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Chemical Vapor Deposition of Cobalt Nitride and Its Application as an Adhesion-enhancing Layer for Advanced Copper Interconnects

Jing Yang[1], Harish B. Bhandari[1], Roy Gordon[1 2], Qing Min Wang[3], Jean-Sebastien Lehn[3], Deo Shenai[3].

Abstract

Copper damascene technology has been widely used for interconnecting microelectronic circuits. Barrier layers such as tantalum nitride (TaN) or tungsten nitride (WN) can prevent the diffusion of copper into surrounding insulators and also protect copper from oxidation. As interconnects are scaled to smaller sizes, sputtering has more difficulty placing thin, conformal and continuous seed layers of copper on the barrier layers prior to electroplating. Chemical vapor deposition (CVD) can make thin, conformal and continuous seed layers of copper, but adhesion between CVD copper and nitride barriers has been found to be too weak. The adhesion at the interface between two metals is expected to be strong if their lattices match both in structure and size. Because of the near-perfect match between the lattice structures of copper and face-centered cubic (fcc) cobalt nitride (Co4N), copper adheres strongly to fcc Co4N. At the same time, cobalt nitride adheres strongly to nitride barriers. Thus fcc-Co4N can serve as an adhesion-enhancing layer between TaN or WN and copper seed layers. This fcc phase of Co4N was prepared by chemical vapor deposition (CVD) using a cobalt amidinate precursor and a reactant mixture of ammonia (NH3) and hydrogen (H2) at substrate temperatures from 100 to 200 oC. The N/Co atomic ratio and the phase of cobalt nitride films can be modified by adjusting the ratio of the co-reactant gases NH3 and H2. The cobalt nitride films prepared by CVD are smooth, highly conformal inside holes with aspect ratios over 30:1, and stable against intermixing with copper up to at least 400 oC. CVD fcc Co4N shows very strong adhesion to CVD copper deposited on top of it, as well as to substrate nitride barriers under it. These CVD copper films can be used a seed layers for filling the copper lines by electroplating. Alternatively, copper lines can be created by bottom-up filling of narrow trenches and vias using iodine-catalyzed CVD of copper. Thus CVD Co4N interlayers between copper and surrounding diffusion barriers can stabilize copper wires against failure by electromigration.

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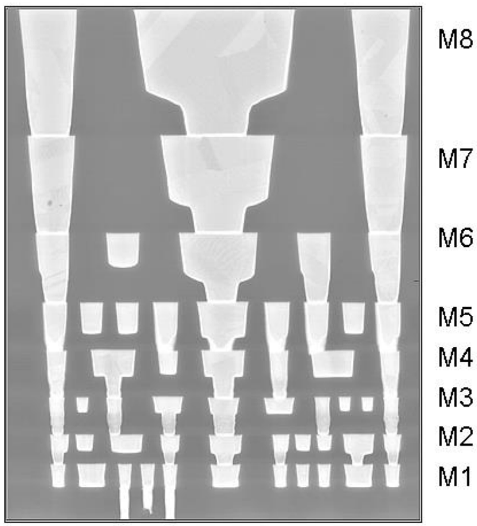
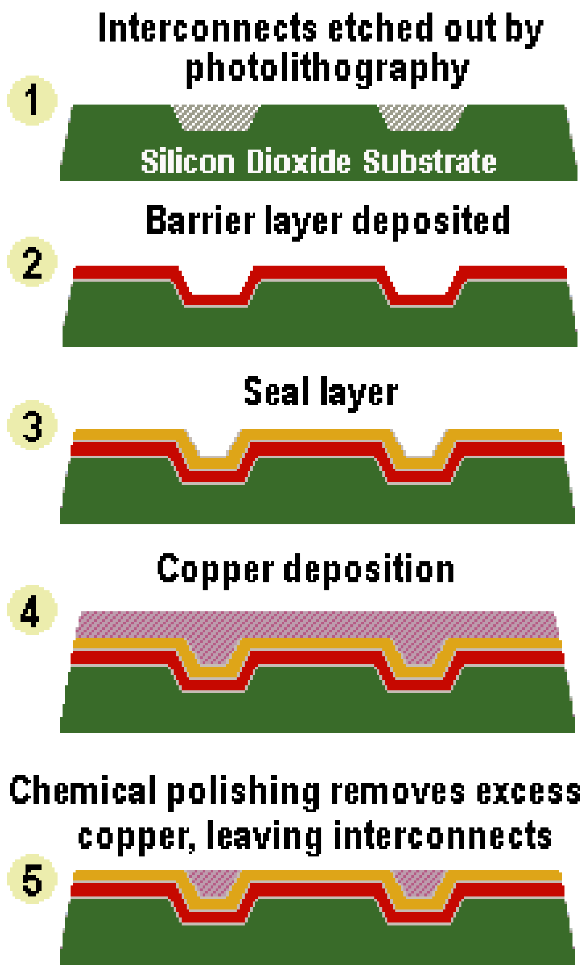
APRIL 11, 2012

Diffusion Barriers and Adhesion layer for Integrated Copper Metallization





- Copper Metallization replaced aluminum alloy metallization since 1997
  - low resistivity
  - better electromigration reliability
- **Challenges**
- Copper Diffuse Through and Degrade the Dielectric
- Copper adhere poorly to dielectrics

Image Credit: Internet

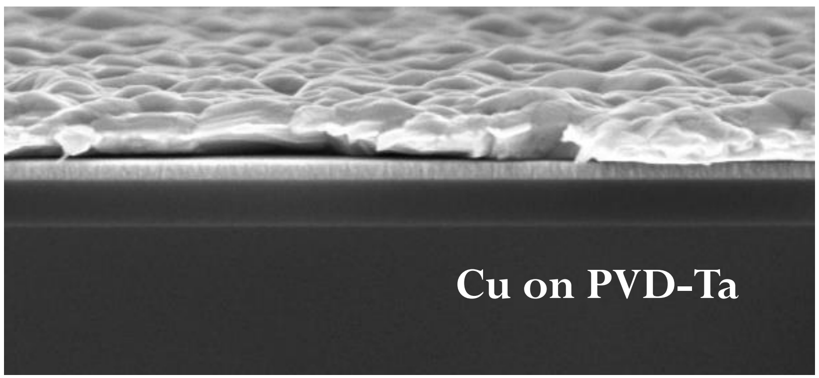
Selection of adhesion layer for CVD Cu seed layer

Tantalum (Ta)

- Poor adhesion with CVD Cu seed layer
- Poor step coverage of PVD-Ta/TaN layer

Ruthenium (Ru)

