AN ALD SOLUTION FOR COPPER BARRIER/SEED LAYERS ON POROUS LOW-K DIELECTRICS

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Copper Interconnects in Microelectronics

Why Cu Interconnections?

Cu has higher conductivity than Al

Cu resists electromigration better than Al

=> higher speed
=> lower power consumption

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Problems of Copper Interconnects

- Cu diffuses easily => thin barrier needed
- Thin barrier => pores in low-k dielectric must be sealed
- Cu adheres poorly => adhesion layer needed
- Cu nucleates poorly => seed layer needed

ALD can solve all these problems efficiently!

Outline

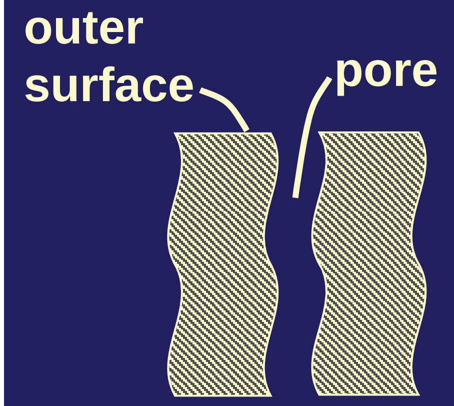
Sealing porous low-k dielectrics: SiO_2

Diffusion barrier: WN

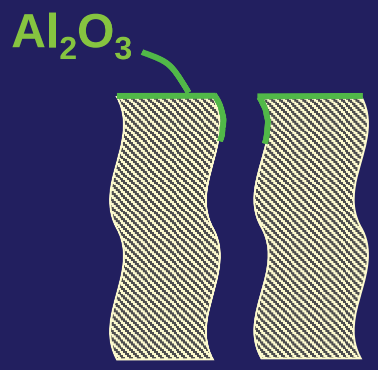
Adhesion layer: Co

Seed layer: Cu

Sealing Pores in Low-k Dielectrics With $AlMe_3$ and $(^tBuO)_3SiOH$



porous low-k dielectric



1 dose of $AlMe_3$ => sub-mono-layer of alumina catalyst with low exposure for low step coverage[a]

1 dose of $(^tBuO)_3SiOH$ => a few nm of silica that seals pores[b]

[a] Roy G. Gordon, Dennis M. Hausmann, Esther Kim, Joseph Shepard, *Chem. Vapor Dep.* (2003), 9, 73

[b] Philippe de Rouffignac, Zhengwen Li, Roy G. Gordon, *Electrochem. Solid State Lett.* (accepted, 2004)

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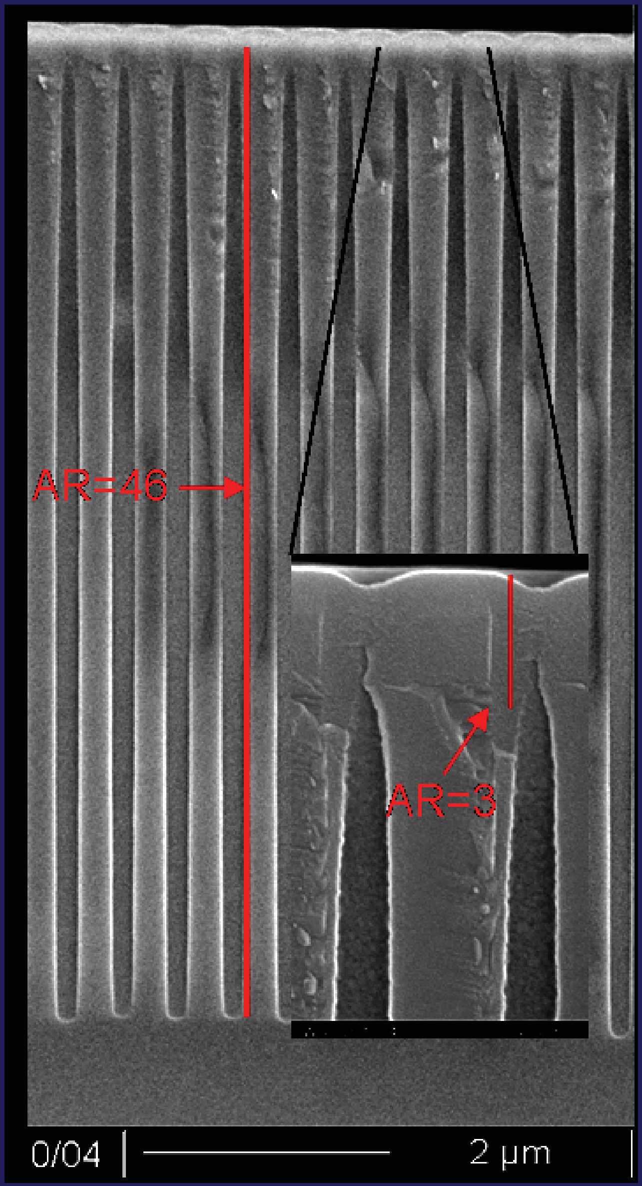
Visualizing Sealed Pores in Test Holes

