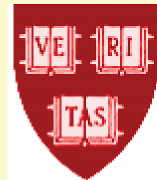

Atomic Layer Deposition of Copper And Copper Nitride Thin Films From Copper(I) Amidinate Precursors

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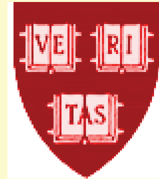
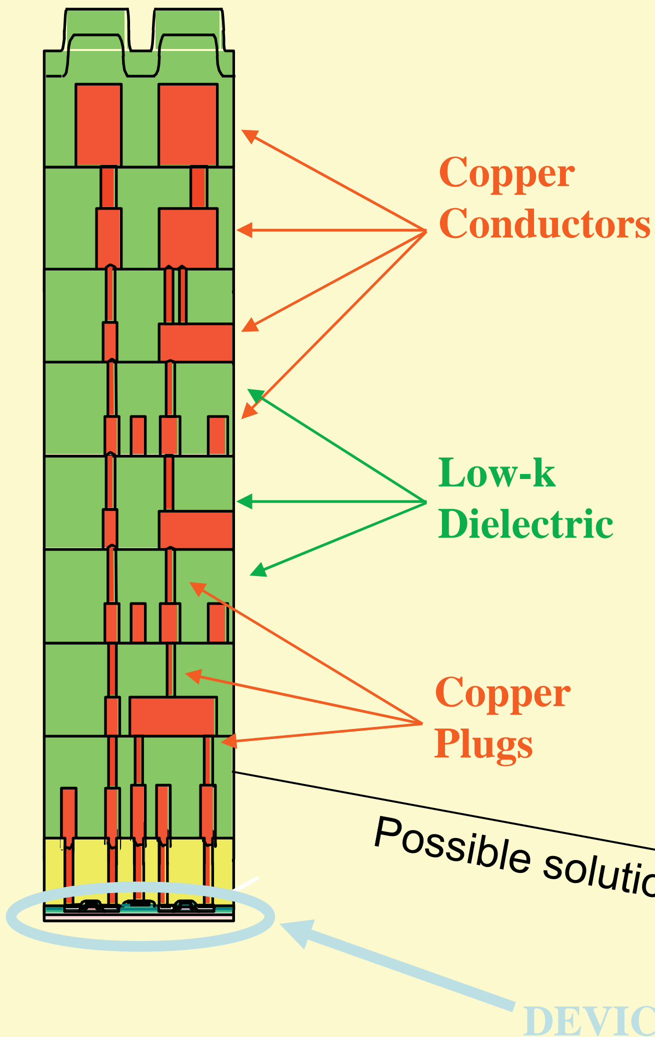


Why ALD Copper Layer?

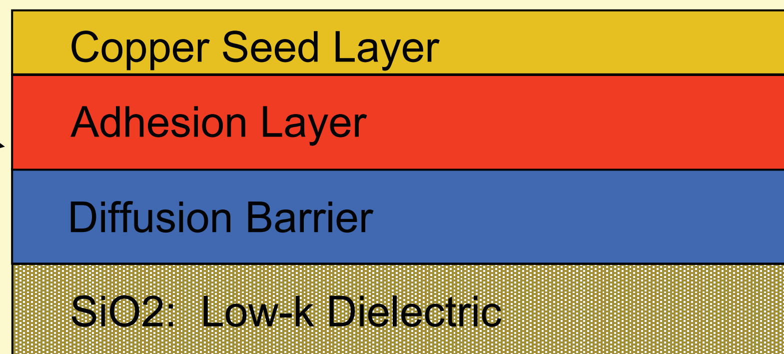


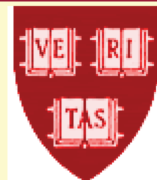
Copper is replacing Aluminum as the standard interconnect metal in microelectronics:

- Lower resistivity.
- Better electromigration.

Advantage of Atomic Layer Deposition

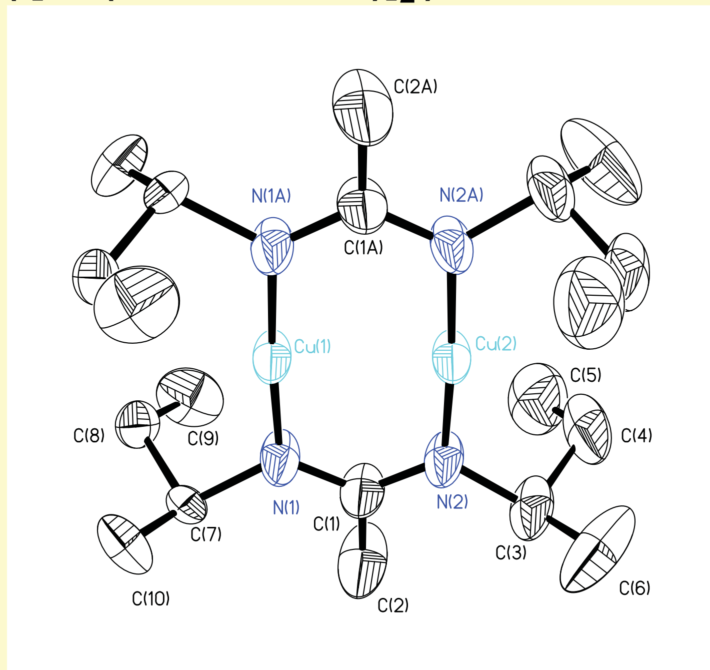
- Conformal coating
- Barrier/adhesion/seed layer together





ALD Copper(I) Amidinate Precursors

Copper(I) N,N'-disec-butylacetamidinate ($[Cu(sBu\text{-}Me\text{-}amd)]_2$)