- Very expensive
- Limited in supply



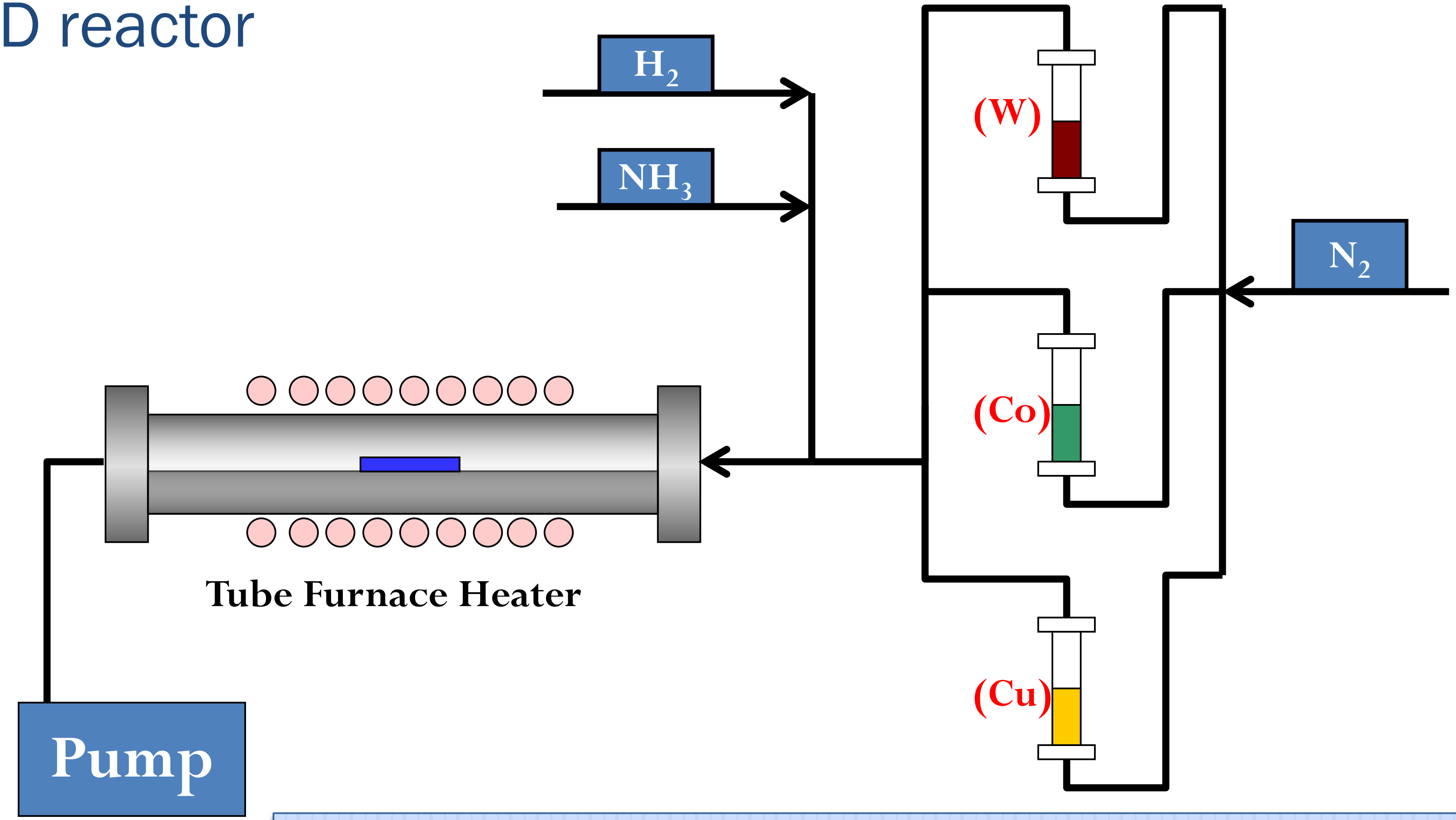
CVD-Cobalt Nitride (Co_4N)

- Inexpensive
- Available in abundance
- Good step coverage
- Resistivity ~ 100 μΩ-cm
- Good adhesion and stable with Cu

Image Credit: Yeung (Billy) Au

Chemical Vapor Deposition of Co_xN, WN, Cu

-CVD reactor



Novel Amidinate Precursors for Future Copper Interconnects

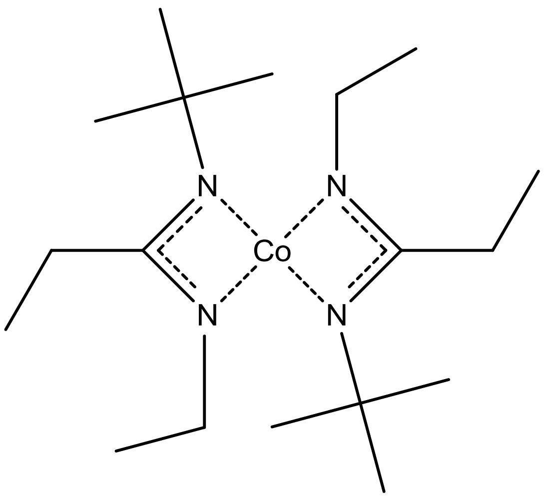
(W) Bis(*tert*-butylimido) bis(dimethylamido)tungsten(VI)

(Co) Bis(n-*tert*-butyl-N'-ethyl-propionamidinato)cobalt(II)

(Cu) (N,N'-di-*sec*-butylacetamidinate)copper(I)

Volatile **liquid** cobalt amidinates Precursor

- **bis(*N*-*tert*-butyl-*N*'-ethyl-propionamidinato)cobalt(II)**



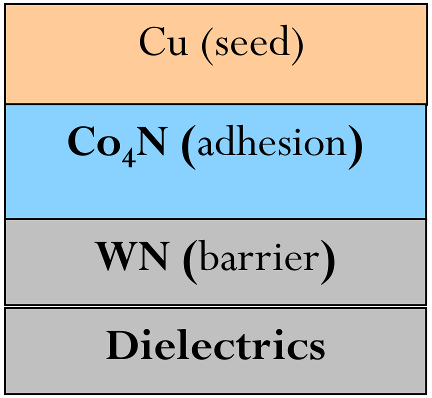
- **Liquid** at room temperature
- High thermal stability - years
- Clean evaporation < 1% residue