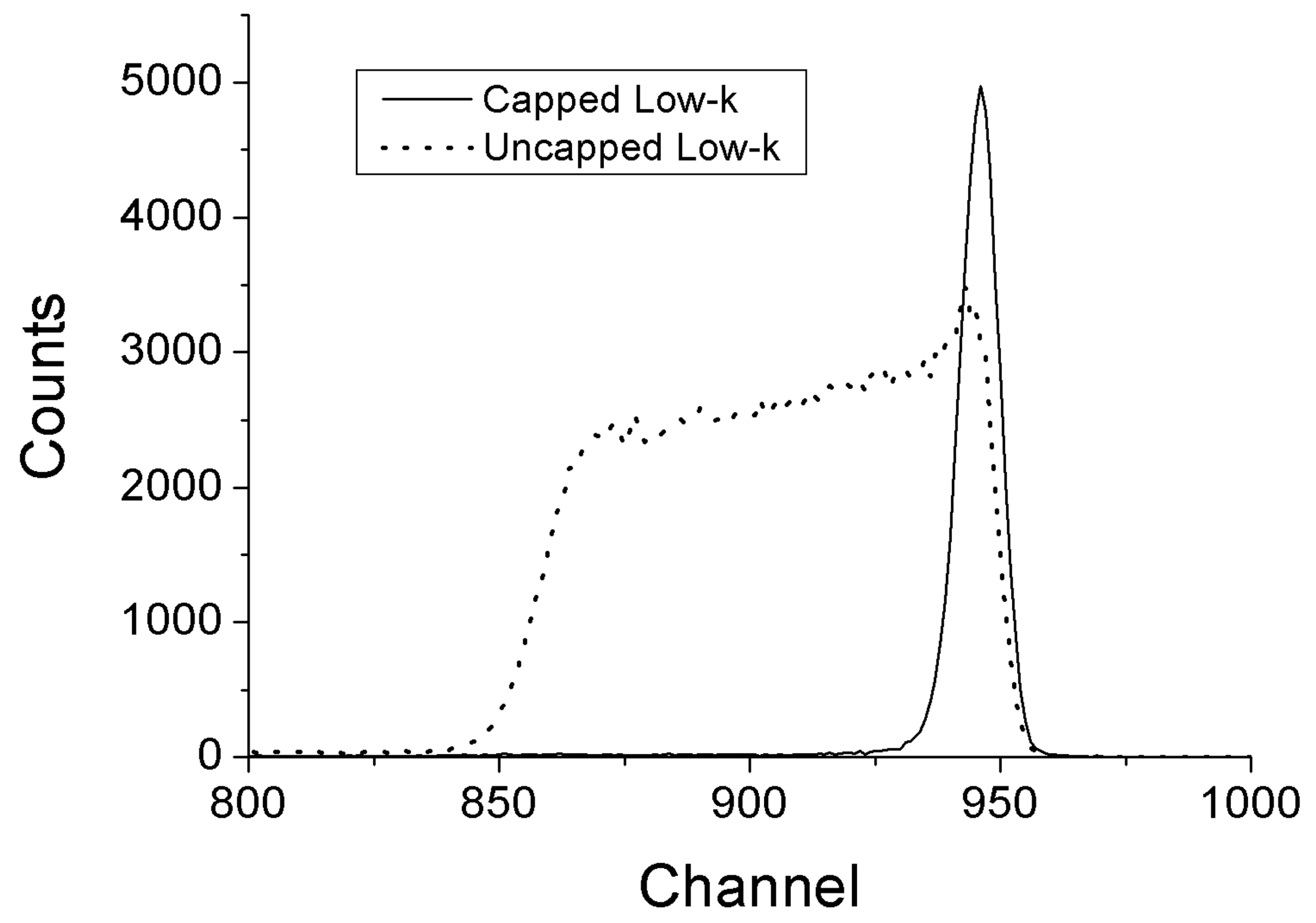
Cross section of DRAM trenches sealed by 10 nm of ALD silica