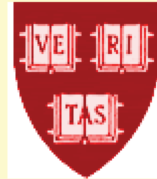
ALD Cu Precursors

Copper Precursor	Melting Point (°C)	Vapor Pressure (°C/Torr)	Half life-time (days, in C6D6, @190°C)
Cu_3Cl_3	430	--	--
$Cu(thd)_2$	198 (dec.)	--	--
$Cu(hfac)_2.xH_2O$	130-134	60/0.25	--
$[Cu(^iPr\text{-}Me\text{-}amd)]_2$	147	70/0.05	45
$[Cu(^sBu\text{-}Me\text{-}amd)]_2$	77	85/0.1	33
$[Cu(^nPr\text{-}Me\text{-}amd)]_2$	65	55/0.05	--

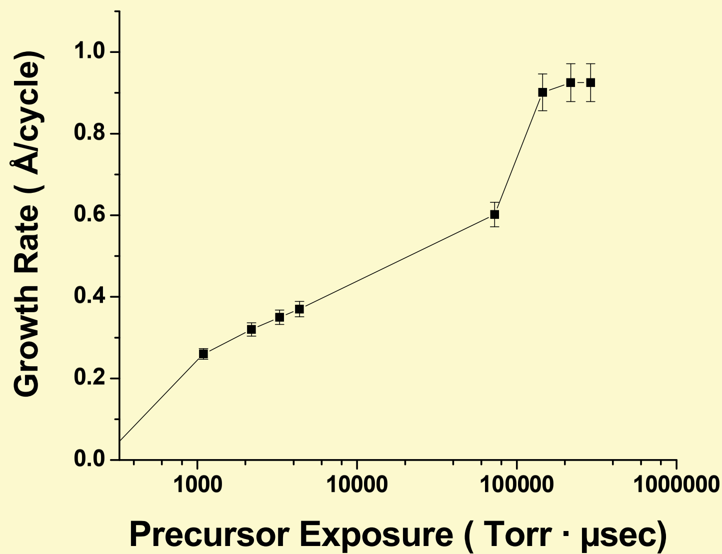
Advantages of Cu amidinates as precursors

1. High volatility and low melting points
2. Low deposition temperature (130-250 °C)
3. Thermally stable, NMR half life-time ~ 30 days @190 °C
4. Pure copper films (< 1% carbon or oxygen impurity)

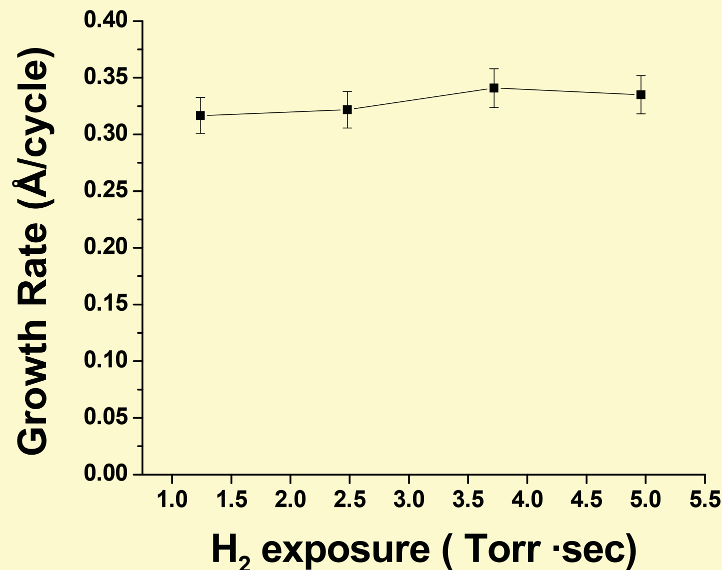
--Zhengwen Li; Sean Barry; Roy G. Gordon *Inorg. Chem.* **2005**, 44, 1728-1735



Saturation Growth of ALD Copper with H_2 as the Reducing Agent



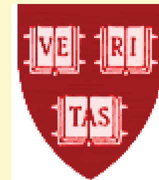
Flowthrough and Close Valve



Flowthrough

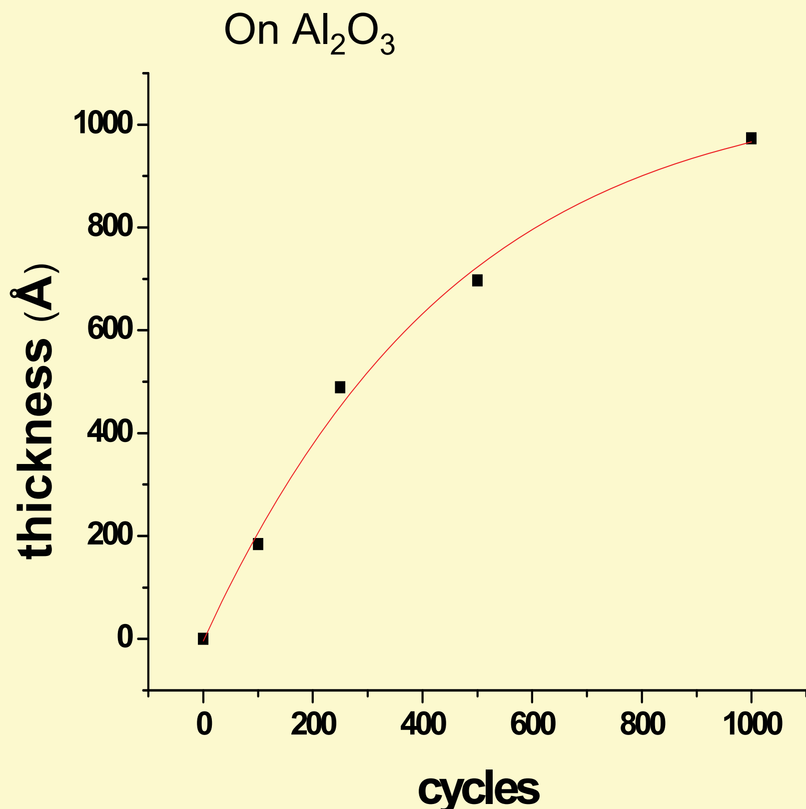
Results:

- Growth rate depends on the precursor exposure time:
  Close valve (2 sec) vs. Flowthrough (~ 30 ms)
- Surface nucleation to ALD metal.
- Self-limited growth at high exposure.



