Supercritical Fluid Technology for Semiconductor Device Fabrication: Deposition of Metals and Mesoporous Silicates from Carbon Dioxide

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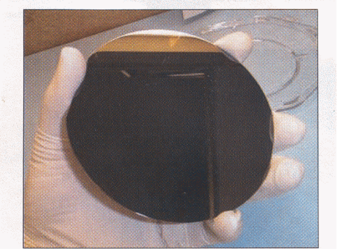
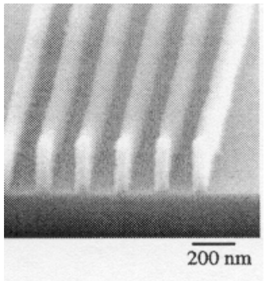
Can SCFs Play an Enabling Role in Device Fabrication?

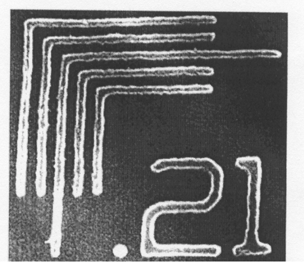
Resists and Cleans



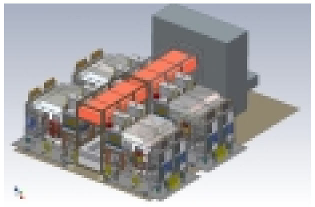
(UNC/NC State)



(Namatsu, NTT)

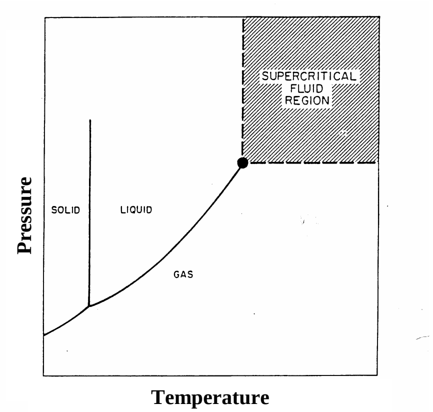


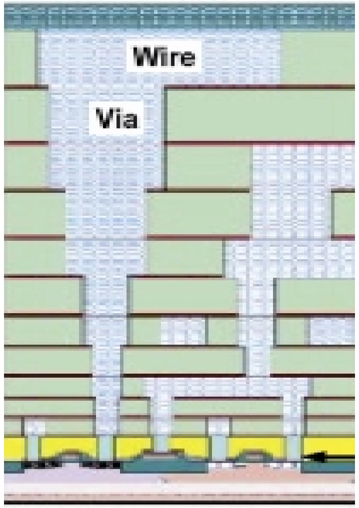
(Ober, Cornell)



(SSI/TEL)

(SC Fluids)

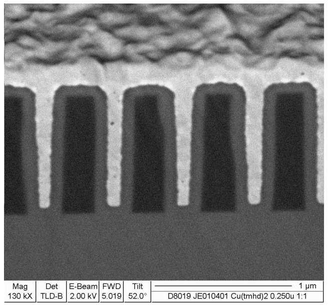




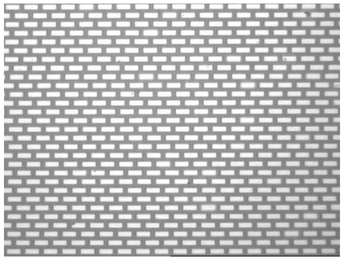
Dry Etch (UMass, Micell)

Low k Silylation (Reidy/UNT))

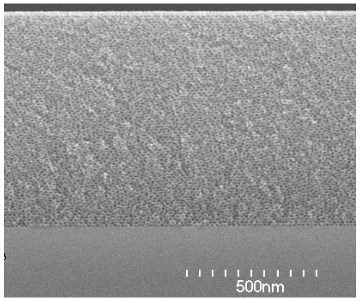
Deposition Chemistry at UMass



(Conformal Fill)



(Caps / Barriers)



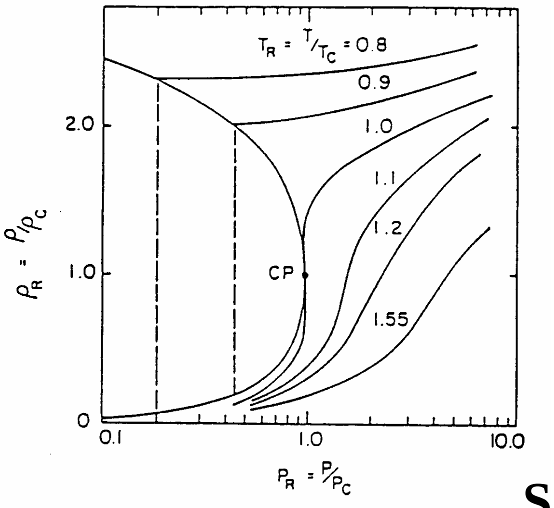
(Ordered ULK Films)

SCFs are Ideal Solvents for Materials Chemistry and Processing in Confined Geometries

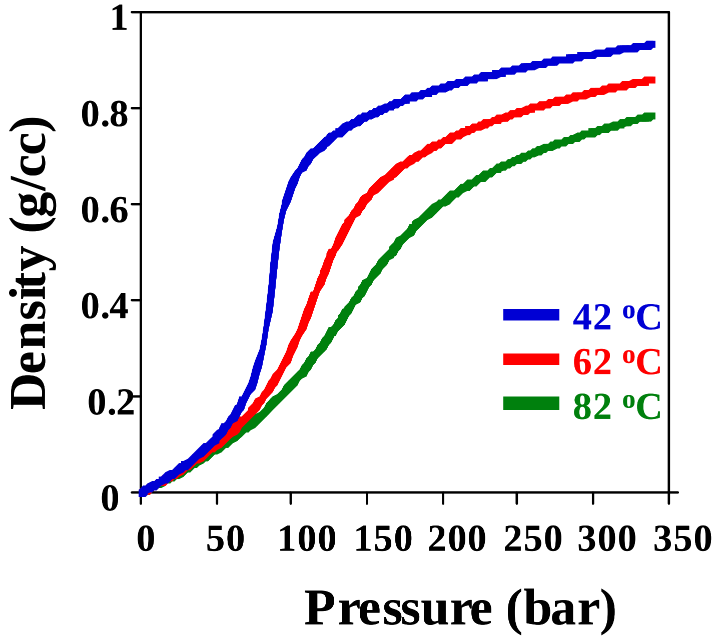
Carbon Dioxide

$T_c = 31.1\ ^0C$

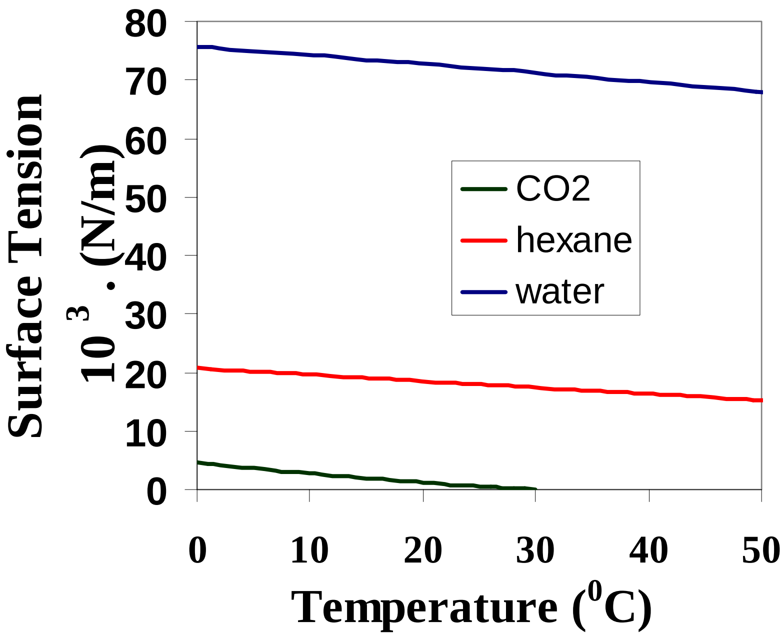
$P_c = 73.8$ bar



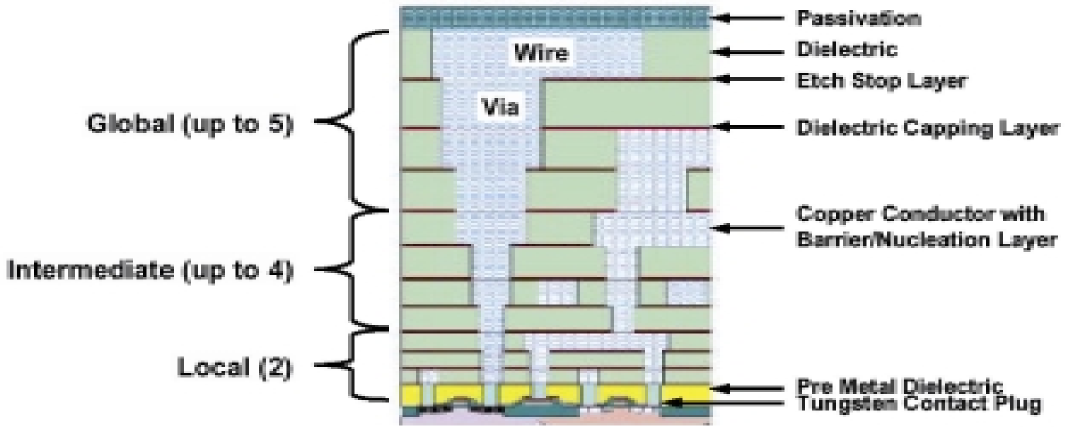
Density of CO_2



Solvent Surface Tension

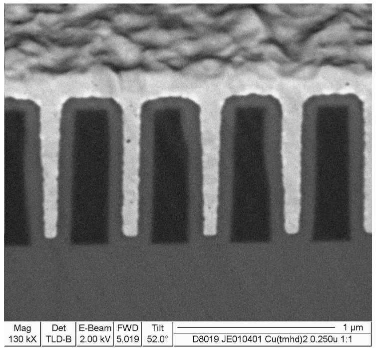


Reactive Deposition from SCFs for Device Fabrication
Developments at UMass



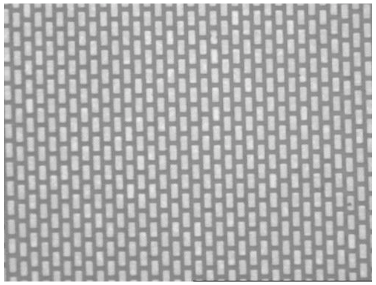
Cross-section of Hierarchical Scaling

(2001 ITRS Roadmap)

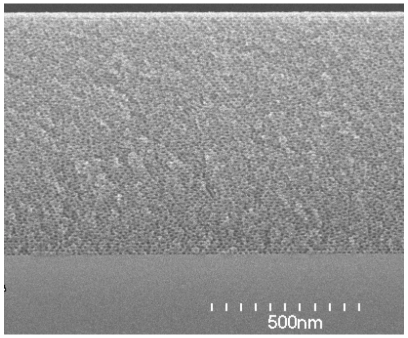


Cu Fill

(Blackburn et al., *Science*, 294, 141, 2001)



Caps/
Barriers



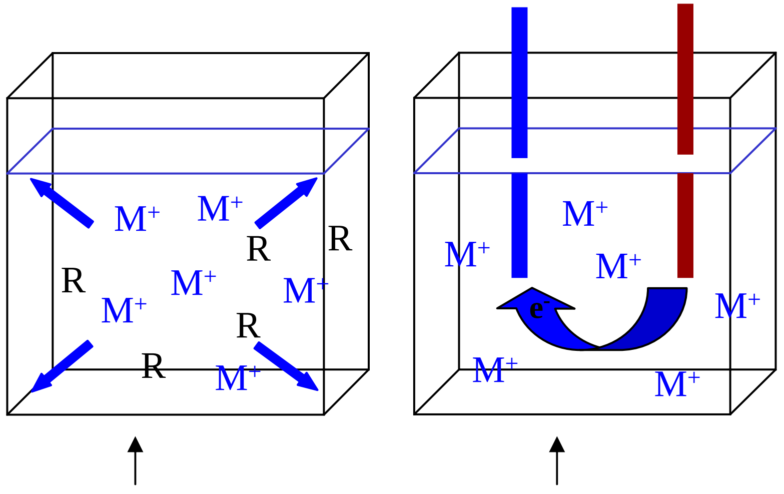
Ordered
ULKs

(Pai et al., Science, 303, 507, 2004)