SEM image at lower right shows a higher magnification image of the sealed tops of 2 holes

Faithful larger-scale model of the smaller pores in low-k dielectrics because no gas-gas collisions occur inside either holes.
(mean free path >> hole diameters)



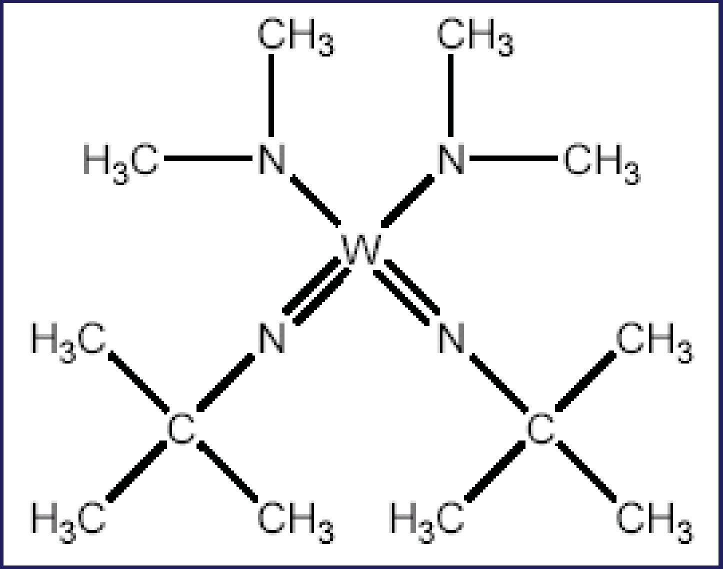
RBS Testing for Penetration of Pores in Low-k Dielectrics by ALD of WN



Why Tungsten Nitride Diffusion Barriers?

- Excellent Cu diffusion barrier properties for films as thin as 1.5 nm!
- Excellent adhesion
- Uniform and dense nucleation
- Resistivity low enough for use as a thin Cu diffusion barrier
- All WN_x phases are electrically conductive (unlike insulating Ta_3N_5)
- CMP with copper (unlike TaN_x, which needs a separate CMP step)
- More effective ALD process for WN than for TaN_x

Precursor for ALD Tungsten Nitride

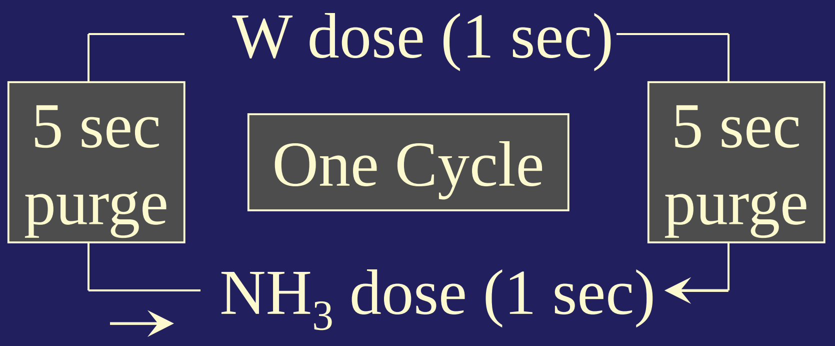


bis(*tert*-butylimido)bis(dimethylamido)tungsten(VI)

- Non-corrosive, low-viscosity, stable liquid
- Sufficient volatility (~40 ºC vapor source)
- High thermal stability and high reactivity
- Commercially available

Jill Becker, Seigi Suh, Roy G. Gordon, *Chem. Mater*. (2003), 15, 2969.