ALD Cu Growth Rate on Different Substrates

On Al_2O_3

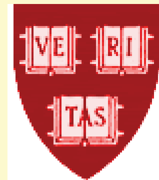


On different substrates

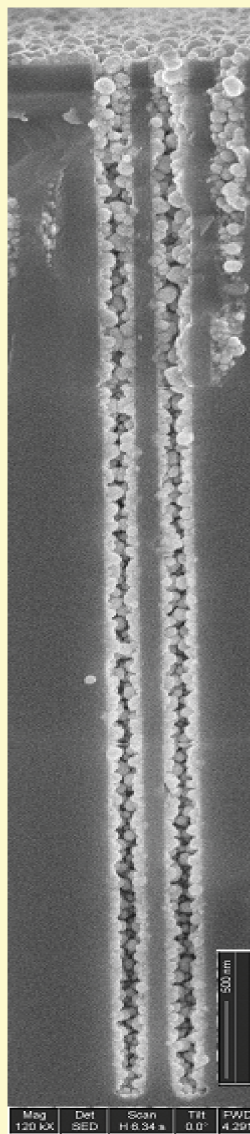
Substrate	Growth Rate (Å/cycle)	$[Cu(sBu\text{-}Me\text{-}amd)]_2$ Exposure (Torr · sec)
Al_2O_3/SiO_2	1.90 (100 cycles)	0.15
Si3N4	1.5 (60 cycles)	0.19
WN	0.54 (30 cycles)	0.28
Ru	~0.20 (300 cycles)	0.57
Co	0.40 (30 cycles)	0.28
Cu	~0.5 (from Al_2O_3 curve)	0.15

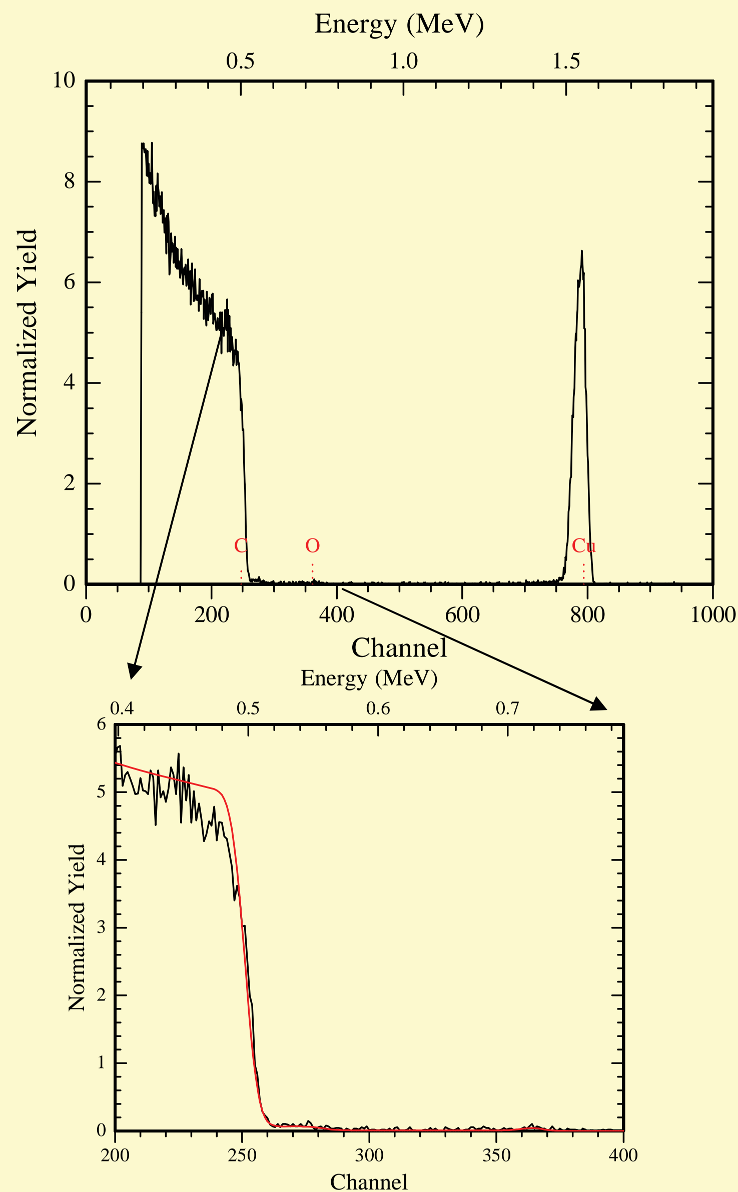
Conclusions:

- ALD Cu growth behavior is different on different substrates.
- The Growth rate is generally larger on oxide surfaces than on metallic surface.
- The initial nucleation stage plays an important role in making continuous Cu film.