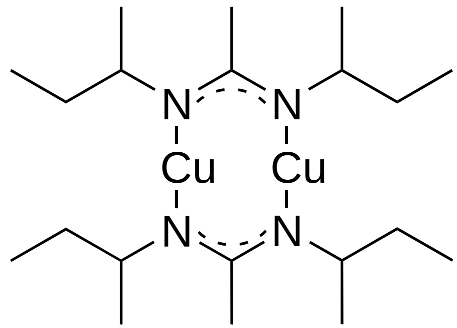
Advantages of using transitional metal amidinates as CVD precursors:

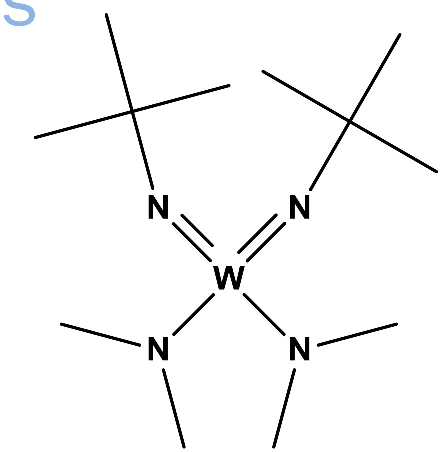
- Bidentate chelating effect enhances thermal stability
- Tunable reactivity and volatility
- Minimal carbon incorporation
- Capability to make metal nitrides
- No corrosive byproducts

Li, Zhengwen;Gordon, Roy G. et. al. ***Dalton Transactions*** (2008),19: 2592-2597z

Copper and tungsten Amidinate Precursors







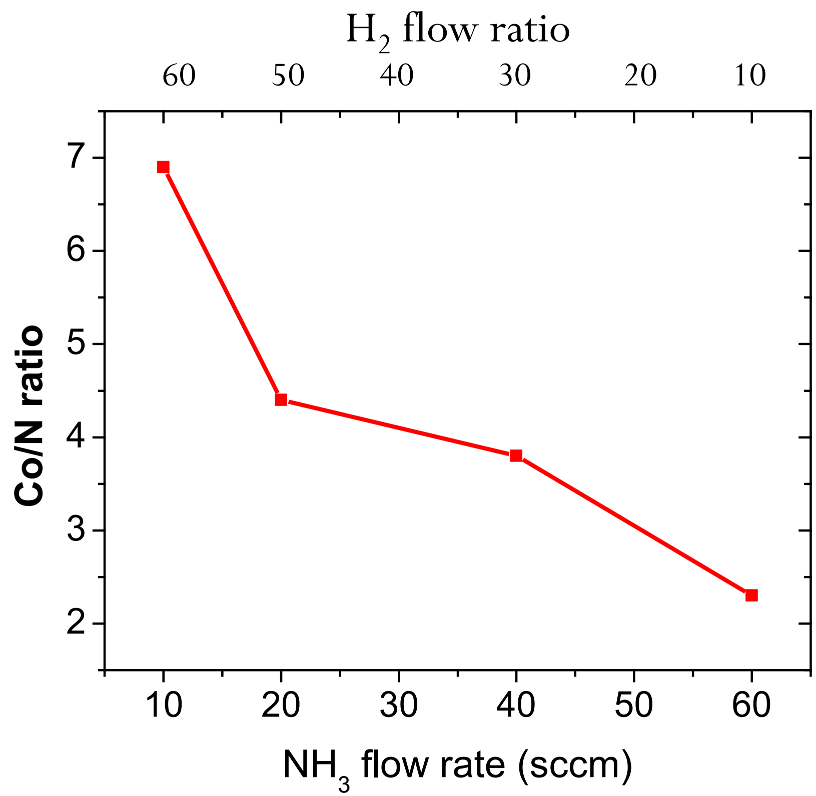
Name	copper (I) N,N'-di-sec-butylacetamidinate	bis(*tert*-butylimido)bis(dimethylamido)tungsten(VI)
Melting Point(°C)	75	
Bubbler Temp. (°C)	130	85
Deposition temperature (°C)	180	390
Pressure (torr)	1	1
N_2 carrier gas (sccm)	40	20
NH_3/H_2 (sccm)	0/40	20/0

Booyong S. Lim, Antti Rahtu, Jin-Seong Park, and Roy G. Gordon, *Inorg. Chem.*, **42 (24),** 7951-7958, (2003).
Becker, Jill S.; Suh, Seigi; Gordon, Roy G., Chemistry of Materials , (2003)15:2969-2976

Chemical Vapor Deposition of Cobalt Nitride

-Tunable Co_xN stoichiometry by adjusting co-reactants

- H_2:
  - Co metal deposited at a high temperature 250□C
  - Thermal Decomposition of cobalt precursor
  - Carbon Contamination
- NH_3/H_2:
  - CoxN deposition at lower temperature 180□C or lower
  - No reactivity with H_2 at 180□C