ALD Results for Tungsten Nitride


W dose (1 sec)

5 sec purge

One Cycle

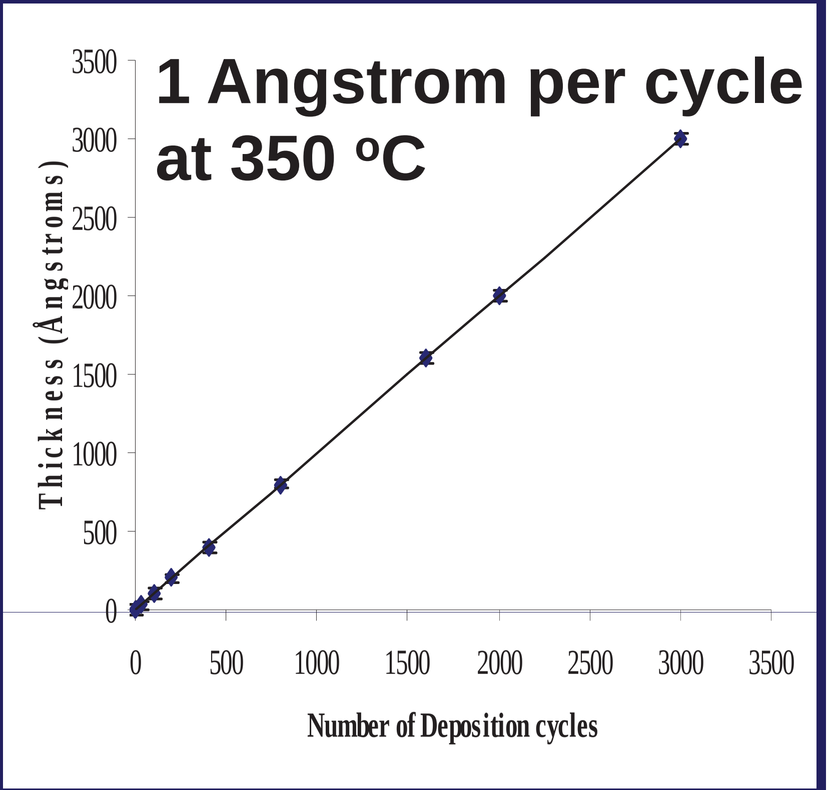
5 sec purge

NH_3 dose (1 sec)

Pure, smooth amorphous WN

Uniform nucleation with no delay

15 cycles => excellent Cu barrier


1 Angstrom per cycle at 350 °C

No WN deposition on reactor walls kept below 250 °C!

Roy G. Gordon, Jill Becker, *Applied Physics Letters* (2003), 82, 2239.

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Co as Adhesion Layer

Why Co as an adhesion layer for Cu?

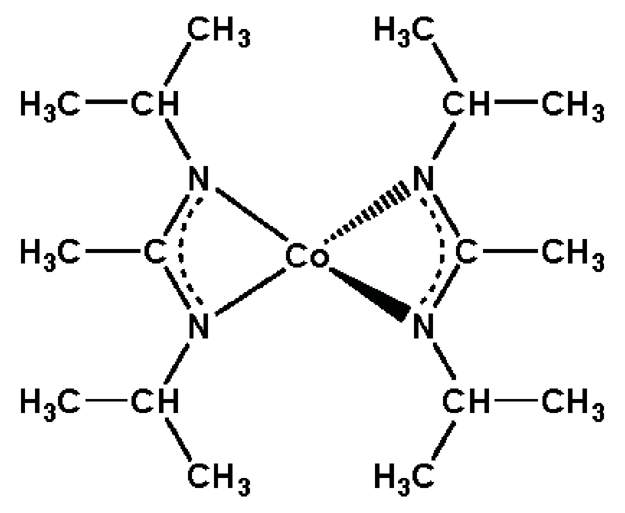
Cu (seed layer)

Co (adhesion layer)

WN (diffusion barrier layer)

- Co adheres to Cu just as well as the industry standard Ta does.
- Cobalt oxide is easily reduced by H_2, unlike more stable Ta_2O_5.
- Co has lower electrical resistivity than Ta.
- Co removed by Cu CMP, eliminating extra CMP step needed for Ta
- ALD Co easily done with H_2; ALD Ta requires difficult H atoms

Cobalt Precursor Properties



Novel Cobalt Precursor:
Co(II) N,N'-diisopropylacetamidinate
$Co(^{i}Pr_2\text{-AMD})_2$