Deposition Techniques for Seed and Fill

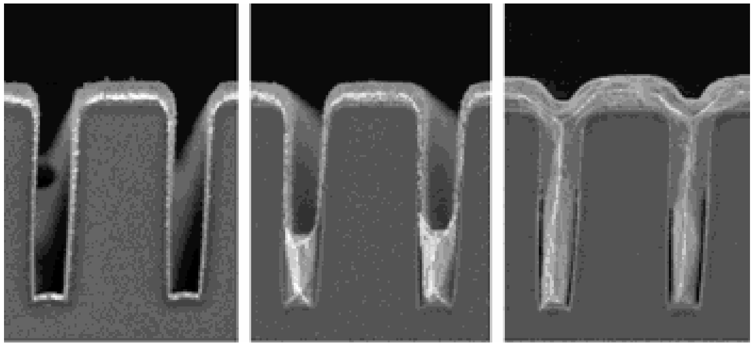
Sputter Seed and Plate

Liquid Phase Techniques



Electroless Plating

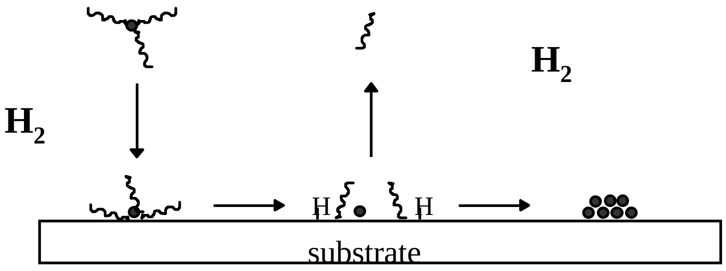
Electrolytic Plating



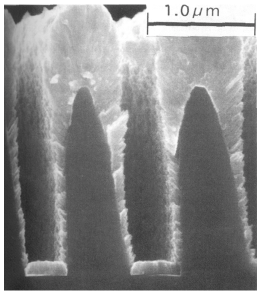
IBM web site

Vapor Phase Techniques

MOCVD



- Step Coverage?
- Issues with Precursor Design, Fluorine
- Adhesion



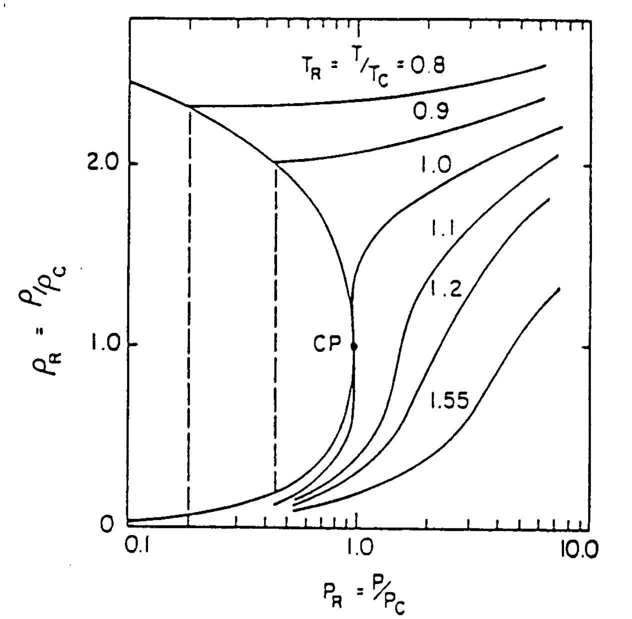
Pd from Pd(hfac)$_2$
on Si via CVD

(Bhaskaran, CVD 1997, 3, 85)

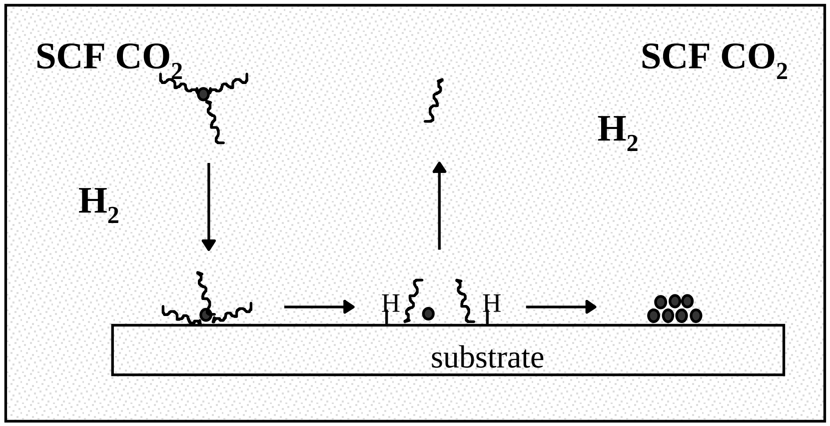
ALD

- Excellent Step Coverage
- Rate?

Chemical Fluid Deposition



Deposition via Reduction of Organometallics in Supercritical CO_2 (T_c= 31 ^{0}C, P_c = 74 bar)



Comparison of Reduction Media for Deposition of Metal Films

	Liquid	SCF (CFD)	Gas (CVD)
Density (g/cm^3)	1	0.1- 1	10^{-3}
Viscosity (Pa-S)	10^{-3}	10^{-4} - 10^{-5}	10^{-5}
Diffusivity (cm^2/sec)	10^{-5}	10^{-3}	10^{-1}
Precursor Conc. (mol/cm^3)	10^{-5}	10^{-5}	10^{-8}
Hydrogen Conc. (mol/cm^3)	10^{-4}	10^{-2}	10^{-4}
Surface Tension (Dynes/cm)	20-50	0	0
Deposition Temperature (^{0}C)	25-80	40-300	250 +

Transport in Solution ❒ Zero Surface Tension ❒ Rapid Diffusion

Cu Deposition - Familiar Chemistries from CVD

Reduction of Cu(II) Compounds

- $Cu(II)L_2$: $Cu(hfac)_2$, $Cu(tmhd)_2$

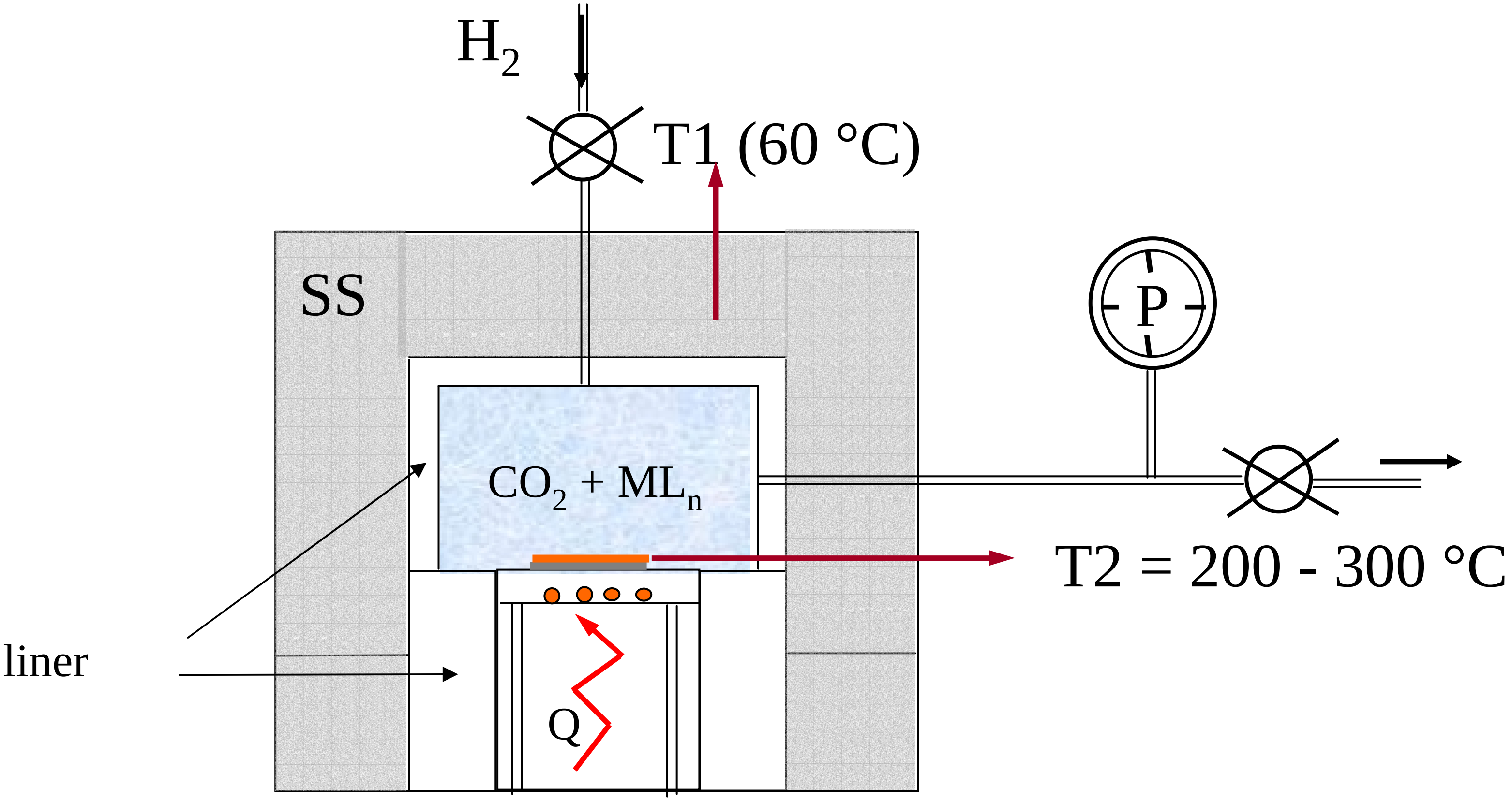
$$\boxed{Cu(II)L_2 + H_2 \xrightarrow{\text{Reduction}} Cu + 2\,HL}$$

Thermal Disproportionation of Cu(I) Compounds

- $Cu(I)LL'$: - $Cu(hfac)(L')$ where L' = 2-butyne, COD, VTMS

$$\boxed{2\,Cu(I)LL' \xrightarrow{\text{Thermal disproportionation}} Cu + Cu(II)L_2 + 2\,L'}$$