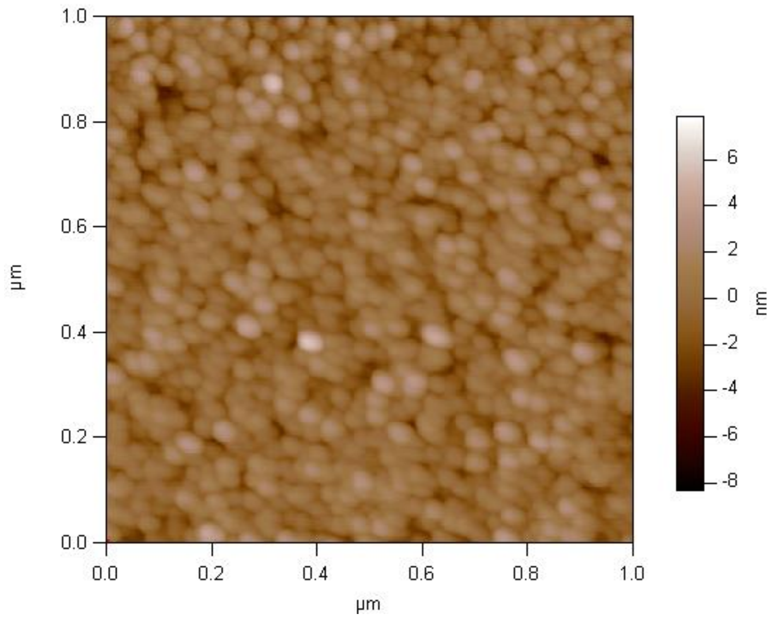


Tune the NH_3/H_2 Ratio → Controls N incorporation in Co-N films

Smooth Cobalt Nitride film

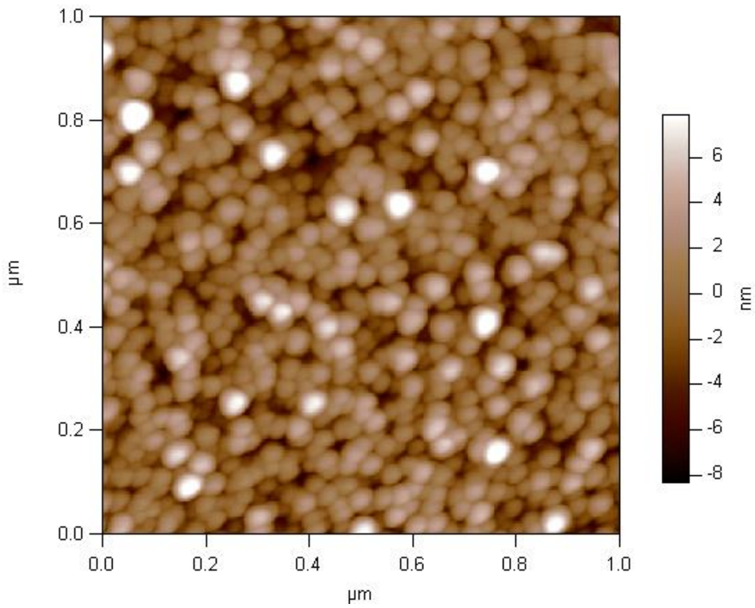
20 nm Co_4N film on SiO_2

RMS roughness = 1.3 nm (6.5%)

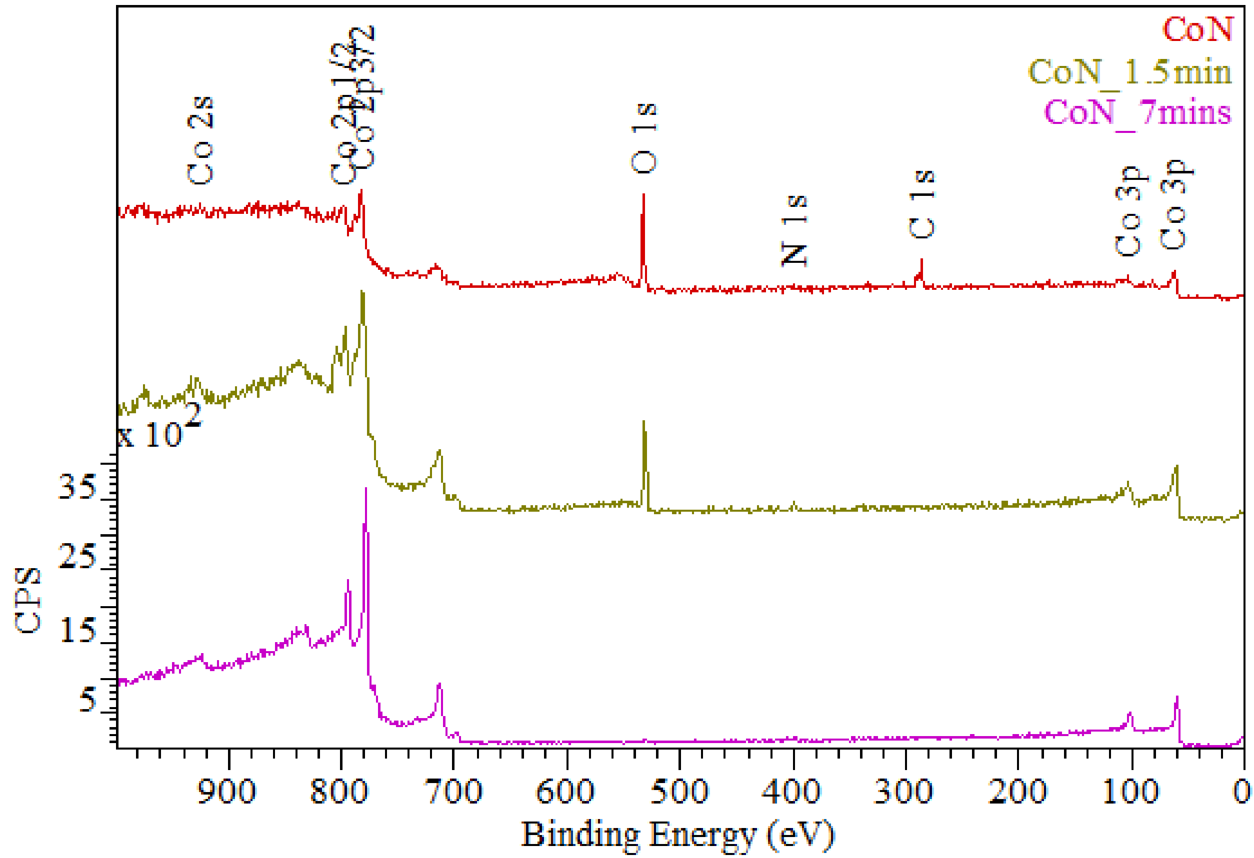


20 nm Co film on SiO_2

RMS roughness 2.7 nm. (13.5%)