Vapor pressure: 60 °C/ ~0.2 Torr

Reactive to molecular hydrogen, H_2

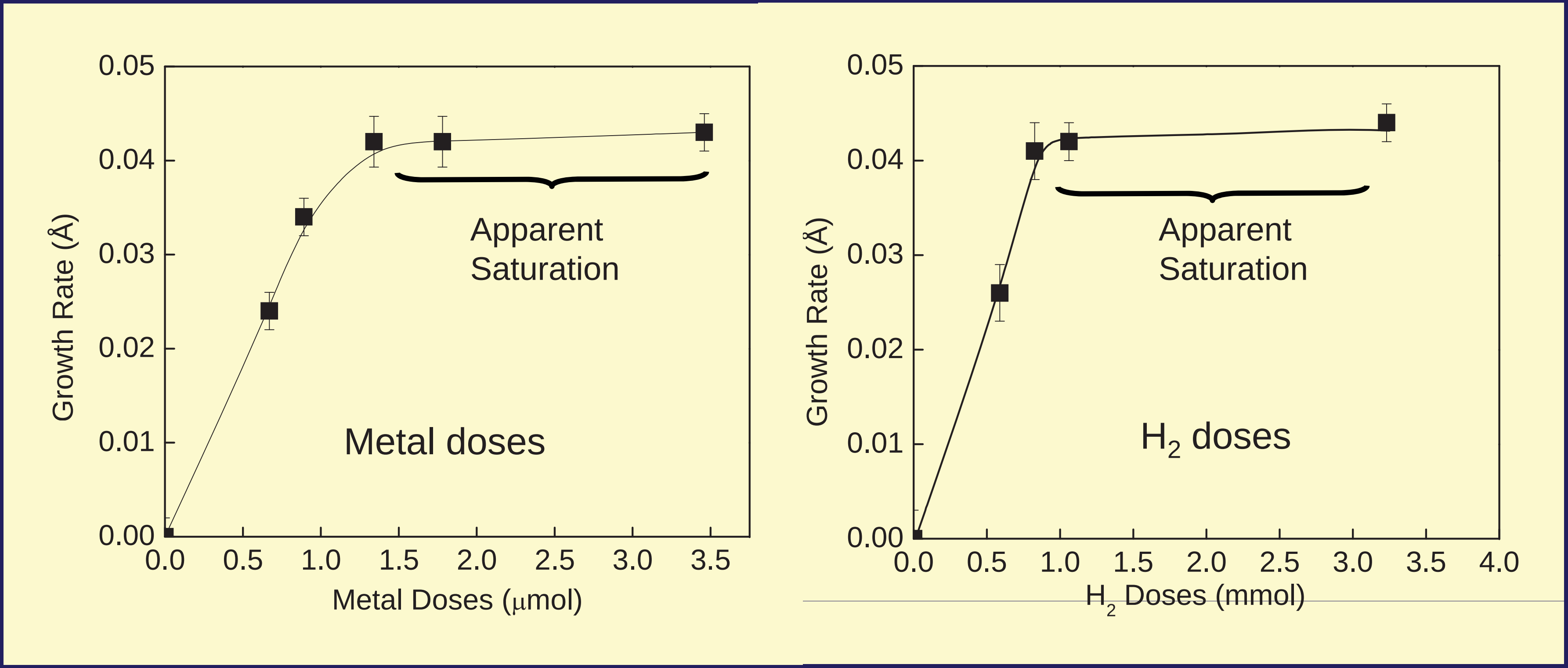
0.2 Angstroms/cycle at 300 °C

No deposition on walls kept at $T < 250$ °C

⇒ No cleaning of reactor walls

Booyong S. Lim, Antti Rahtu, Roy G. Gordon, *Nature Materials* (2003), 2, 749.