Cold Wall CFD Reactor



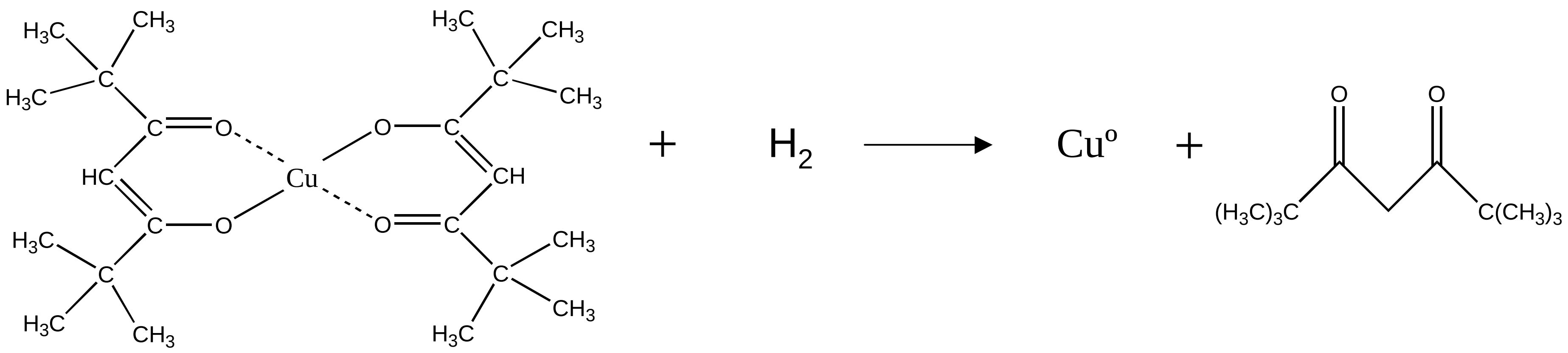
T1 and T2 controlled independently

↓

Substrate selectivity

Deposition via H_2 Reduction of Copper(II) β-diketonates in CO_2

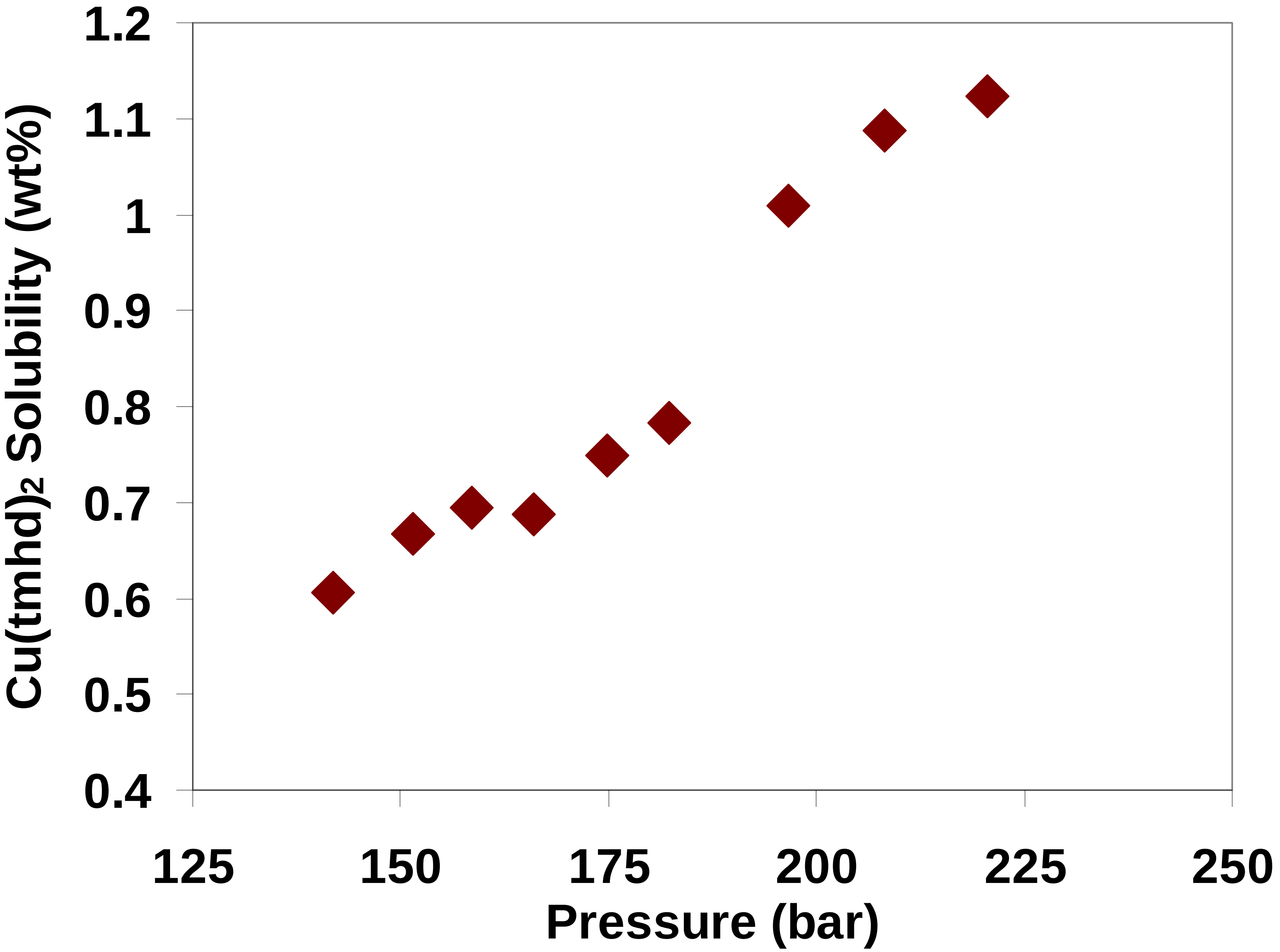
Cu(tmhd)$_2$ – An Attractive Precursor
Not practical via CVD due to low volatility



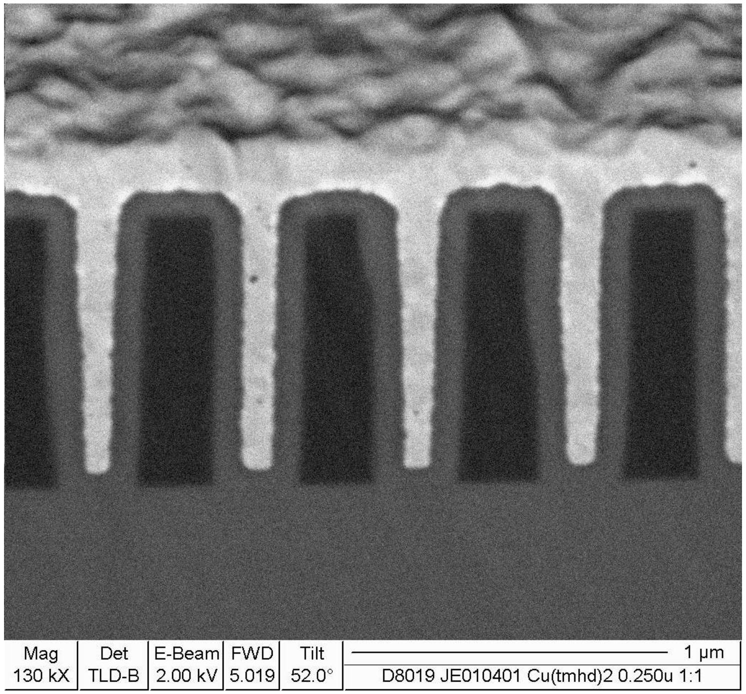
Deposition on Pd-Seeded Si, TiN; Temperature < 225 °C
Deposition on Si (native oxide), TiN, Ta, TaN; Temperature > 225 °C

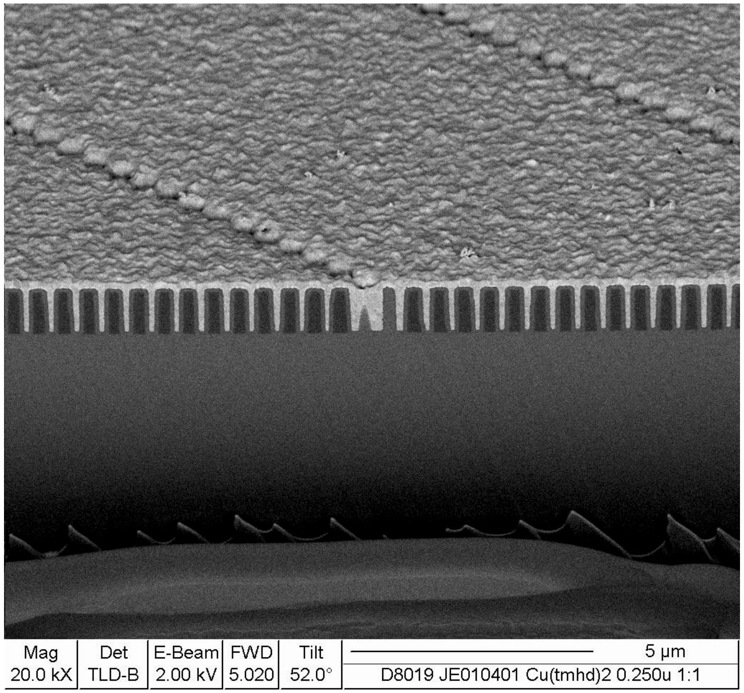
No F Contamination, Fluid Phase Concentrations in CO_2 > 1000x that of CVD

$Cu(tmhd)_2$ Solubility in CO_2 at 50 ^{0}C



Copper Deposition by H_2 Reduction of Cu(tmhd)$_2$ on Pd-Seeded Si in CO_2 (200 ^{0}C)

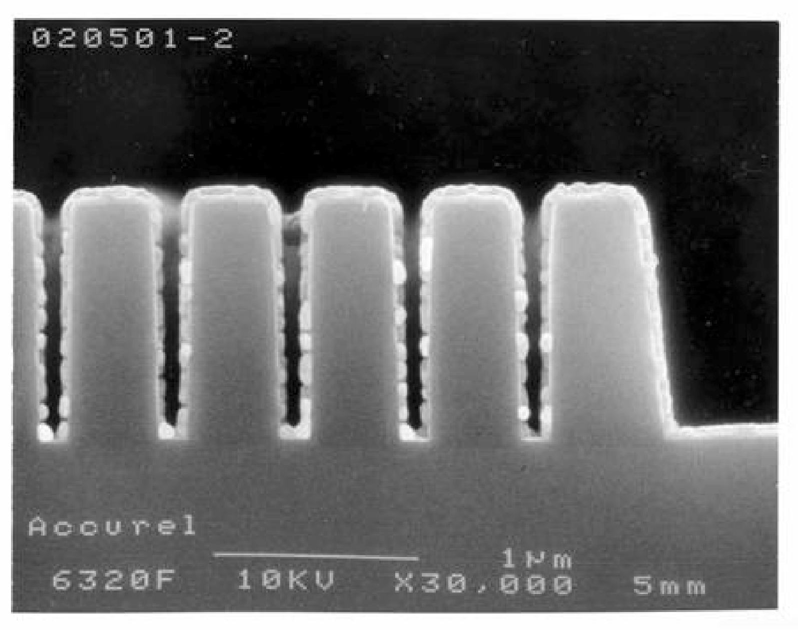




- **Exceptional Gap Fill**

(*Science*, 294, 141, 2001)

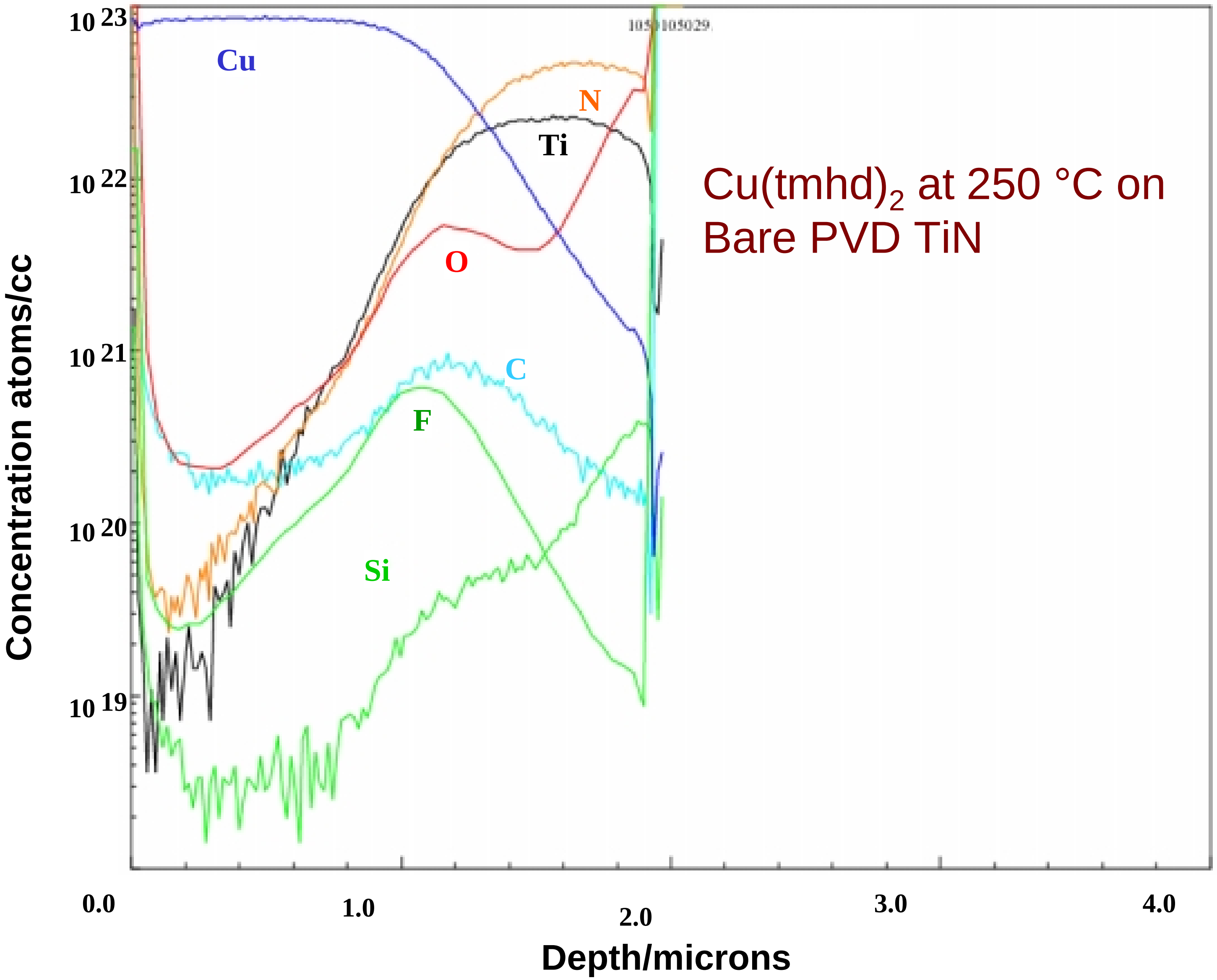
Copper Deposition by H_2 Reduction of Non-fluorinated Cu β-diketonates in CO_2 on Un-Seeded Ta