Highly pure Cobalt Nitride film

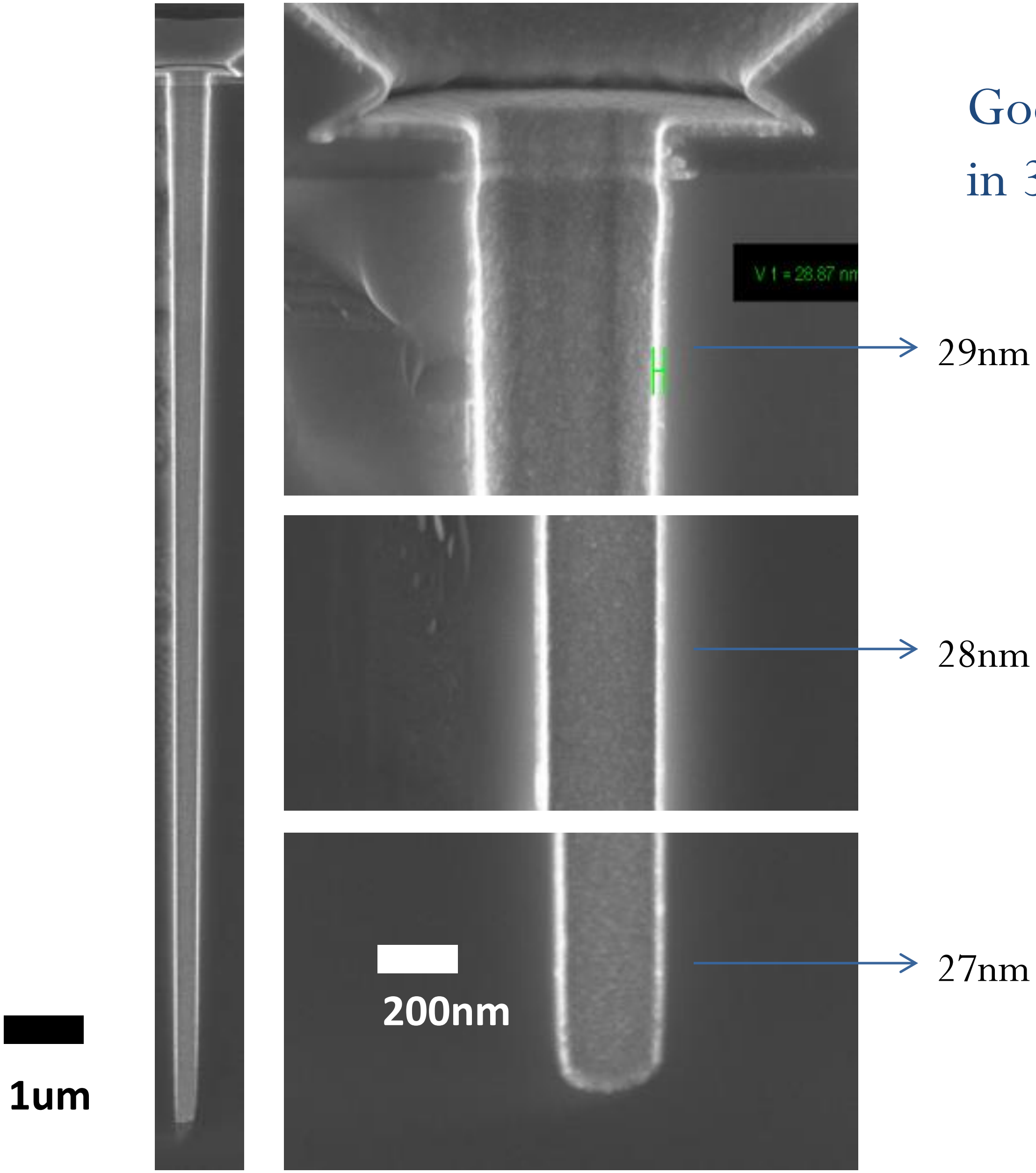


Surface Carbon Contamination:

- Disappearance of Carbon 1s peak after 1.5min sputtering

Surface Oxidation – Affect the adhesion energy

Good step coverage of CVD-Cobalt Nitride film



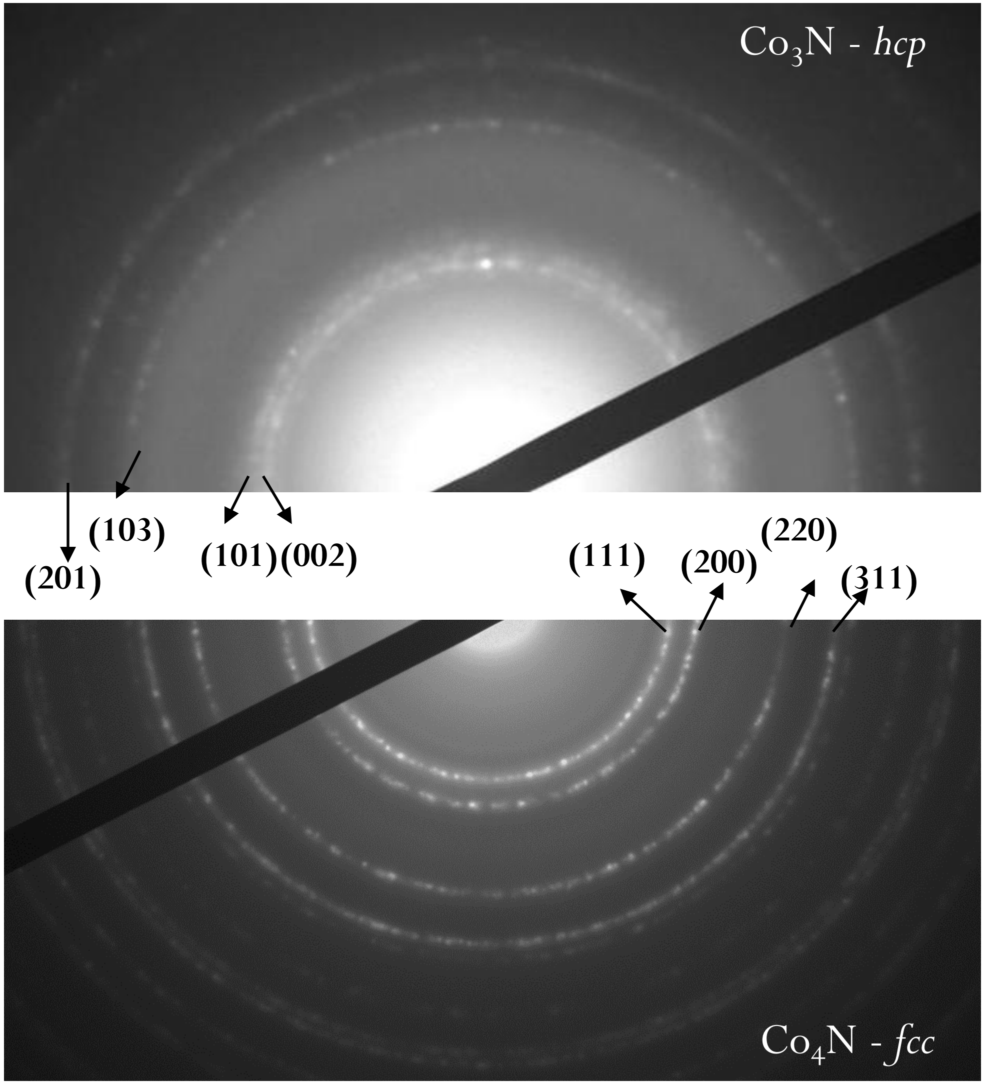
Good Conformality
in 30:1 aspect ratio feature.