ALD of Cobalt Films

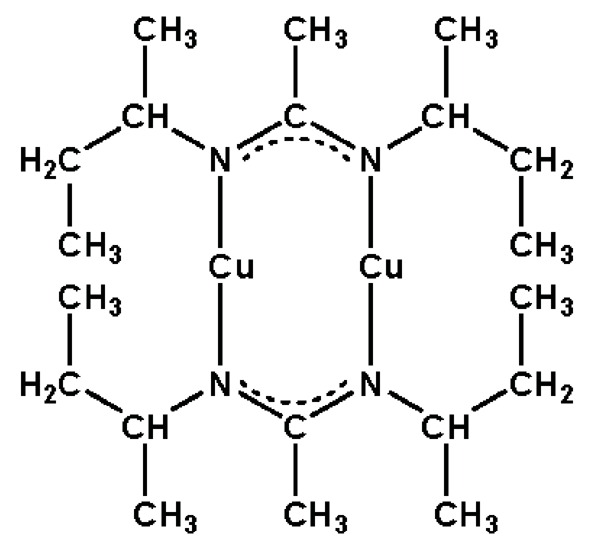


Increasing the exposure (but not the dose) by 100 times increases the thickness by 3 X, to about 0.12 A/cycle.

⇒ these saturation curves are not complete.
⇒ heterogeneous surface reactivity or H dissolved in film

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

1 Angstrom per cycle at 180 °C

	Cu	H_2
Dose (nano-moles/cm^2)	2.5	5×10^3
Exposure (Torr-seconds)	1	1.2×10^2

Zhengwen Li, Roy Gordon, unpublished results

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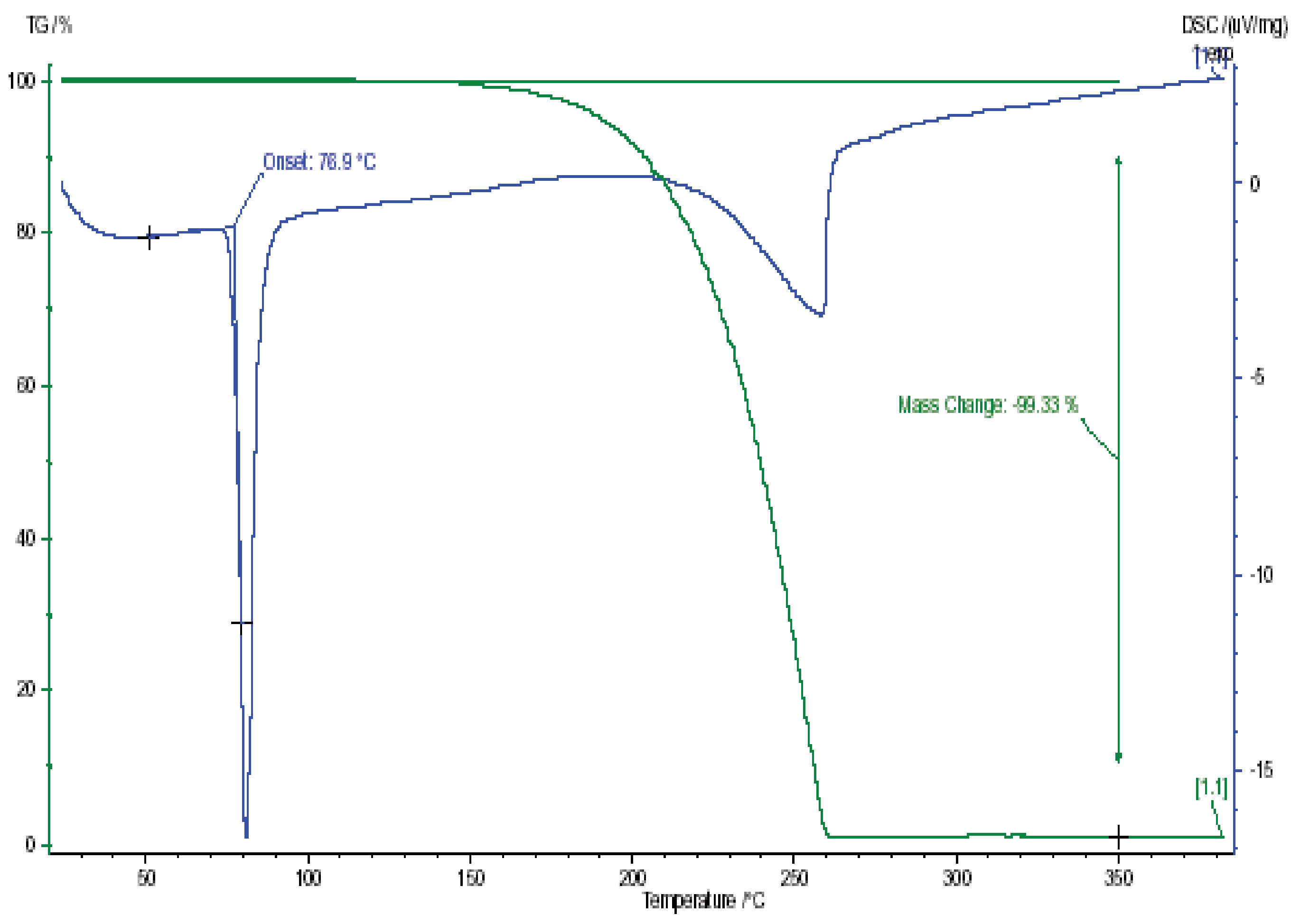
TGA/DSC of Cu(I) N,N’-di-*sec*-butylacetamidinate