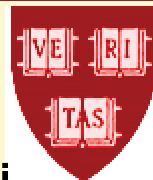
Film quality: High Aspect Ratio coating and Low impurities



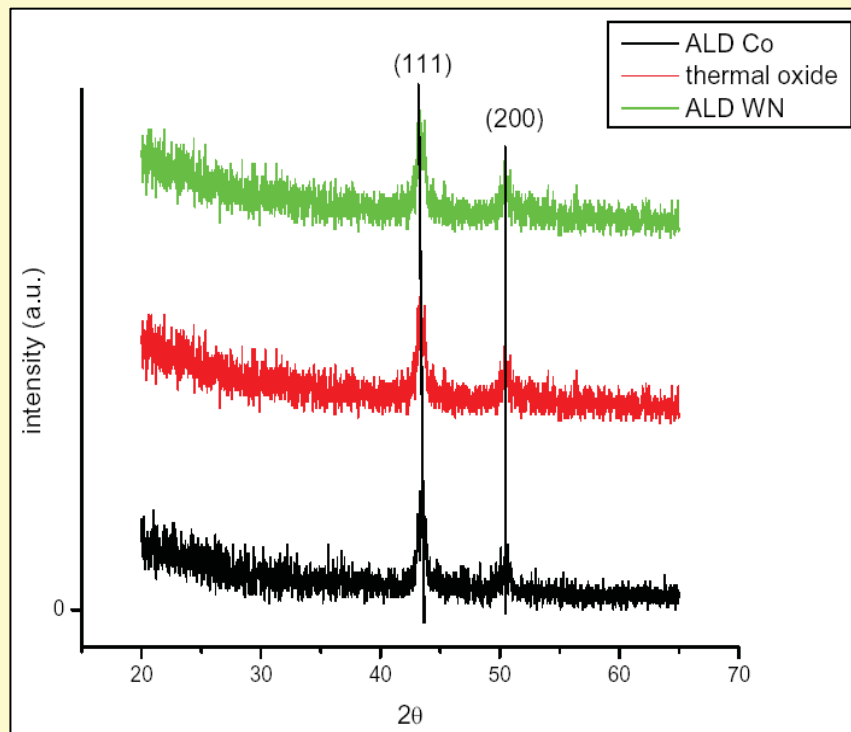


- AR = 40;
- Uniform and conformal coating;
- maximum aspect ratio can go to above 150;
- Carbon impurity below RBS detection limit (< 1%);

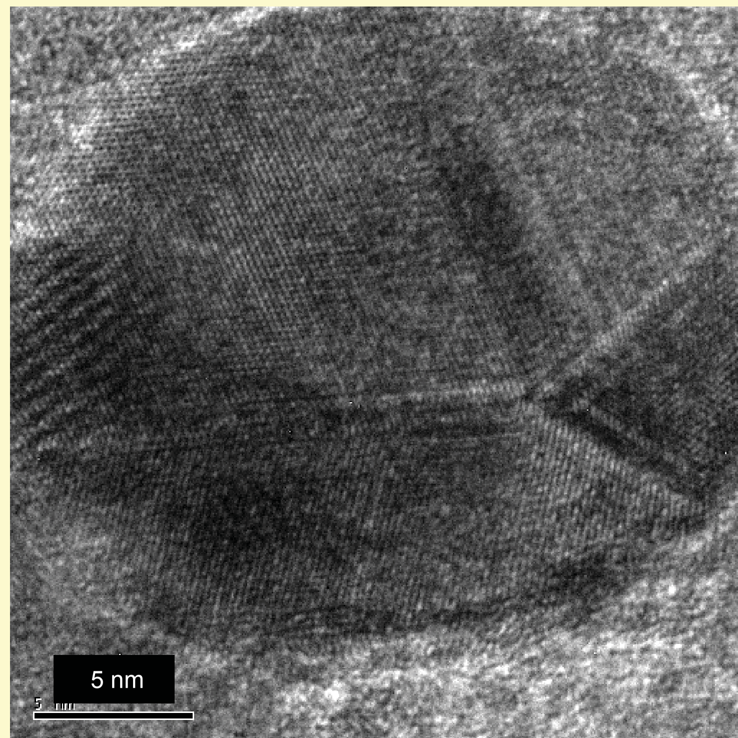
Crystal Structure Study of Cu by XRD and TEM



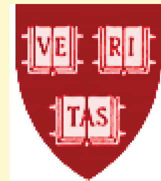
X-ray Diffraction: polycrystalline Cu



High Resolution TEM: Cu nuclei



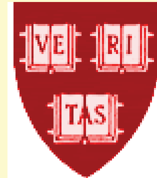
---- Zhengwen Li; Roy G. Gordon; et al. *Electrochem. Solid-state Lett.* 8(7) G182 (**2005**)