- **Large Grains in Thick Films, No Seam, 2.0 μΩ-cm**
- **Conformal Thin Films - Viable Cu Seed Layers**
- **Excellent adhesion w/ surface pretreatment**

(Blackburn et al., *Science*, 294, 141, **2001**; Cabanas et al., *Microelec. Eng*, 64, 53, **2002**; Cabanas et al., *2002 AMC Proceedings*, (MRS) 409)

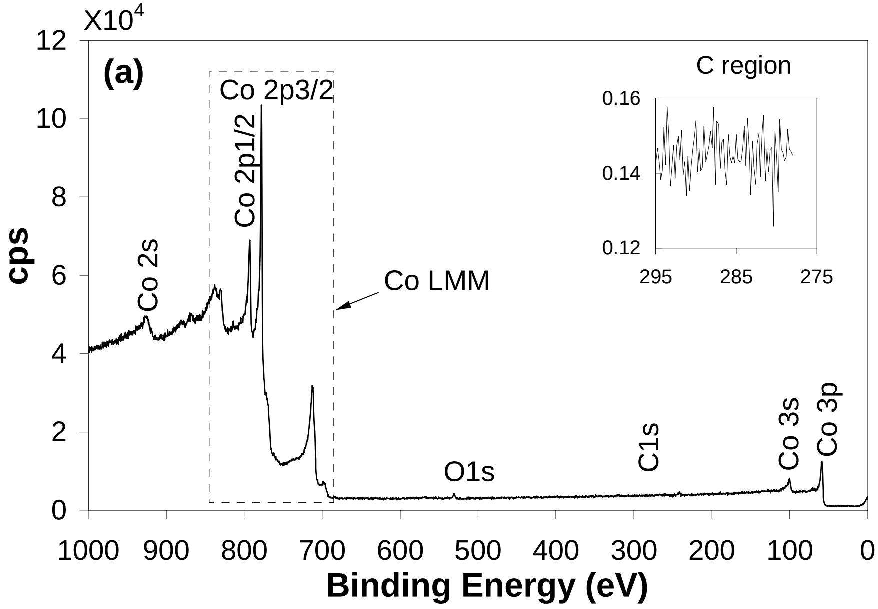
Copper Deposition from Cu(II)(tmhd)$_2$



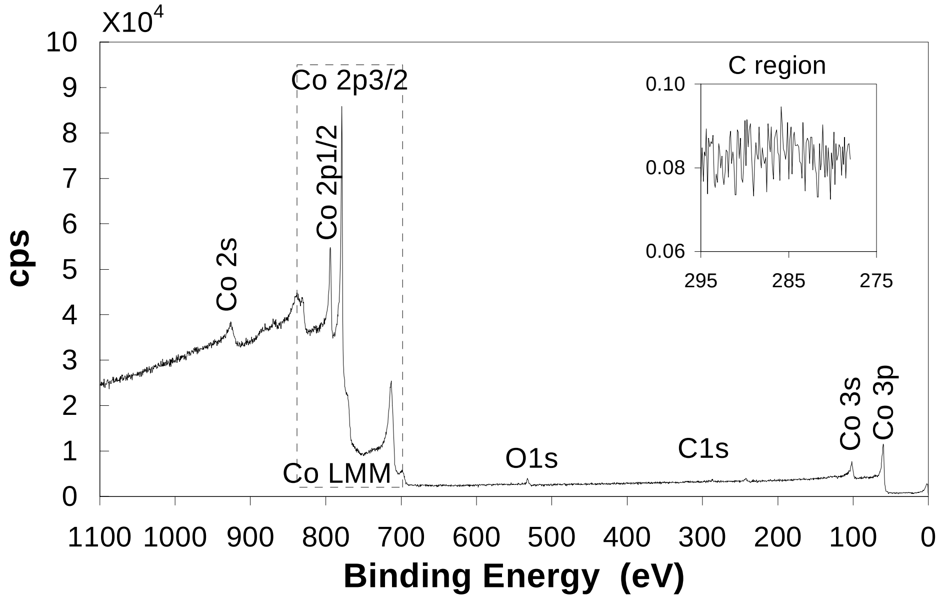
Cu(tmhd)$_2$ at 250 °C on
Bare PVD TiN

Deposition of Co from Carbon Dioxide

Deposition of Co on Cu, TaN, TiN, and Si(SiO_2) via H_2 Reduction of Co(tmhd)$_3$ or $CoCp_2$



Co film deposited at 225 °C and 245 bar onto Cu/TaN/Si from Co(tmhd)$_3$ (0.30 wt %) by H_2 reduction in CO_2 solution



Co film deposited at 300 °C and 224 bar onto native oxide of Si from $CoCp_2$ (0.20 wt %) by H_2 reduction in CO_2 solution

Co(tmhd)$_3$ - tris (2,2,6,6-tetramethyl 3,5-heptanedionato) cobalt(III)

$CoCp_2$ - bis(cyclopentadienyl)cobalt (II)

(Hunde and Watkins, Chem. Mater., **2004**, 16, 498)

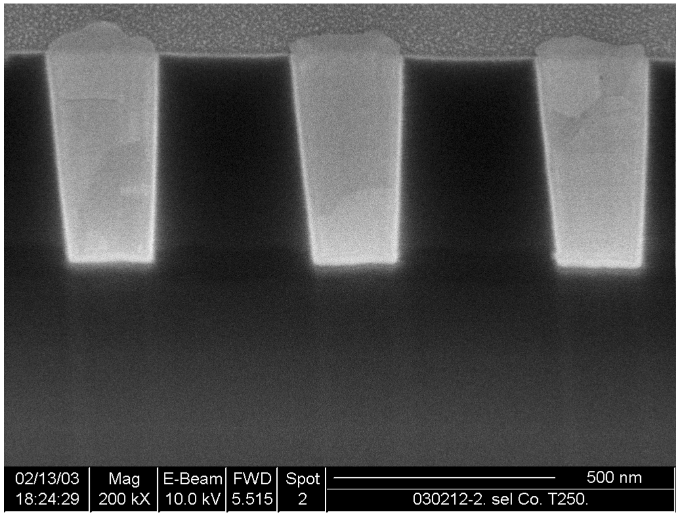
Selective Co and Co(P) Caps on Cu, Post CMP
Co(tmhd)$_3$ 300 ^{0}C, H_2 Reduction, P Source = TPP

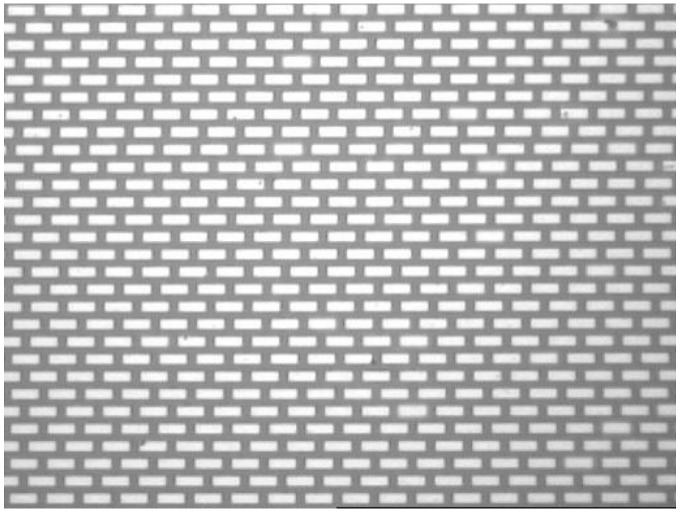
(with J. Blackburn et al., Novellus, 2003 AMC Proceedings)

SEM

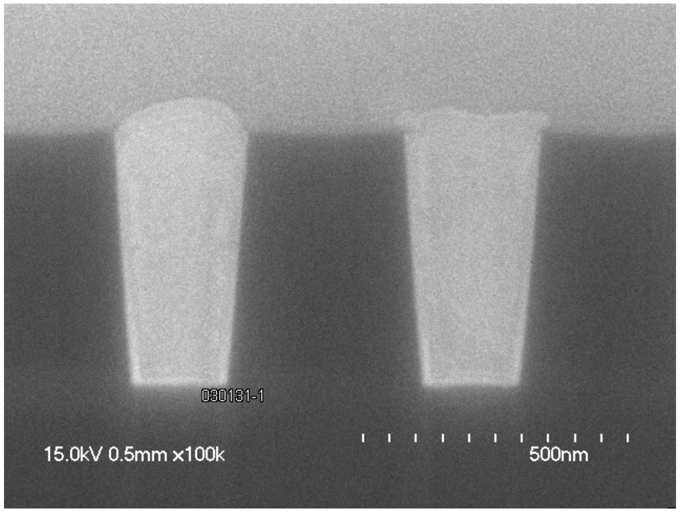
Optical

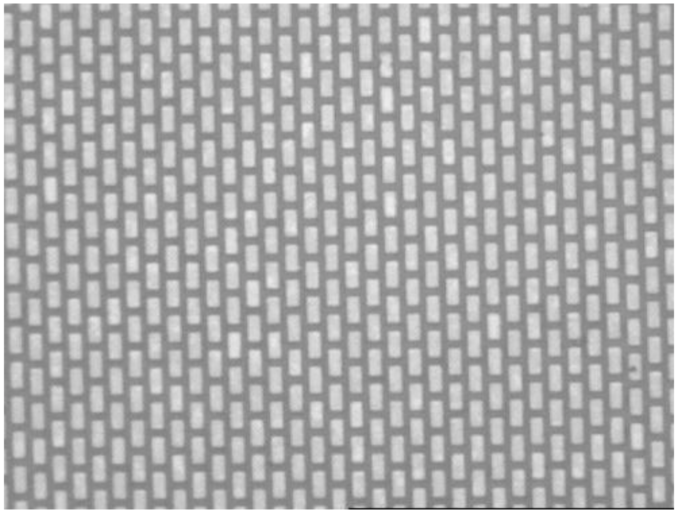
Selective Co





Selective Co(P)
(10% P)





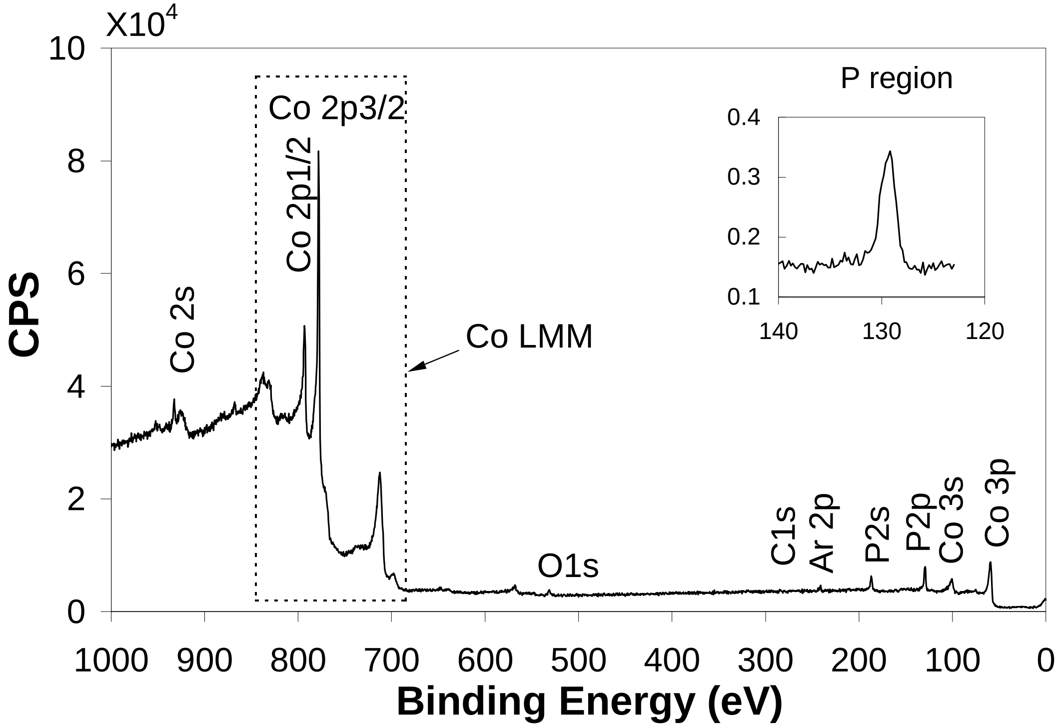
NOVELLUS

UMASS

Deposition of Phosphorous Doped Cobalt Films

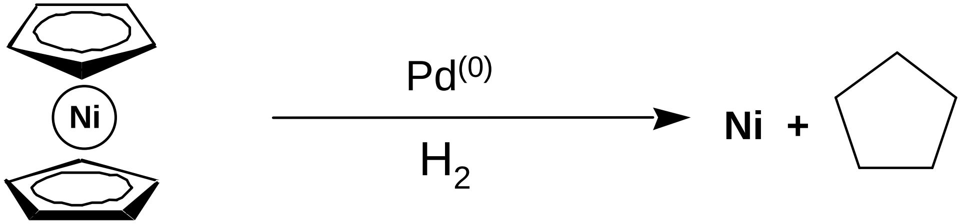
- Triphenyl phosphine (TPP) was used as P source
- P doped Co films from TPP + $CoCp_2$ mixtures or TPP + $Co(tmhd)_3$ in SC CO_2
- Carbon free films with 4 -20 at % P were deposited on, Cu/TaN, native oxide of Si,TaN/Si substrates