Melting point: 77 °C

Liquid evaporates with negligible residue (<0.7%)

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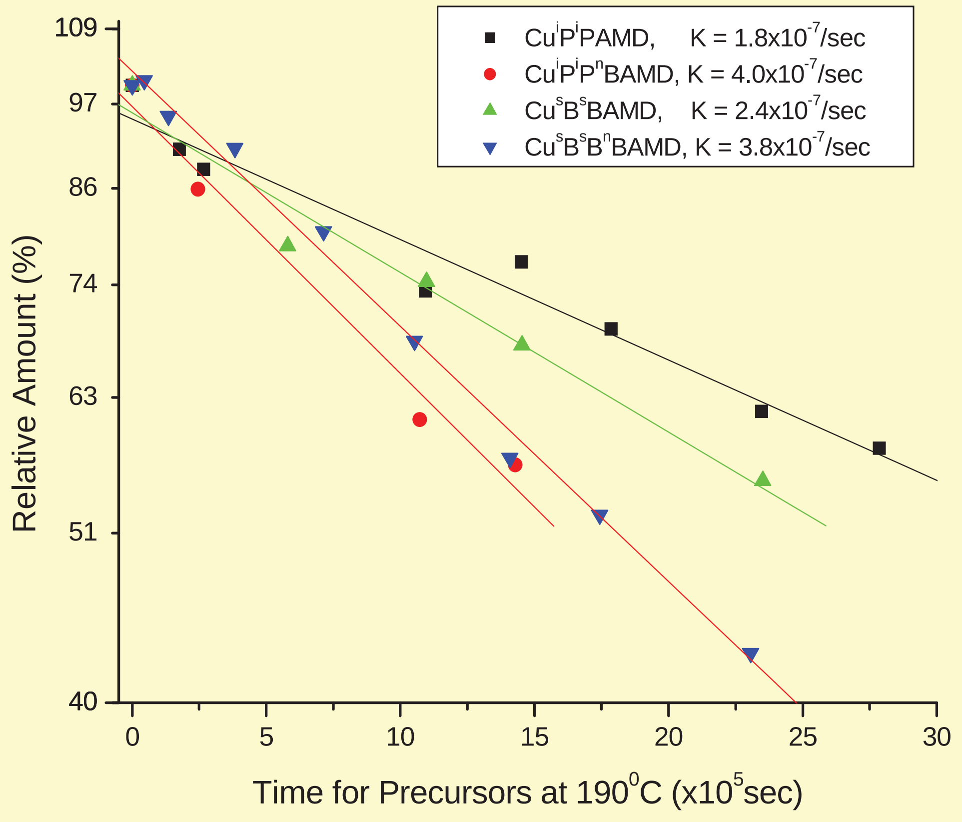
Thermal Stability of Copper Precursors by NMR