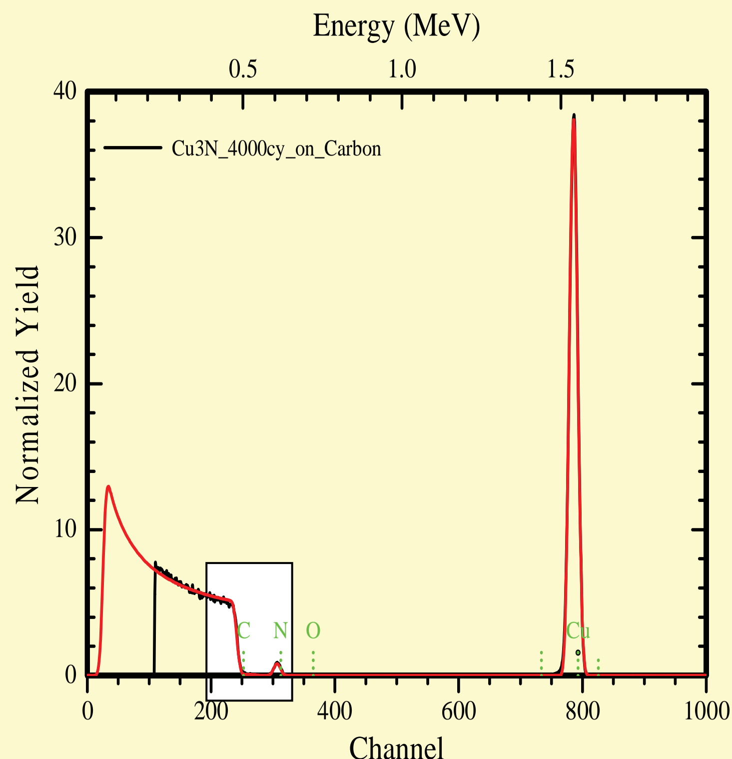


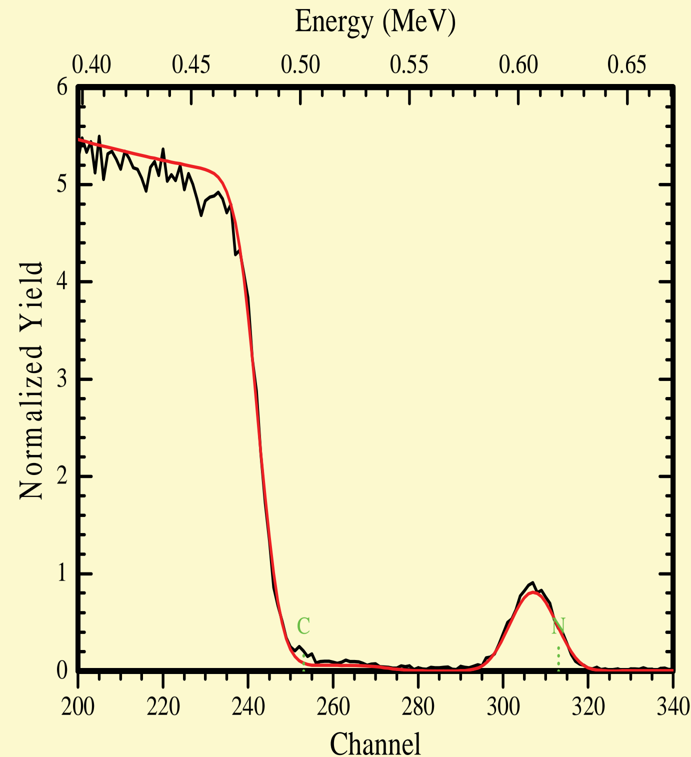
Above results used H_2 as the reducing agent.

What will happen if NH_3 is the reducing agent?

RBS of ALD Cu_3N Using NH_3 as the Reducing Agent



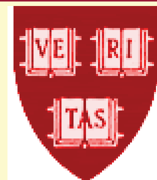




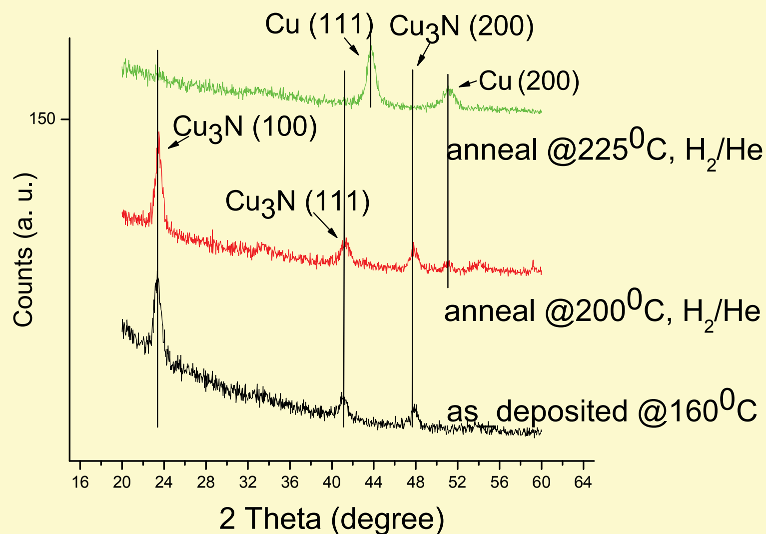
RBS Spectrum of the Cu_3N film on Carbon substrate

- The simulated curve ratio: Cu : N = 3:1.
- No obvious Oxygen peak, below RBS detection limit, < 1%.
- Carbon contamination < 1 %.

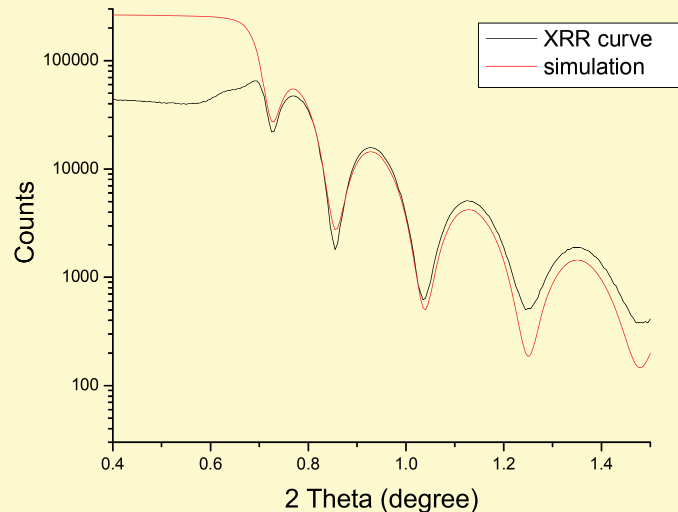
X-ray analysis of Copper nitride structure