XPS Survey - Co(P) film deposited at 300 ºC on Cu

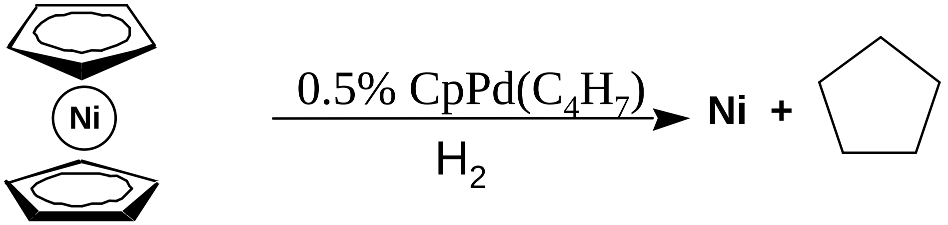


Flexible Deposition System:
Deposition of Ni from $NiCp_2$ in CO_2

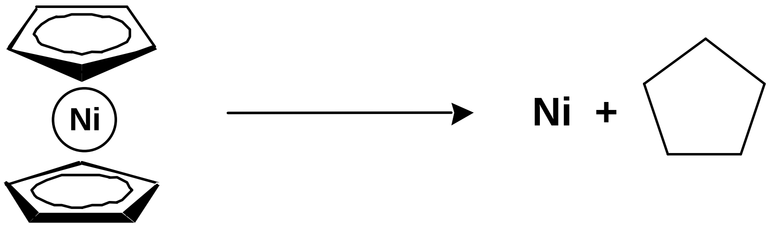
60 ^{0}C, Seeded Deposition



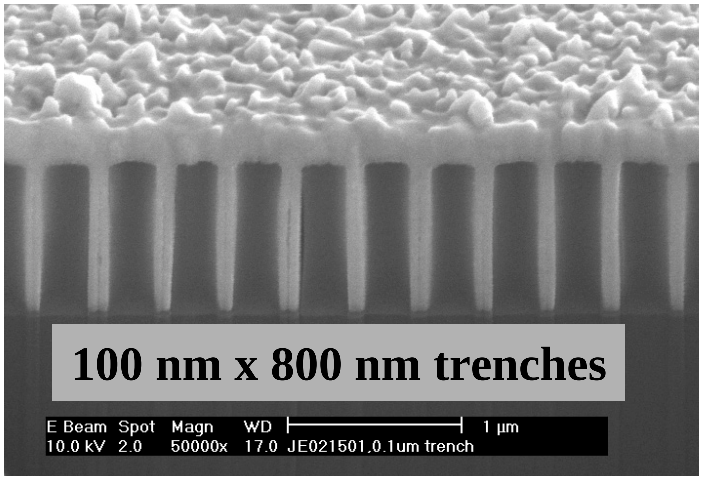
60 ^{0}C, Co-Deposition

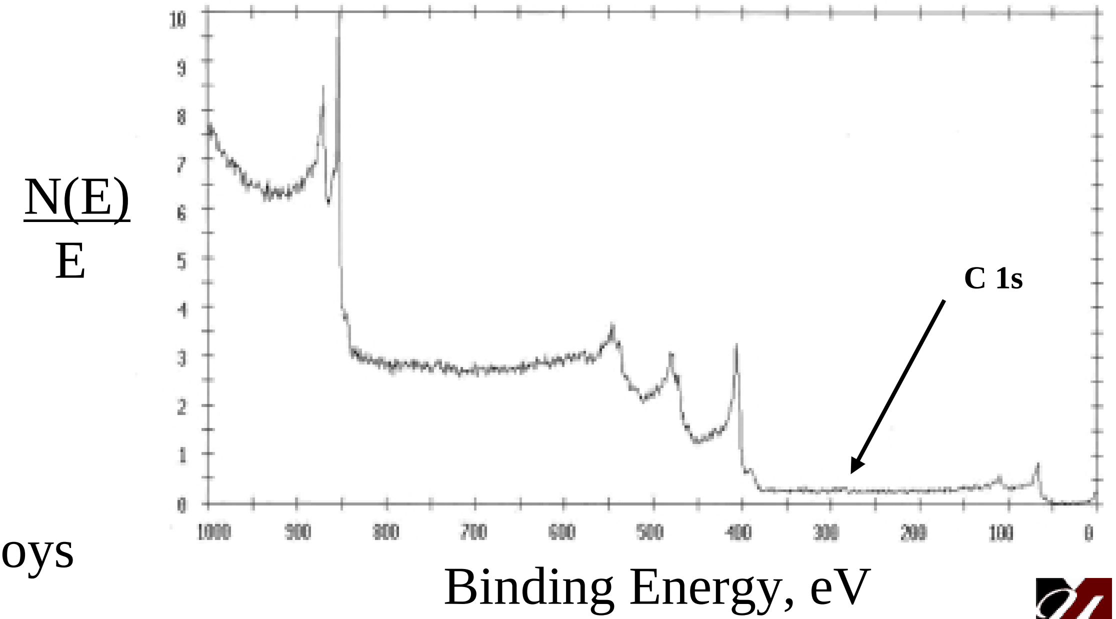


175^{0}C, Non-selective Deposition



(*Science*, 294, 141, 2001)



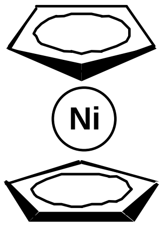


Also: Pt, Pd, Ir, Au, Rh, Co and alloys

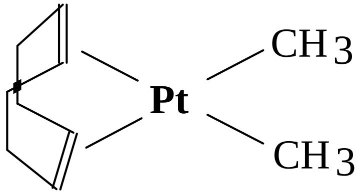
(*Chem. Mater*. 1999, 11, 213; Chem. *Mater*., 2000, 12, 2625; *Adv. Mater*. 2000, 12, 213, submitted, 2003)

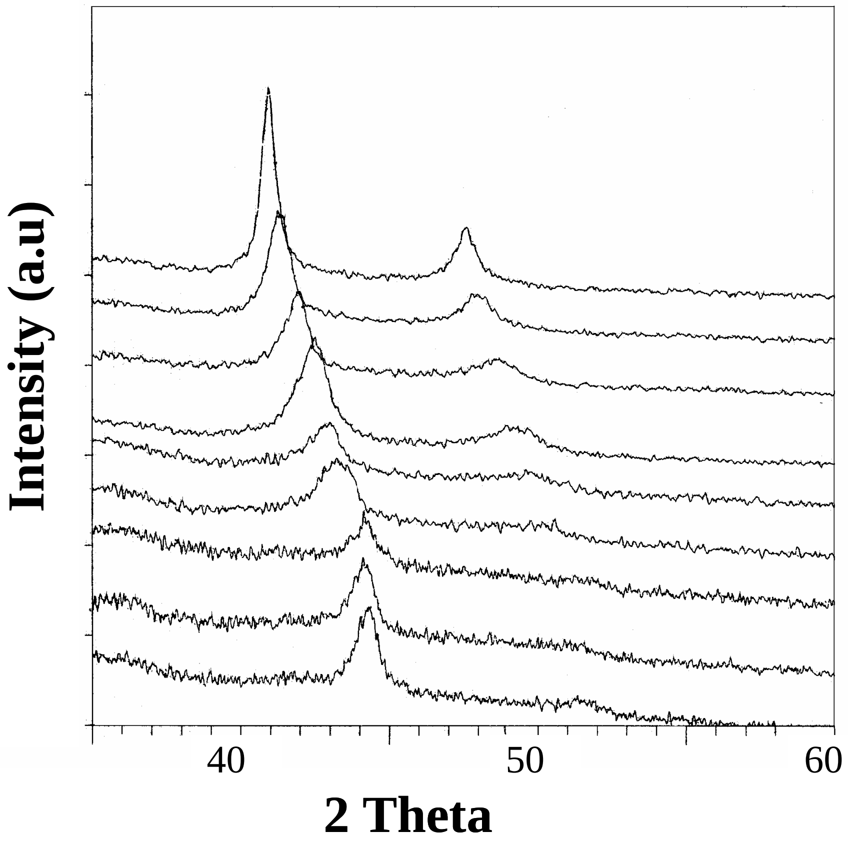
Deposition of Ni/Pt Alloys from $NiCp_2$ + $CODPt(CH_3)_2$ in CO_2