Thickness profile along
a 14 μm deep hole (a/r=30)

hcp-Co_3N & fcc-Co_4N

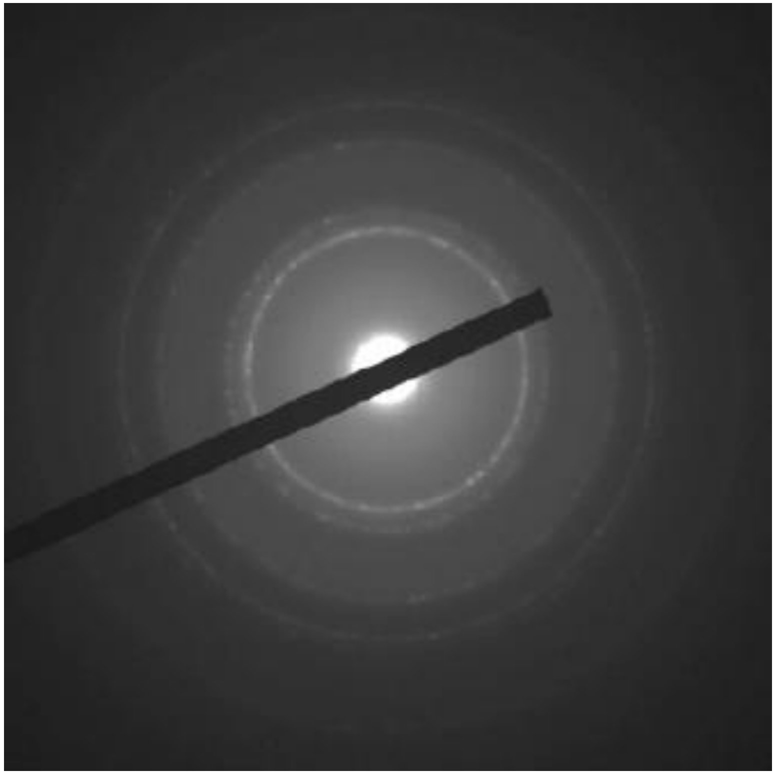
NH_3 (sccm)	H_2 (sccm)	Co_xN	Phase
60	0	2.3	hcp-Co_3N
40	20	3.8	fcc-Co_4N
20	**40**	**4.4**	**fcc-Co_4N**
10	50	6.9	fcc-Co_4N

- Co-rich film exhibit a fcc structure.

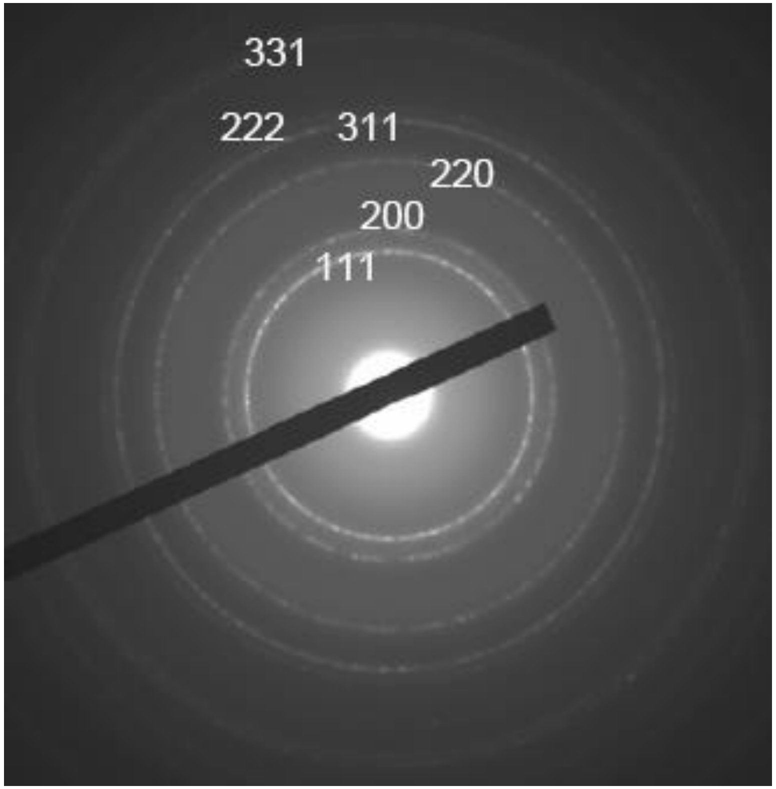


Electron diffraction patterns of polycrystalline Co_3N and Co_4N

Cobalt Nitride film structure (FCC) is stable at 400°C

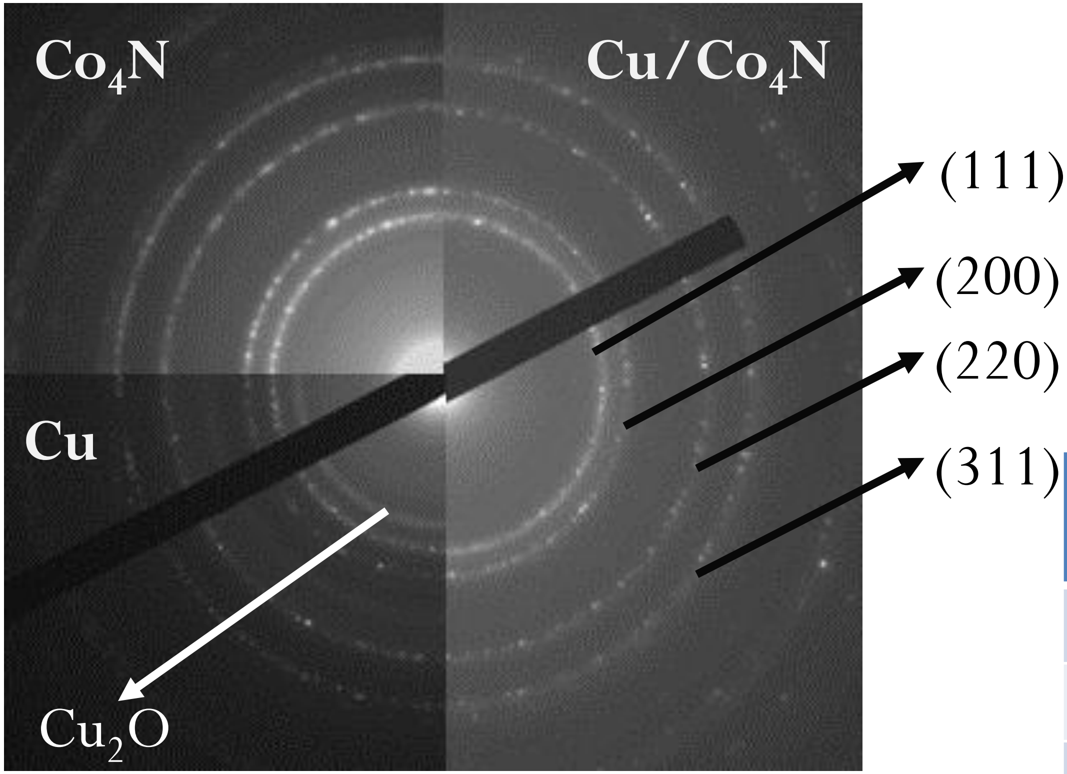


Co_4N as-deposited at 180°C



Annealed at 400°C in N_2

Small lattice mismatch between Co_4N and Cu (-2%)