XRD structure study of annealing temperature effect



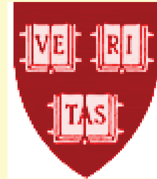
X-ray Reflection Spectrum

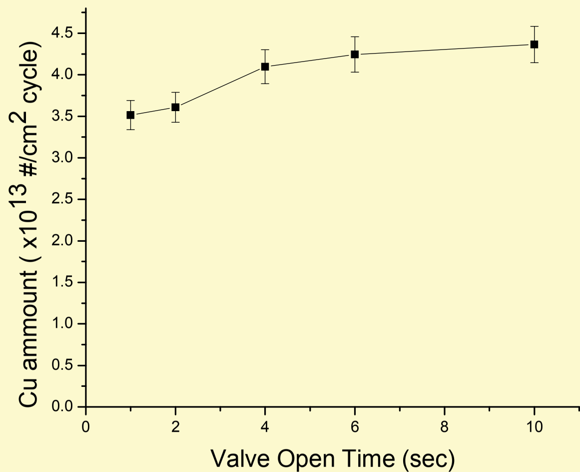


Conclusion:

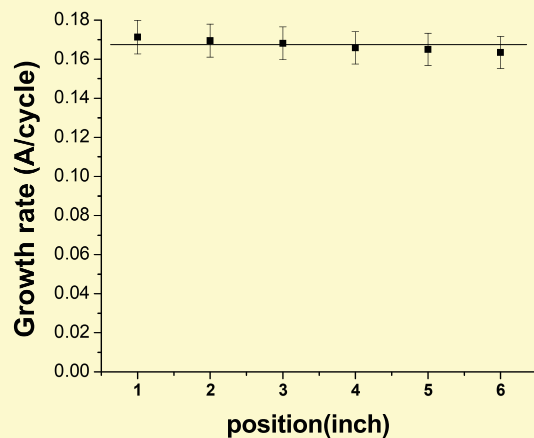
- As-deposited film is stoichiometric Cu_3N, anti ReO_3 structure, predominant at (100).
- Anneal at 200^{0}C, the film begins to decompose to copper.
- At 225^{0}C, the film totally converted to copper. (for bulk material, decomposition ~300^{0}C).
- The density of the as-deposited films is 5.30 g/cm^3 (bulk 5.84g/cm^3.)

ALD Growth Behavior Characterization of Cu_3N Film

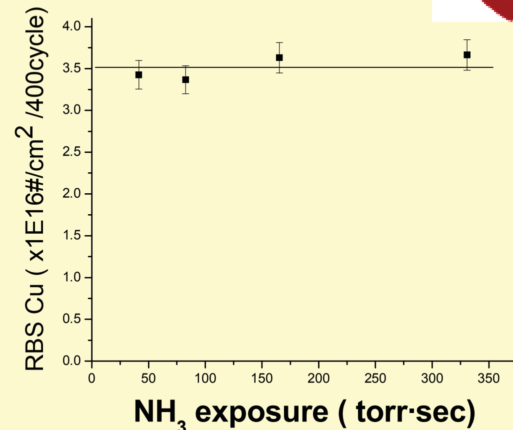




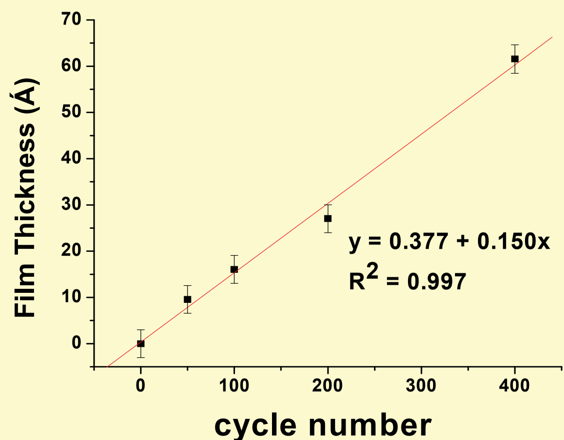
Varying valve open time, 200⁰C



Different positions at 160⁰C for 4000 cycles



Varying NH_3 pressure @ 200⁰C

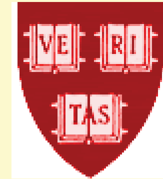


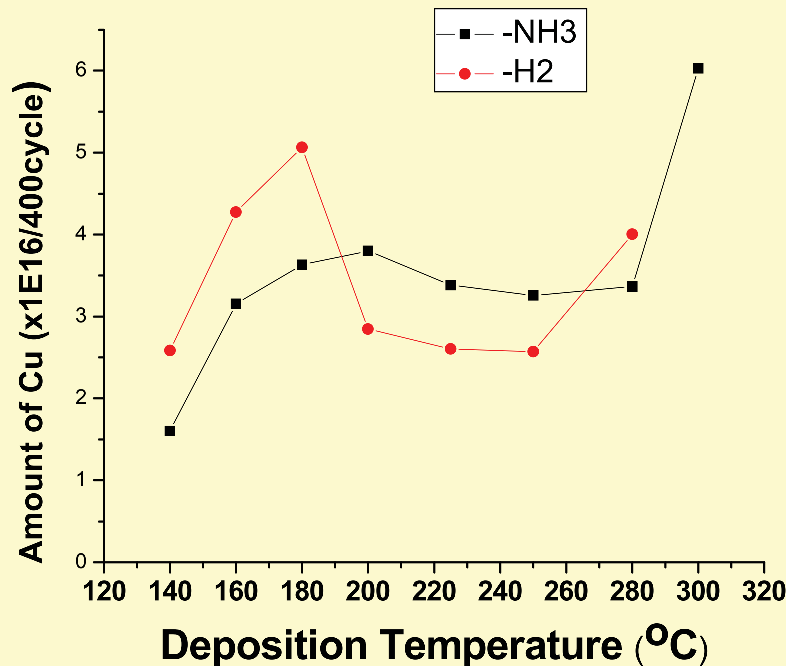
precursor 3.2 nmole/cm², 160⁰C

Results: growth saturated at

- Precursor bubbler valve open time T_{valve} = ~4s.
- Uniform growth at different locations.
- Ammonia amount is in large excess.
- Linear growth on all the tested substrates, Ru, SiO_2, Co, NiSi, *et. al.* growth rate 0.15A/cycle at 160⁰C.