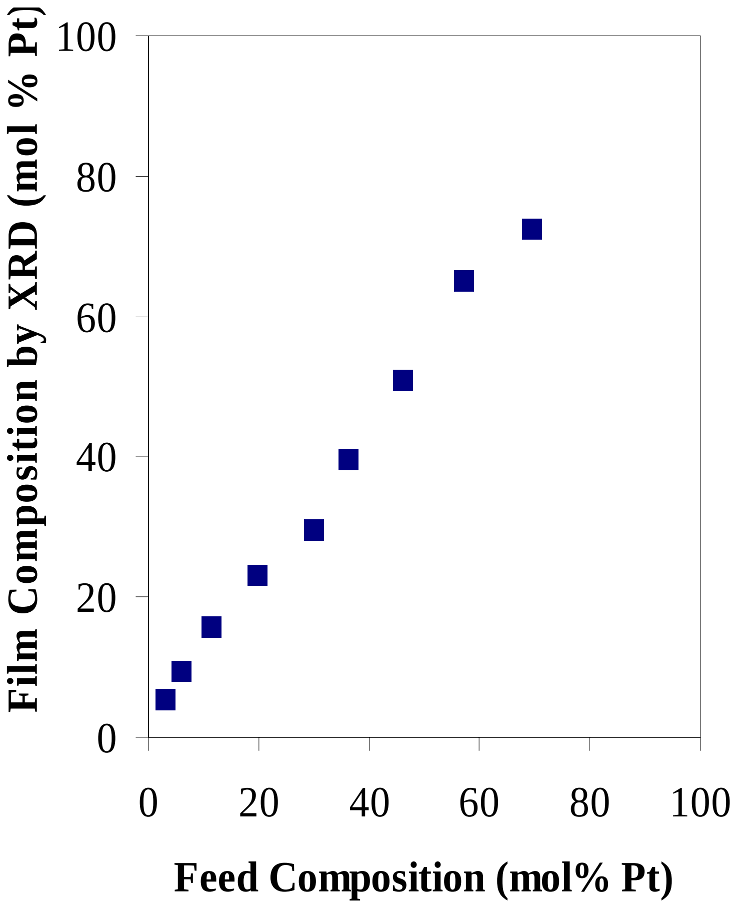
60 °C, 140 bar, Polyimide Substrate



X-Ray Diffraction

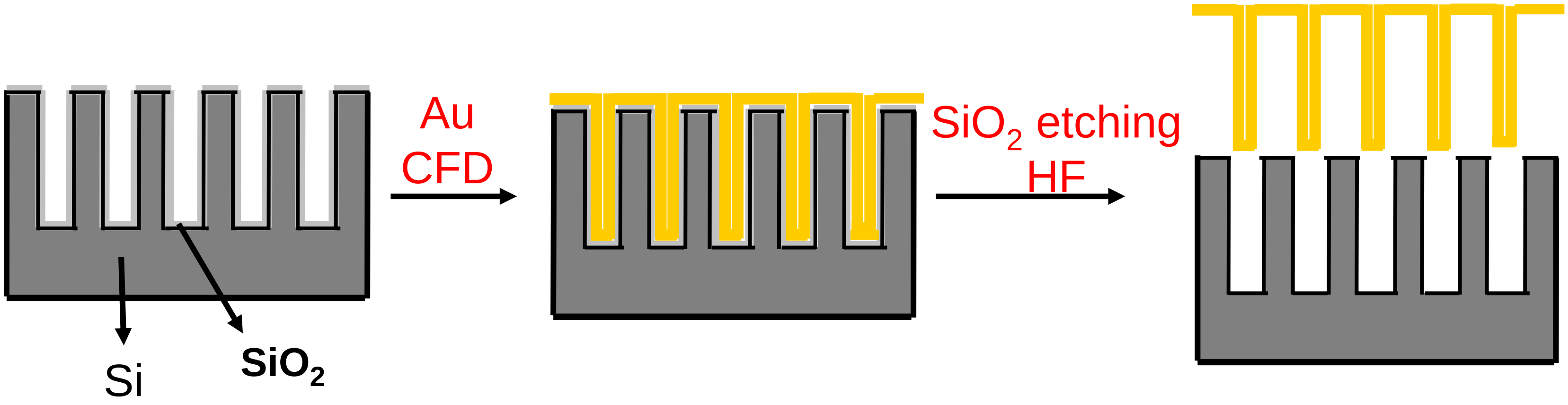


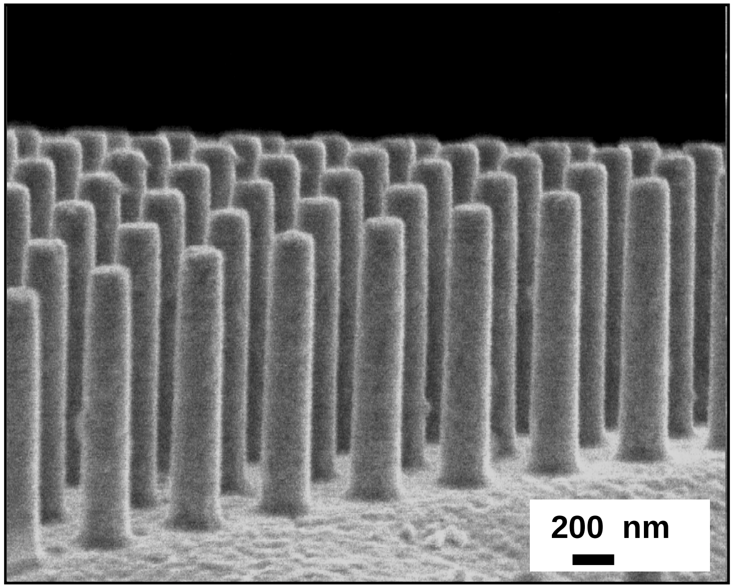


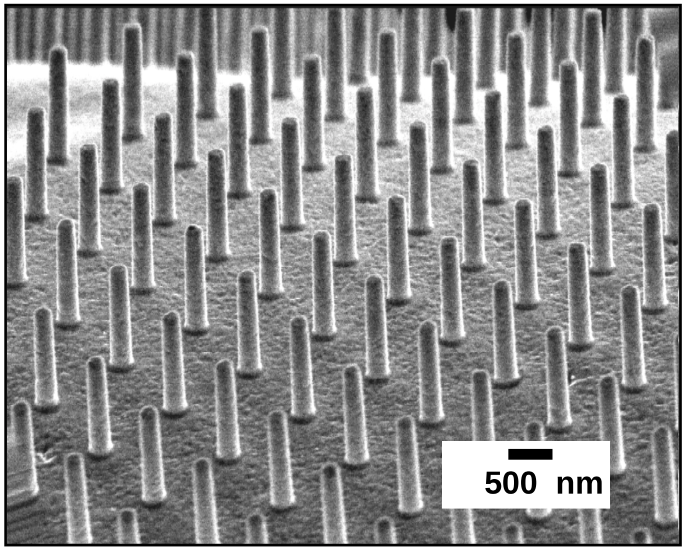


Fabrication of Metal Posts
Deposition of Gold in High Aspect Ratio Vias and Template Removal
(just for fun)

Au by H_2-assisted CFD of $Au(CH_3)_2(acac)$ at 125 °C and 200 bar

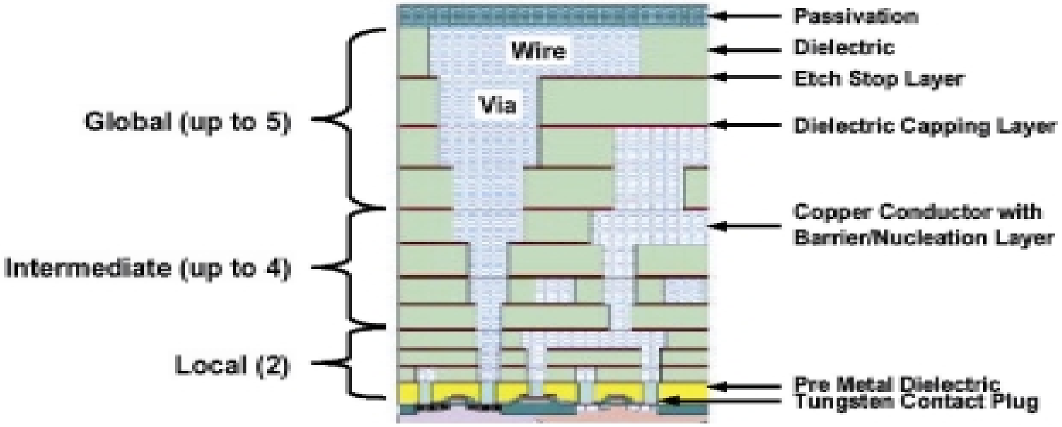






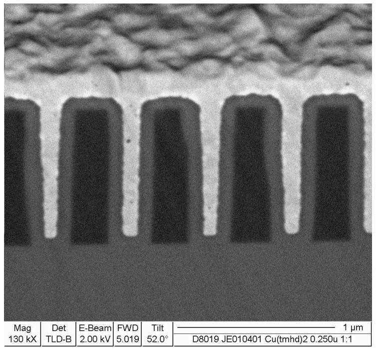
(*Chem. Mater*. **2004**, in press)

Role of SCFs in Semiconductor Device Fabrication

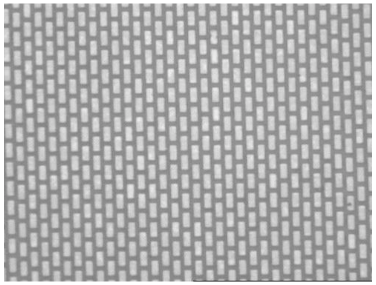


Cross-section of Hierarchical Scaling

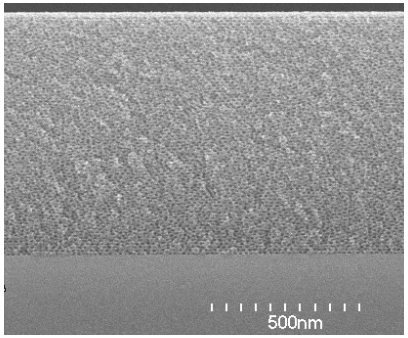
(2001 ITRS Roadmap)



Cu Fill

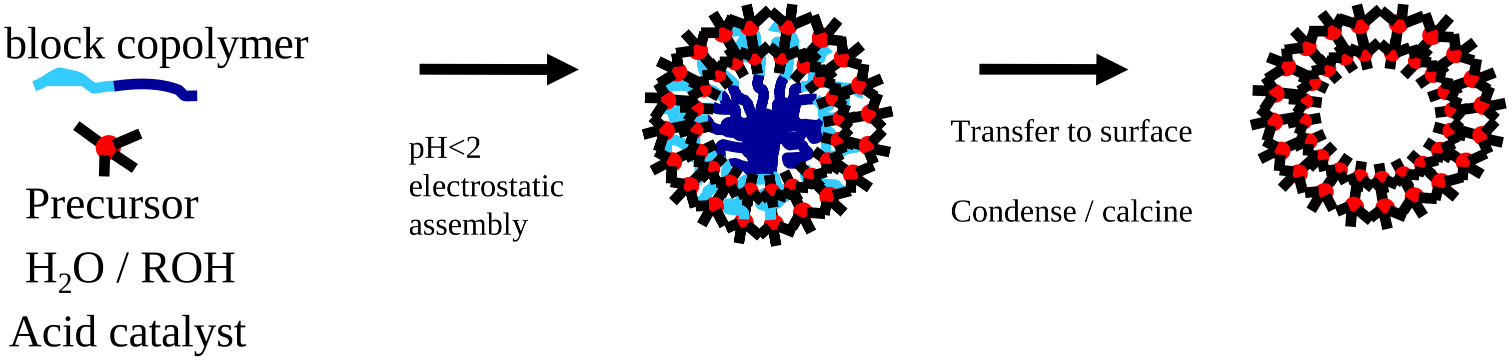


Caps/
Barriers



Ordered
ULKs

Coordinated Self Assembly / Evaporation-Induced Self Assembly
Good Control Over Local Structure


block copolymer

Precursor

H_2O / ROH

Acid catalyst

pH<2
electrostatic
assembly

Transfer to surface

Condense / calcine

Sol-Gel Chemistry

M-O-R + H_2O $\longleftrightarrow$ M-O-H +R-O-H **(Hydrolysis)**

M-O-H + H-O-M $\longleftrightarrow$ M-O-M + H_2O **(Water Condensation)**

M-O-R + H-O-M $\longleftrightarrow$ M-O-M + R-O-H **(Alcohol Condensation)**

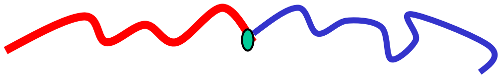
- Usually acid or base catalyzed

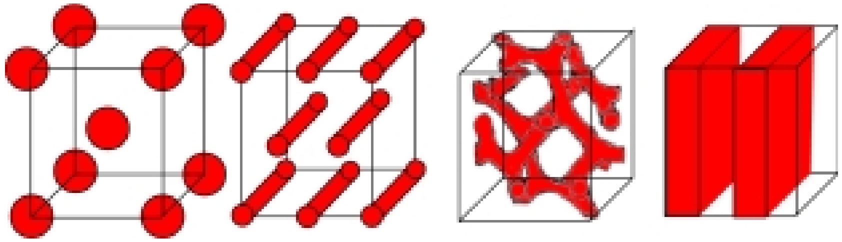
Issues

- Aging Periods / Presence of Excess ROH and H_2O
- Mutual Solubility of Template and Precursors
- Control of Pore Orientation, Long Range Order, Patterning Requires External Fields
- Structure Evolution and Network Formation are Coincident

