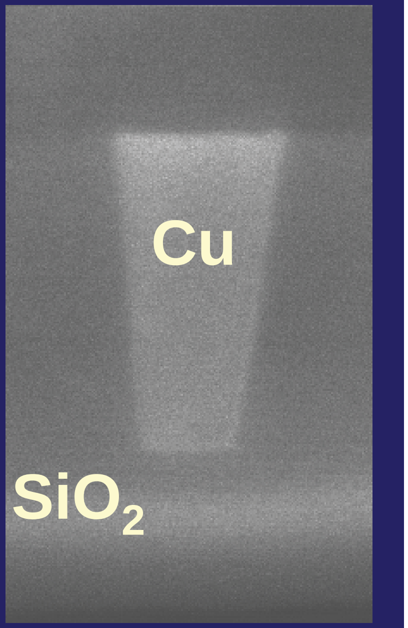
SEM by Daniel Josell, NIST

=> Adhesion strong enough to survive CMP

Before CMP



After CMP



Interconnect Summary

ALD of SiO_2 pore sealant / WN barrier / Ru glue / Cu seed

- **Extendable to the end of the roadmap**
- **No deposition on chamber walls => no chamber cleaning**
- **No plasma damage to substrates**
- **Simplified equipment design because no plasma needed**

Acknowledgements

Metals: Booyong Lim, Antti Rahtu, Jin-Seong Park

Nickel: P. Venkateswara Rao, Kyoung-ha Kim

Copper, Cobalt: Zhengwen Li, Sean Barry, Don Keun Lee

Ruthenium: Huazhi Li, Titta Aaltonen

Metal Nitrides: Jill Becker, Seigi Suh, Esther Kim, Kyoung-ha Kim

Metal oxides: Dennis Hausmann, Philippe de Rouffignac, Jin-Seong Park, Kyoung-ha Kim, Leo Rodriguez, Mike Coulter

TEM: Damon Farmer; SEMATECH

Adhesion measurements: Joost Vlassak, Youbo Lin

DRAM trenches supplied by Infineon

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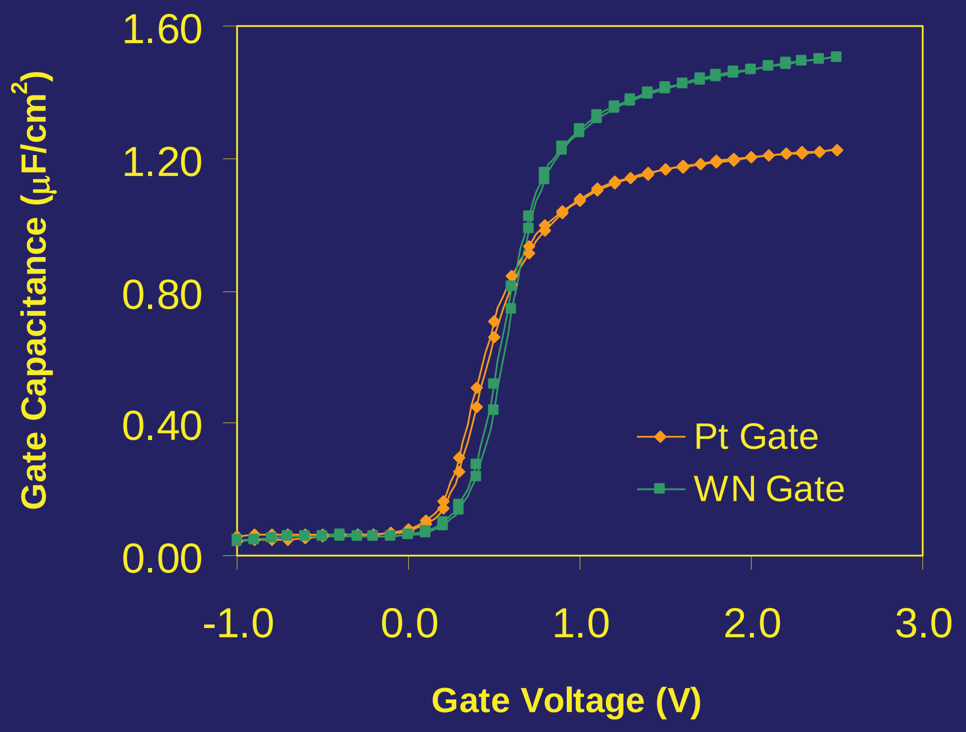
In-situ Deposited WN Gate vs. Ex-situ Deposited Pt Gate



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

Harvard University