Temperature Dependent Growth of Copper and Copper Nitride





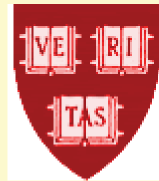
Similar phenomena happened on

- both Cu and Cu_3N deposition
- on all substrates tested: SiO_2, Si_3N_4, Ru, Co, Ti, NiSi, Al_2O_3.

low temperature (~130^{0}C-190^{0}C), mainly controlled by reactivity of the precursor and reducing agent

medium temperature (~200^{0}C-280^{0}C), desorption plays a role

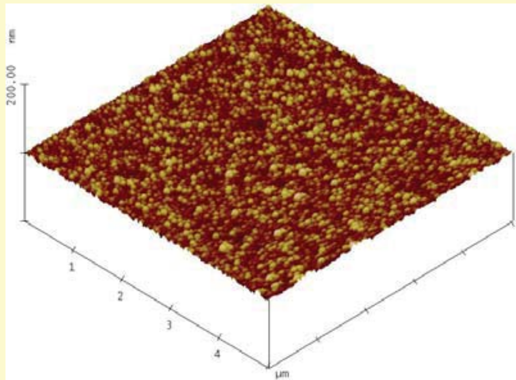
high temperature (>300^{0}C), precursor starts to decompose



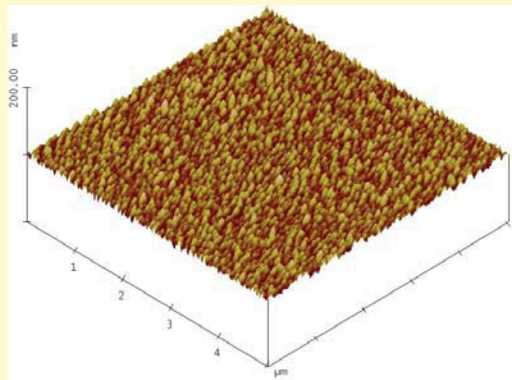
AFM Study of Film Surface Morphology

With H2, Copper

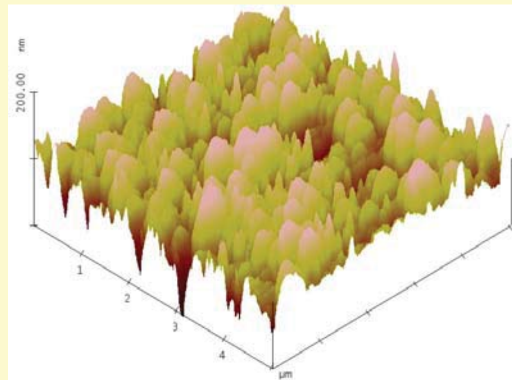
(a). Tdep=160^0C, thickness 5.04 nm
RMS 1.517nm



(b). Tdep=200^0C,thickness 3.36nm
RMS 3.047nm

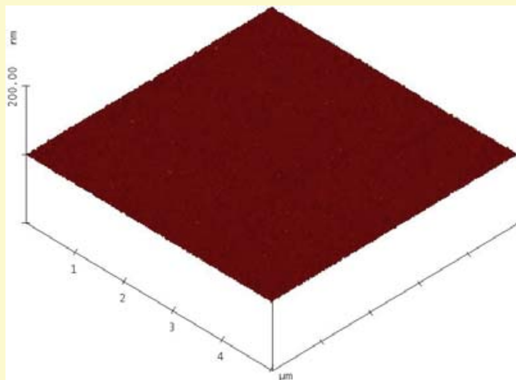


(c). Tdep=280^0C, thickness 4.72nm
RMS 21.109nm

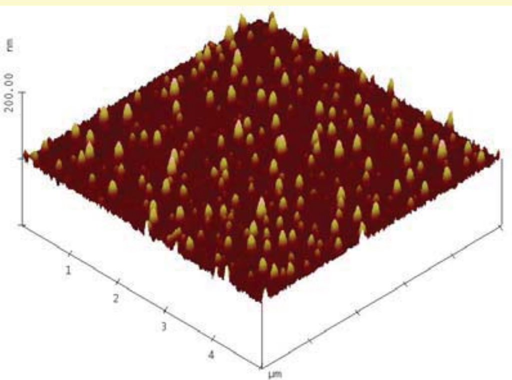


With NH3, Copper Nitride

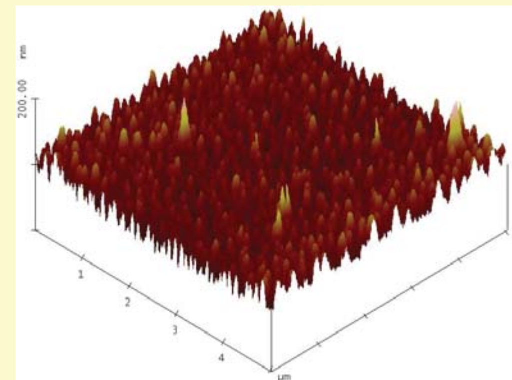
(d). Tdep=160^0C, thickness 6.74 nm
RMS 0.706nm