Controlling Morphology in Block Copolymers

Di-block Copolymer

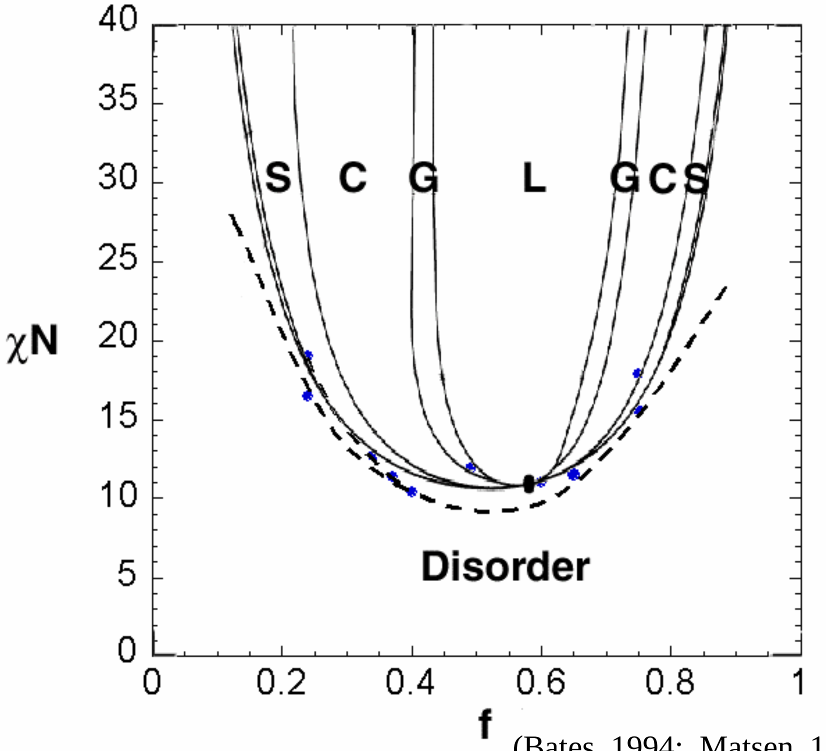




Increasing **f** →

BCP Phase Diagram

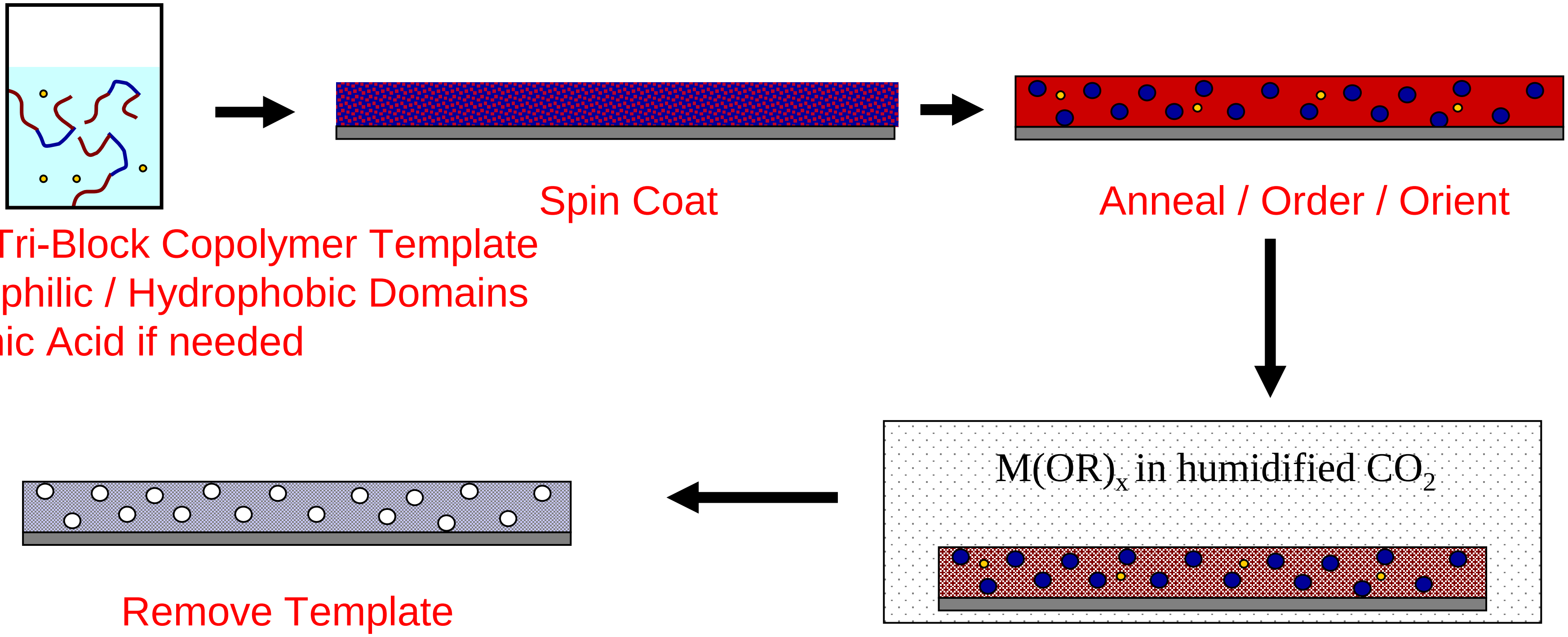
SCFT Theory vs. Experiment (PEP-b-PEE)



(Bates, 1994; Matsen, 1996)

Key Parameters: block volume fraction, f → controls morphology
degree of polymerization, N → controls domain size
Flory Parameter, χ → χN controls segregation

Our Approach to Mesoporous Materials



Spin Coat

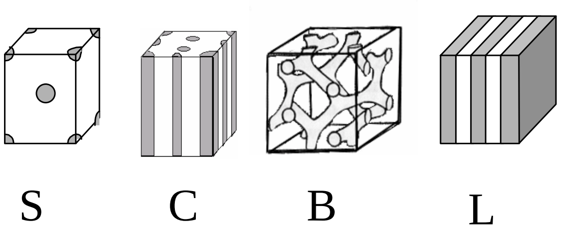
Anneal / Order / Orient

Di or Tri-Block Copolymer Template
Hydrophilic / Hydrophobic Domains
Organic Acid if needed

$M(OR)_x$ in humidified CO_2

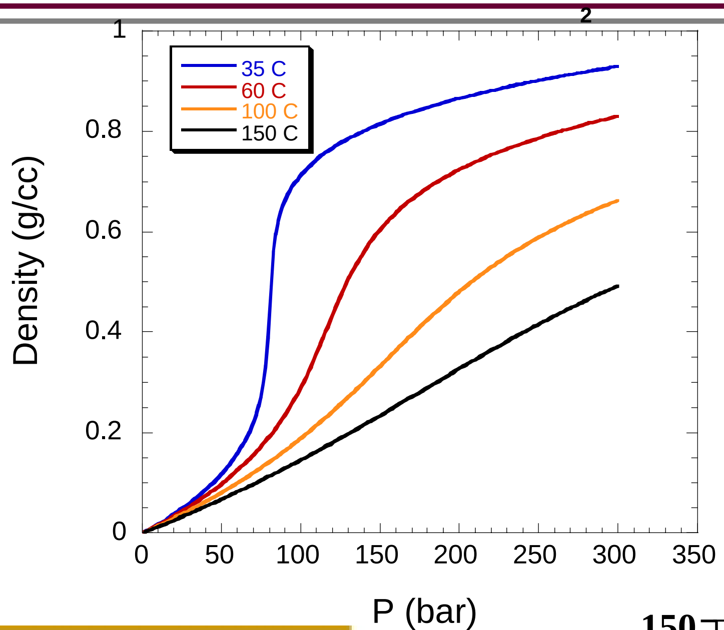
Remove Template

Infuse / Condense Alkoxide



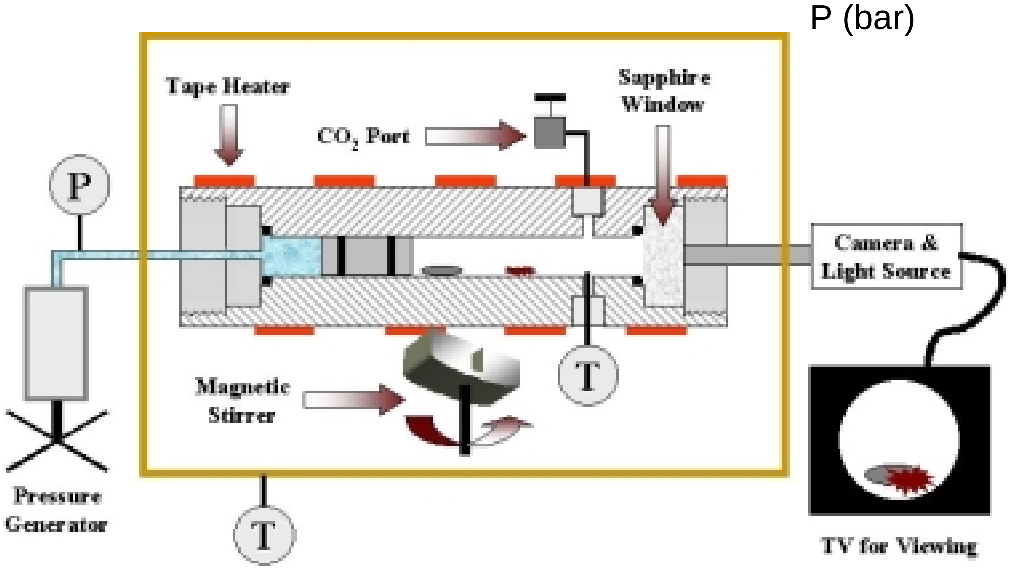
- mutual solubility of template and precursor is not required
- extraction of ROH from incipient film drives condensation
- alkoxide condensation can be decoupled from template self-assembly
- **heterogeneous approach preserves structural details of pre-formed BCP template**

TEOS Solubility in Supercritical Carbon Dioxide

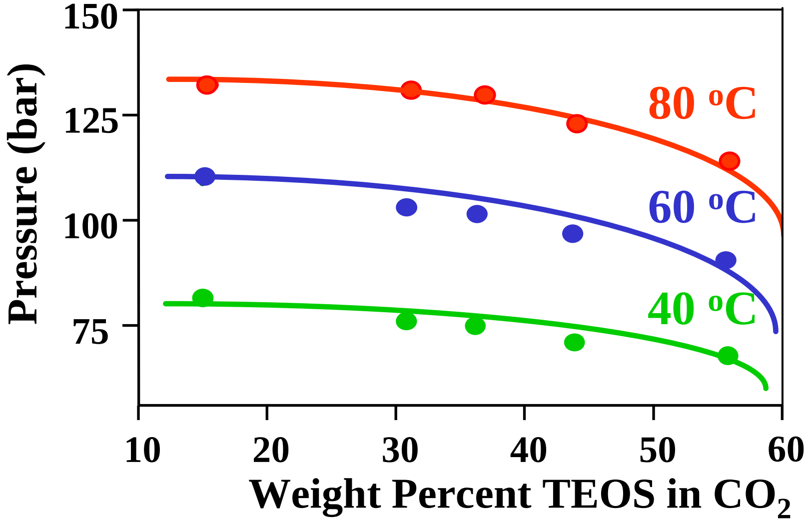


CO_2

T_c=31°C, P_c=73.8 bar



Variable Volume View Cell

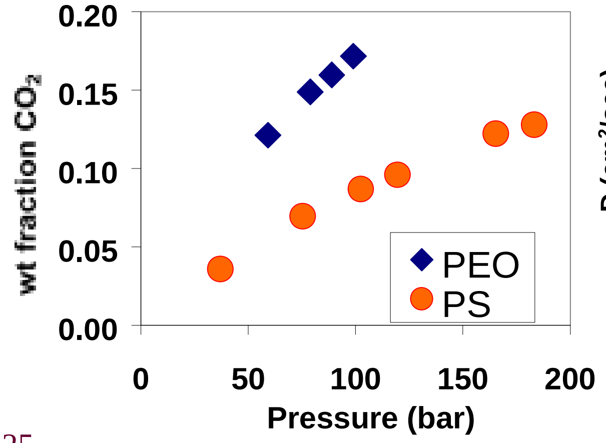


TEOS Solubility in SC-CO_2

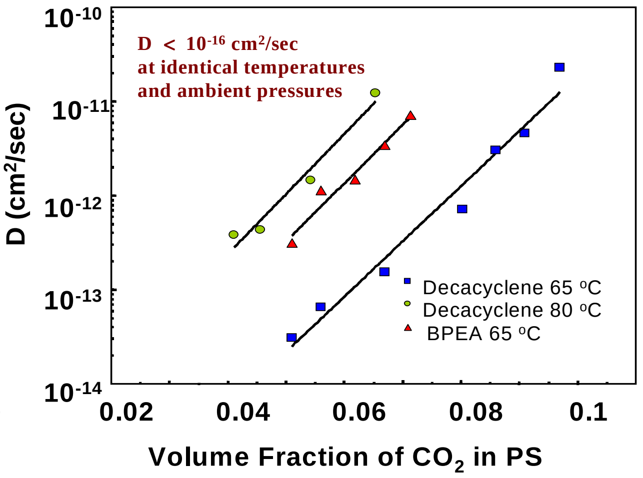
Why are SCFs Enabling?