⇒ **Half-lives ~1 month at 190 °C**

⇒ **Thermally stable at evaporation temperature of 95 °C**

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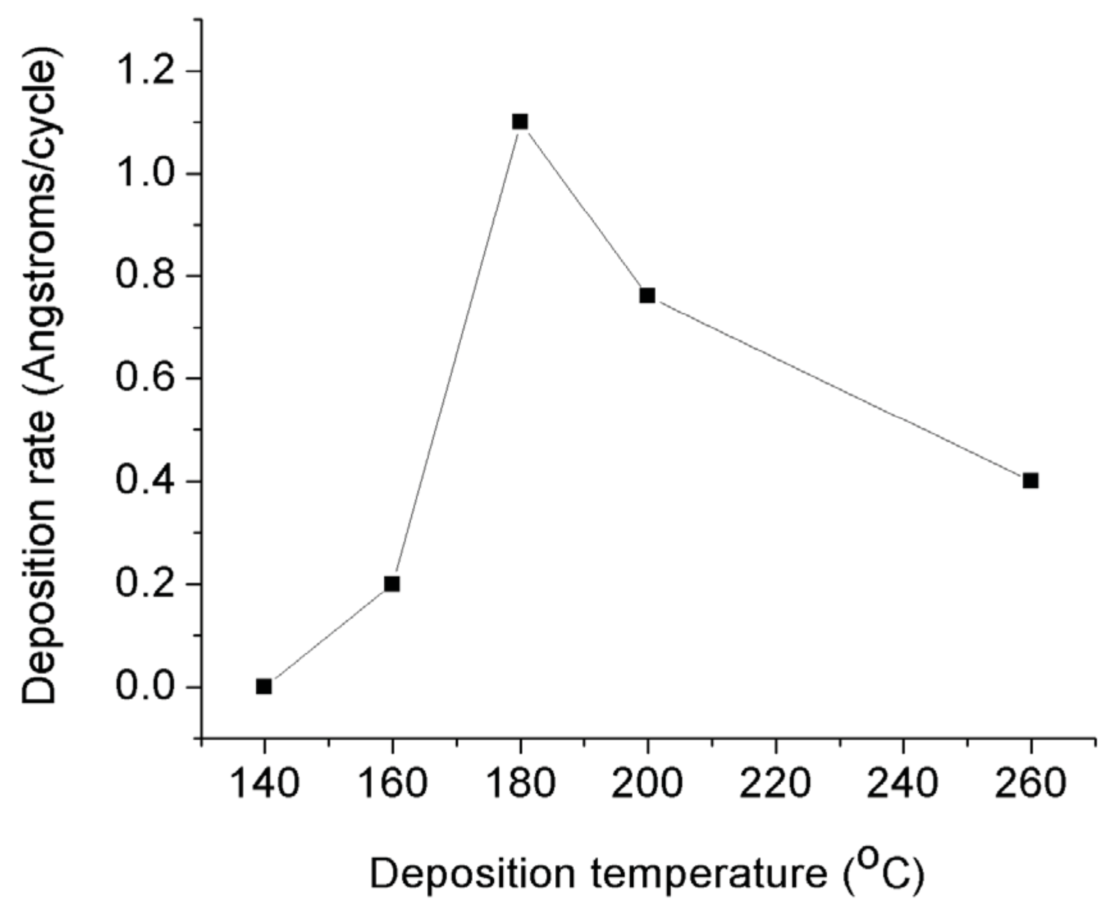
Temperature Dependence of Copper Growth Rate



- At each temperature, self-limited growth demonstrated
- No deposition on “warm” reactor walls (T < 140 °C)

Adhesion of Co and Cu Films

	Scotch Tape Test	4-Point Bend Test
Cu/SiO$_2$	failed	2 J/m^2 [a]
Co/SiO$_2$	failed	
WN/SiO$_2$	passed	> 31 J/m^2
TaN/SiO$_2$	passed	6 J/m^2 [a]
Cu/WN/SiO$_2$	poor nucleation	
Co/WN/SiO$_2$	passed	> 31 J/m^2
Cu/Co/WN/SiO$_2$	passed	> 31 J/m^2

Excellent adhesion even when films exposed to air between depositions

Advantage of Co/WN over Ta/TaN, which fails to adhere after air exposure

[a] Hughey et al., Engineering Fracture Mechanics **71**, 245 (2004)

Summary of ALD for Interconnects

Pores in porous low-k sealed with 1 ALD cycle of SiO_2

WN diffusion barrier with < 15 ALD cycles

ALD Co films are an excellent adhesion layer for Cu films

ALD Cu seed layers at 1 Angstrom per cycle

All depositions at T < 350 °C

Outstanding adhesion between all layers ($\geq$ 31 J/m^2)

ALD Cu/Co/WN/SiO_2/porous low-k is very promising as a future copper seed/diffusion barrier/insulator structure.

Acknowledgements

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WN: Jill Becker, Seigi Suh

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Porous low-k supplied by JSR

TGA/DSC data from Air Products

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