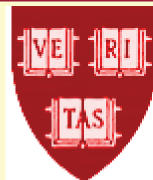


(e). Tdep=180^0C,thickness 7.76nm
RMS 4.474nm



(f). Tdep=280^0C, thickness 4 nm – 7.2nm, RMS 11.647nm

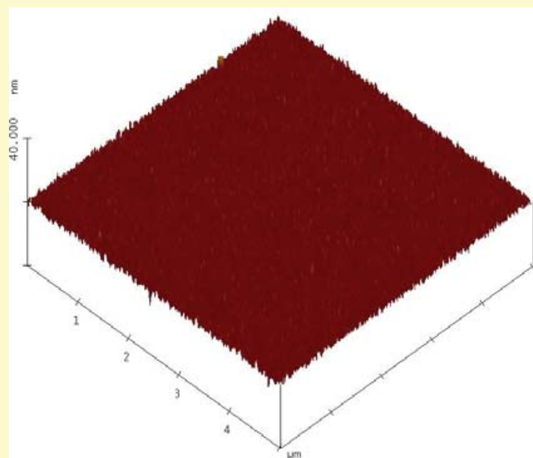




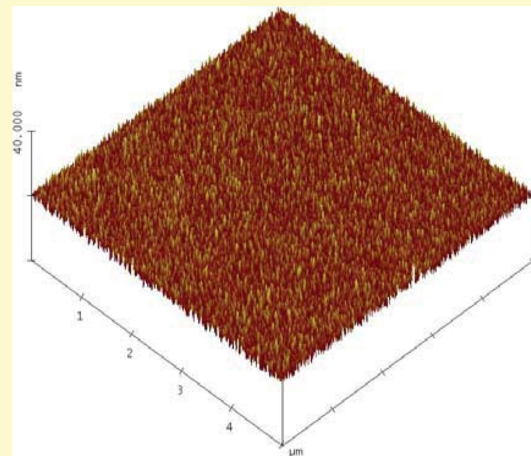
AFM Surface Study of Cu_3N Conversion to Cu

As_deposited Cu3N @160^{0}C,
Thickness 6.74nm, RMS 0.70nm

@225^{0}C, Cu_3N decomposes to Cu.
Thickness ~4nm, RMS 0.91nm



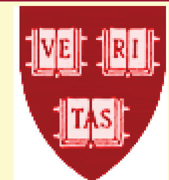
RTA 5 mins
in H_2/He

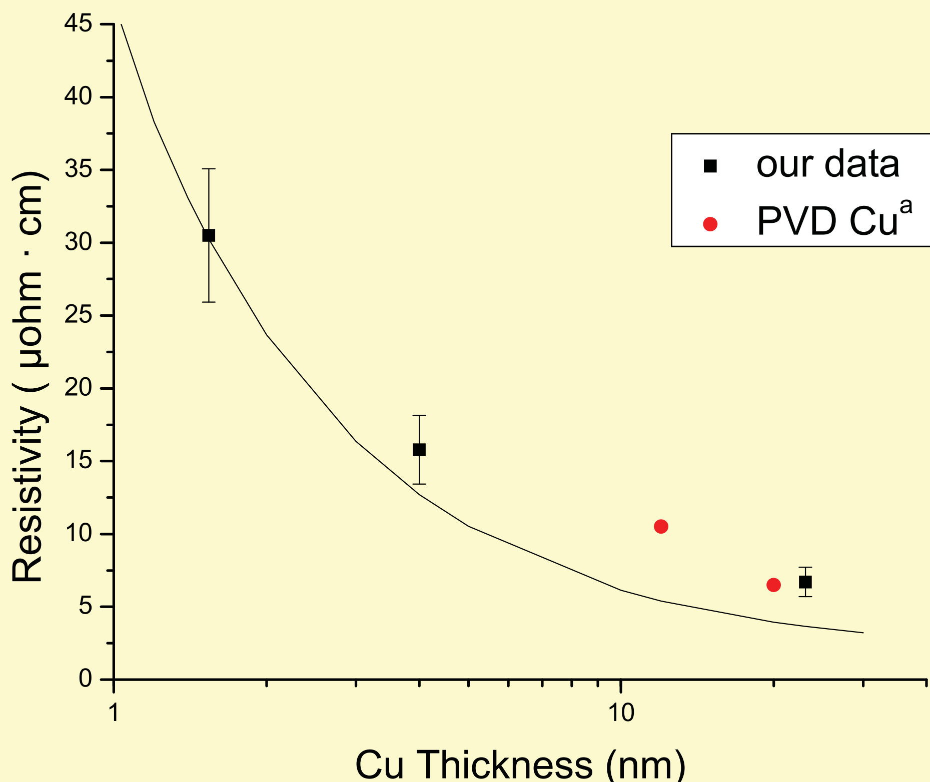


ALD as-deposited Cu made @160^{0}C, thickness 5.0 nm, RMS 1.5 nm.

- **Smooth Cu seed layer made from the conversion of Cu_3N is possible**

Electrical properties of Cu Thin Films from Cu_3N Conversion





Grain Boundary Scattering Model simulation equation [(a)]

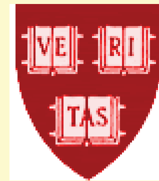
$$\rho / \rho_0 = 1+1.5\{R/(1-R)\} \lambda / g$$

Where g is the average size of the grains, = film thickness

R the scattering coefficient =0.3

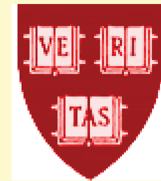
Conversion of Cu_3N to Cu film is as good as high vacuum sputtered Cu film

-- a. Rossnagel, S.; Kuan, T.; *J. Vac. Sci. Tech. B* **22**(1) 240 (2004)



Summary

- ALD Copper/copper nitride film was made from Cu(I) amidinates with H_2/NH_3 as reducing agent. ALD behavior is carefully characterized.
- The growth of ALD Cu is surface-dependent, while copper nitride growth is more or less surface-independent.
- Both films are pure. Carbon and oxygen contamination < 1 atom.%.
- ALD Copper nitride is smoother than ALD copper with similar thickness. This may be used to make smooth copper film from Copper nitride conversion.
- Copper film is conductive, comparable with PVD Cu.



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The Whole Gordon Group

$$: NSF