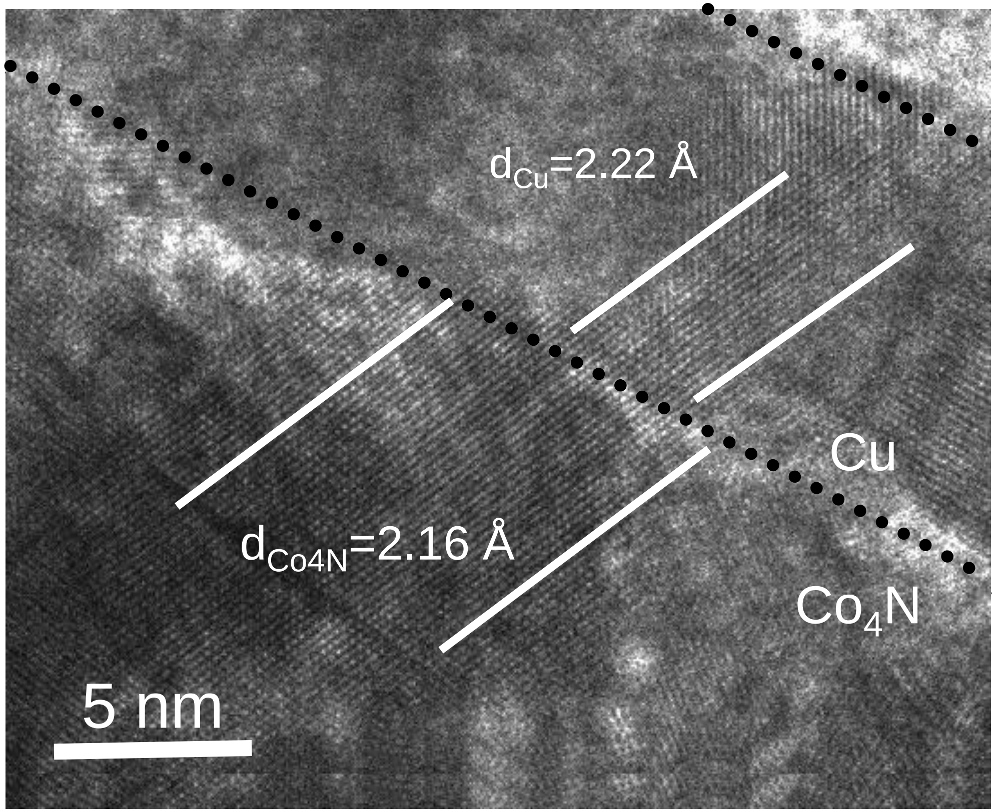
TEM Electron diffraction patterns of a single layer of Co_4N, a bilayer film of Cu/Co_4N, and an oxidized Cu film

- Co atoms placed in a fcc lattice and a nitrogen atom trapped interstitially in the center of a unit cell.

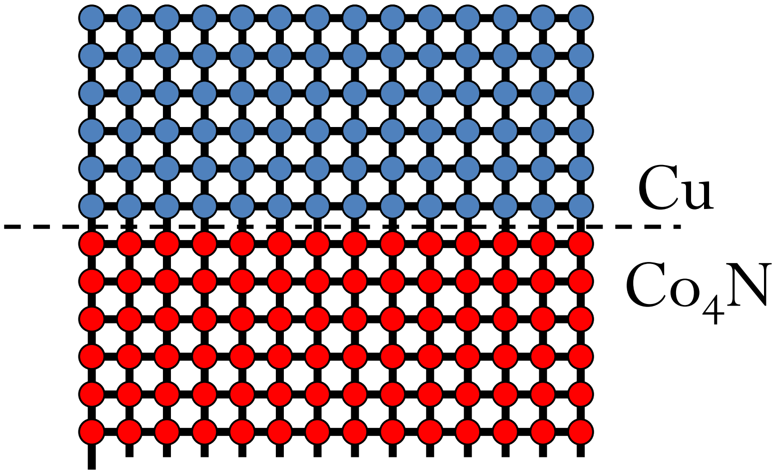
fcc structure	Lattice constant (Å)
Co	3.545
Co_4N	3.548
Cu	3.615

Co_4N	Cu	% diff
3.548Å	**3.615Å**	**~1.9**

Hetero-epitaxial relation between Co_4N and Cu

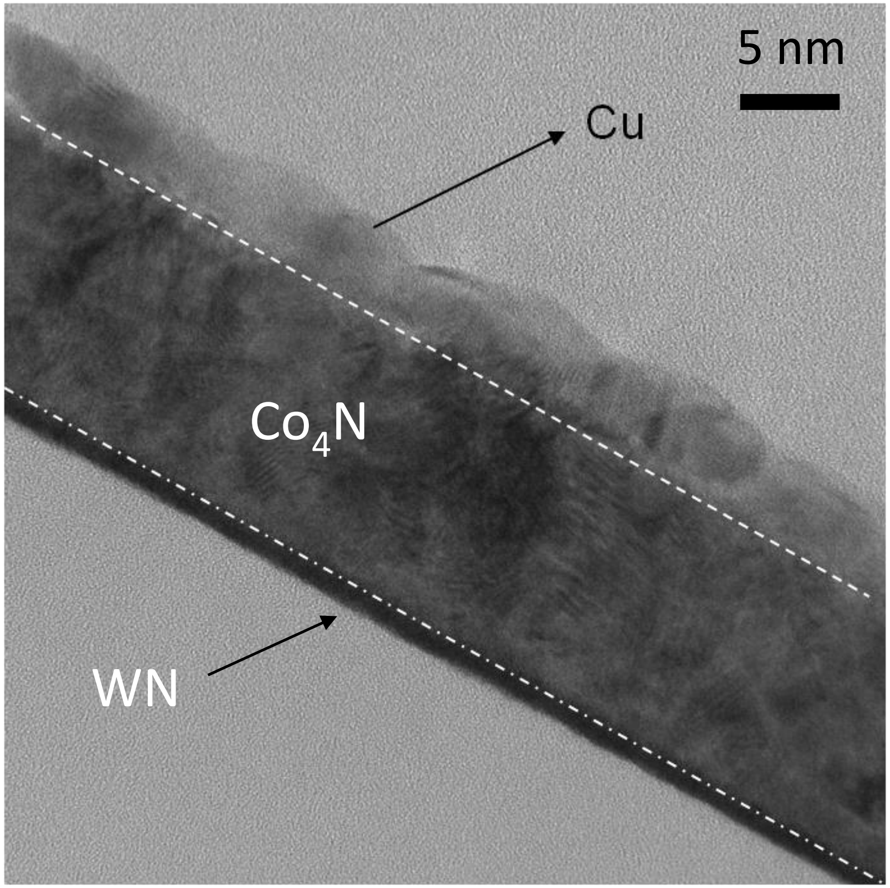


High-resolution cross-sectional TEM of the Co_4N/Cu interface showing the epitaxial relation between the materials.



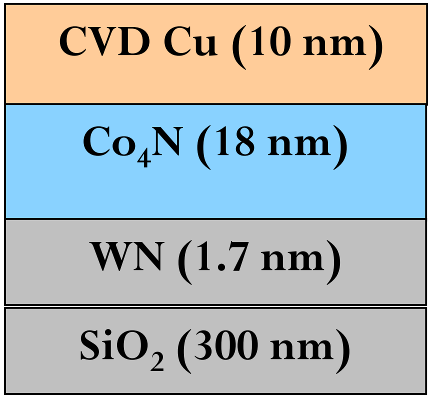
Experiment	*d*-spacing,ratio Cu(111)/Co_4N(111)
Cross-section TEM	2.22/2.16 = **1.03**

Strong Adhesion between Co_4N and Cu



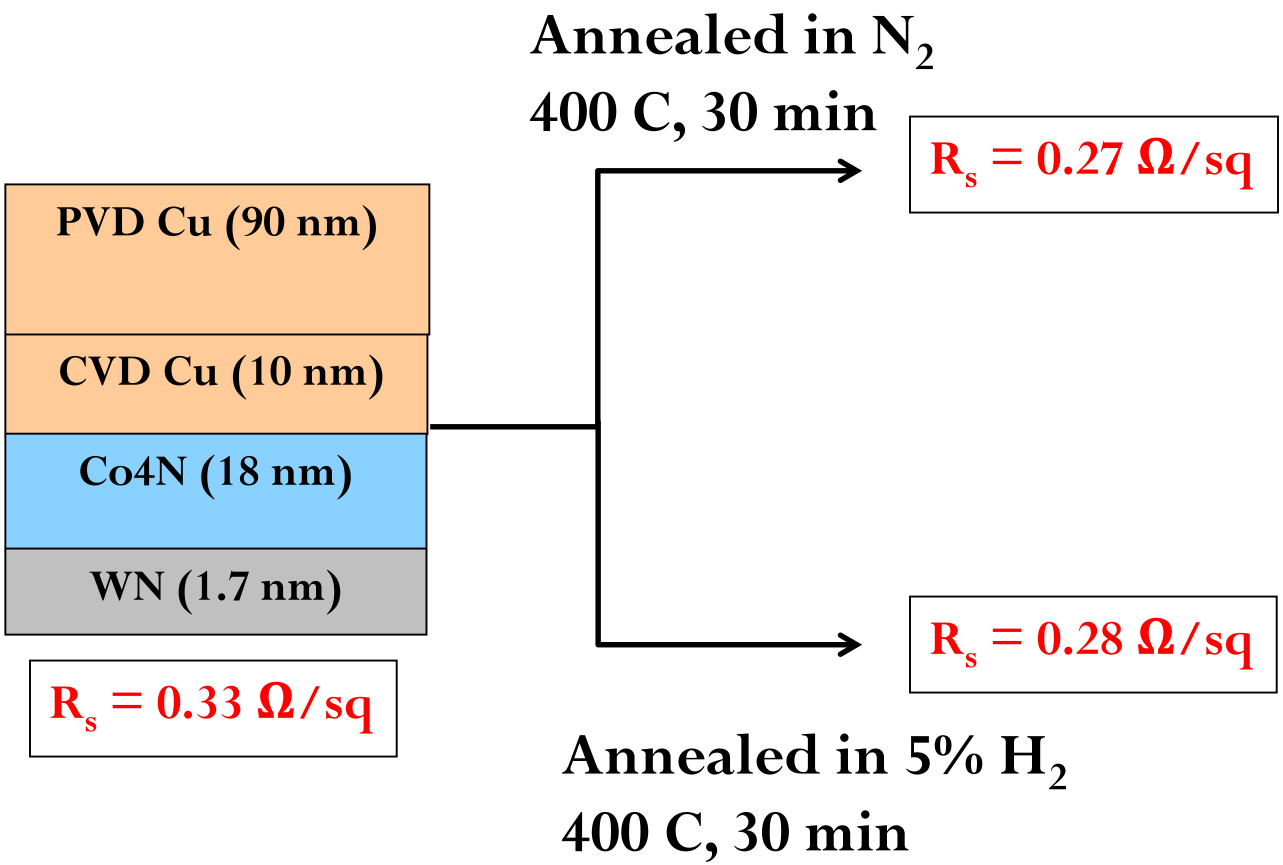
Cross-sectional TEM of SiO_2/WN/Co_4N/Cu

Without Co_4N Adhesion layer,
Cu/WN/SiO_2 **fail** the Scotch tape test.



Adhesion Energy = **10 - 13 J/m^2**

Cu/Co_4N interface is stable at 400°C without any intermixing



lowering of the sheet resistance indicates re-crystallization of Cu.
If any intermixing, the sheet resistance will increase sharply.

Summary

- The structure of as-deposited Co_4N films can be controlled depending on NH_3:H_2 flow rate conditions during CVD
- Face Centered Cubic structure of Co_4N thin films are stable up to 400°C
- Co_4N structure has a low lattice misfit of $< \sim 2\%$ with Cu (Ref: Cu-Ru ~ 4.8% misfit)
- Cu/Co_4N interface is stable up to 400 °C - No Intermixing

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- Members of Gordon Group

Harvard University
Center for Nanoscale Systems

DOW

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