- Template Dilation is Modest, Equilibrium Limited
  - template order is not disrupted
- Diffusion is Enhanced in Dilated Matrices
- Reagent Partitioning is Favorable
- Elimination of Excess Alcohol / Water from Reaction Media
  - rapid condensation, no aging periods

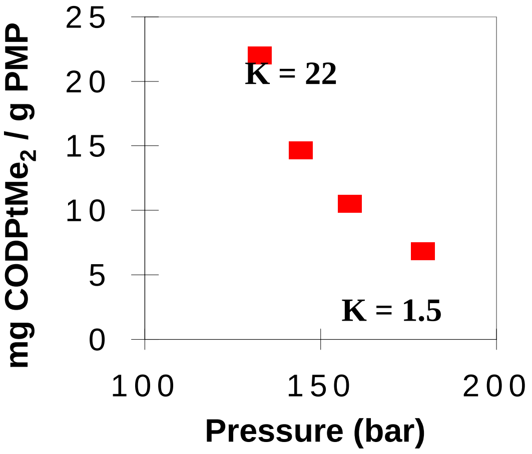
CO_2 Sorption in PS and PEO at 65 ^0C



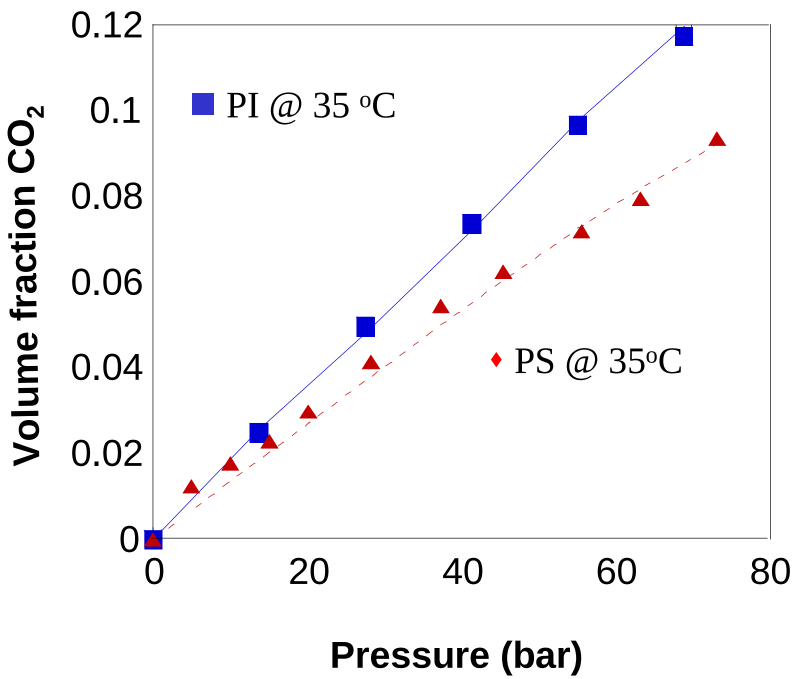
Probe Mobility in CO_2 - Dilated PS

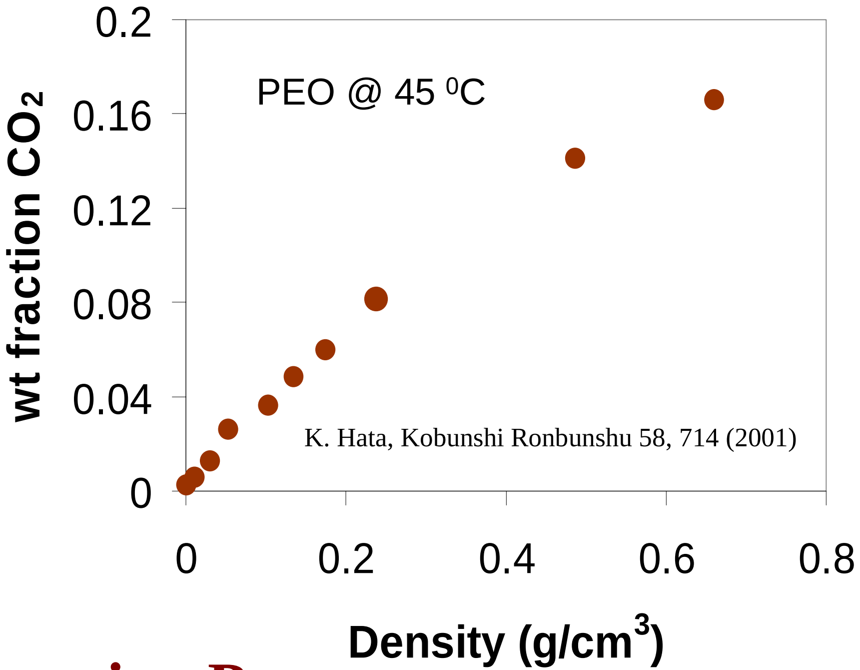


Partitioning of $CODPtMe_2$ between CO_2 and CO_2- Dilated PMP



Polymer/SCF Interactions
CO_2 Sorption Homopolymer Systems



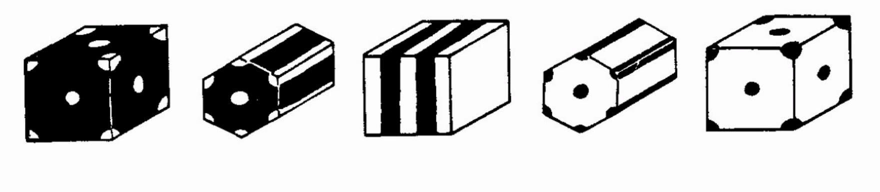


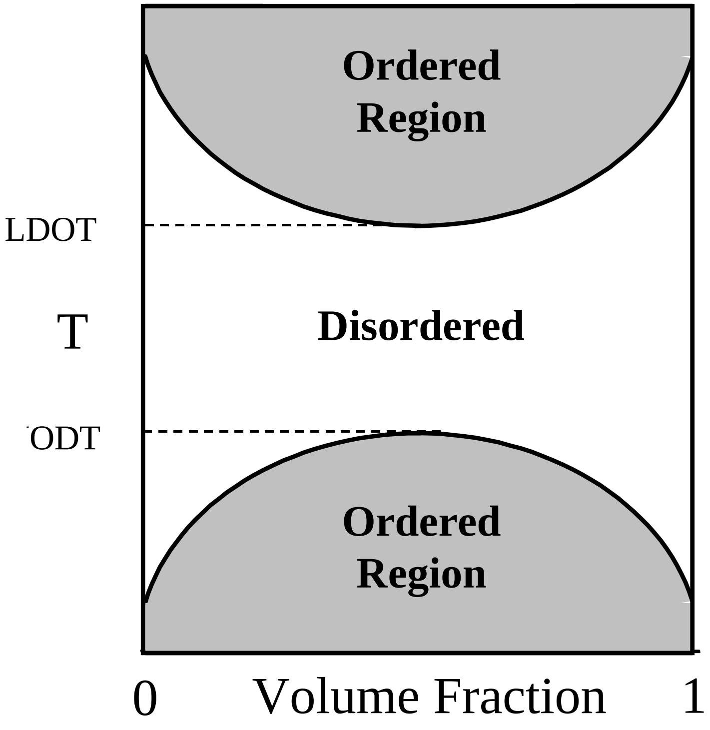
K. Hata, Kobunshi Ronbunshu 58, 714 (2001)

Polymer/CO_2 Interaction Parameters

	Temperature (°C)	χ
polystyrene	35	1.65
poly(vinyl methyl ether)	20	0.90
polyisoprenene	35	1.56
polybutadiene	25	1.62
poly(n-butyl methacrylate)	60	0.90

Phase Behavior of BCPs Dilated with Supercritical Fluids





ODTs => Sorption of SCFs can expand miscibility slightly via solvent screening (enthaplic effect)

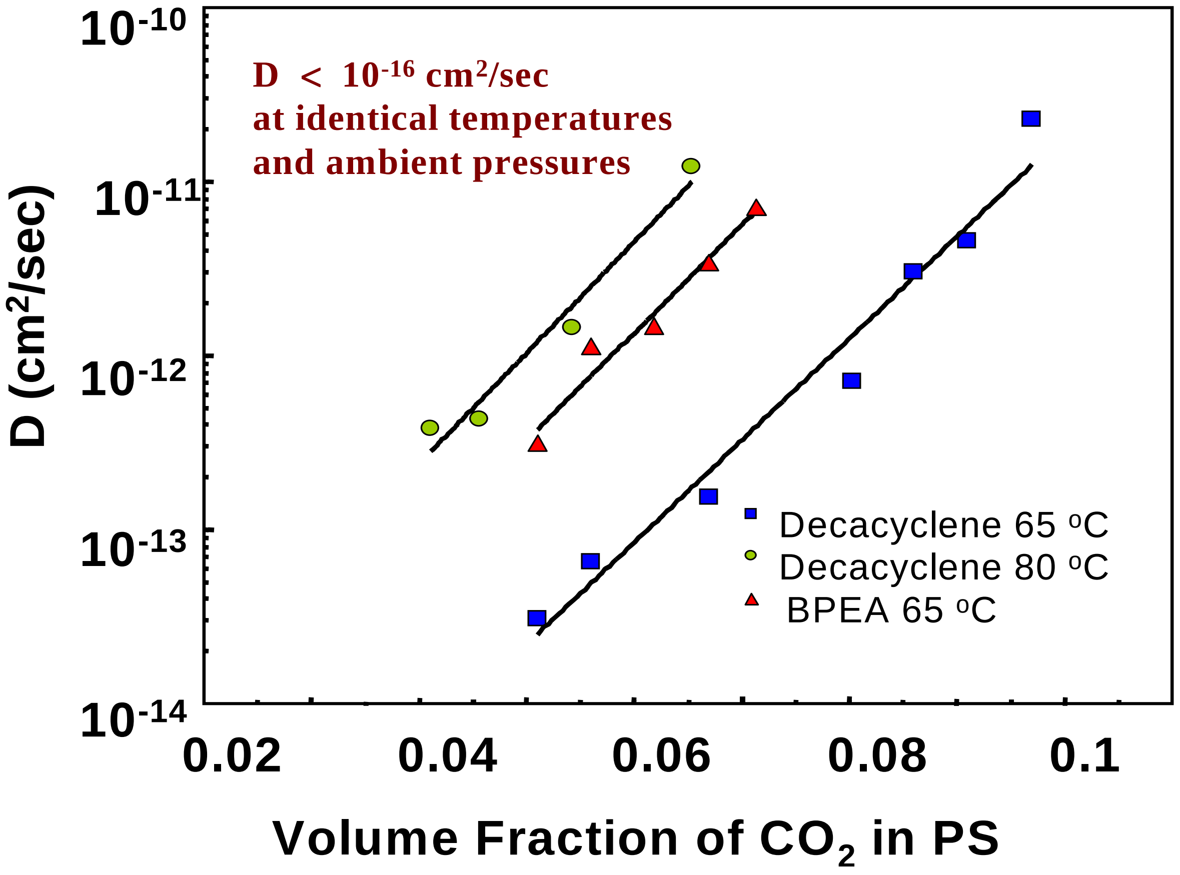
LDOTs => Selective dilation drives segregation through a free volume (entropic effect)

Macromolecules **2003**, 36, 4029
J. Polym. Sci. Polym. Phys. in press
Macromolecules **2002**, 35, 4056
Macromolecules **2000**, 33, 5143
Macromolecules **1999,** 32, 7737
Macromolecules **1999,** 32, 7907

For large χN and modest dilations BCPs remain strongly segregated

Real Time Measurements of Probe Diffusion in CO_2 – Dilated PS Films

High Pressure Fluorescence NRET



(Gupta et al., Macromolecules 2003)

Silica Sol - Gel Chemistry

Hydrolysis

$$Si(OEt)_4 + H_2O \leftrightarrow Si(OEt)_3(OH) + EtOH$$

$$Si(OEt)_3(OH) + H_2O \leftrightarrow Si(OEt)_2(OH)_2 + EtOH$$

$$Si(OEt)_2(OH)_2 + H_2O \leftrightarrow Si(OEt)(OH)_3 + EtOH$$

$$Si(OEt)(OH)_3 + H_2O \leftrightarrow Si(OH)_4 + EtOH$$

Condensation

$$2\,Si(OH)_4 \leftrightarrow (OH)_3Si - O - Si(OH)_3 + H_2O$$

Ethanolysis

$$Si(OEt)_4 + Si(OEt)_3(OH) \leftrightarrow (OEt)_3Si - O - Si(OEt)_3 + EtOH$$

Overall

$$Si(OEt)_4 + 2H_2O \leftrightarrow SiO_2 + 4EtOH$$

- Extraction of Ethanol into CO_2 Drives Condensation Chemistry
- No Aging Periods, Rapid Synthesis

Synthesis of Mesoporous Silica – Generation 1
Precursor and Templates

Si Alkoxide

Tetraethylorthosilicate (TEOS), Others

Pluronic Surfactants $[-CH_2-CH_2-O]_m -[CH_2-CH(CH_3)-O]_n [-CH_2-CH_2-O]_m$

			Volume Fractions	
	m	n	PEO	PPO
Pluronic F127	100	65	0.68	0.32
Pluronic F108	133	50	0.784	0.216

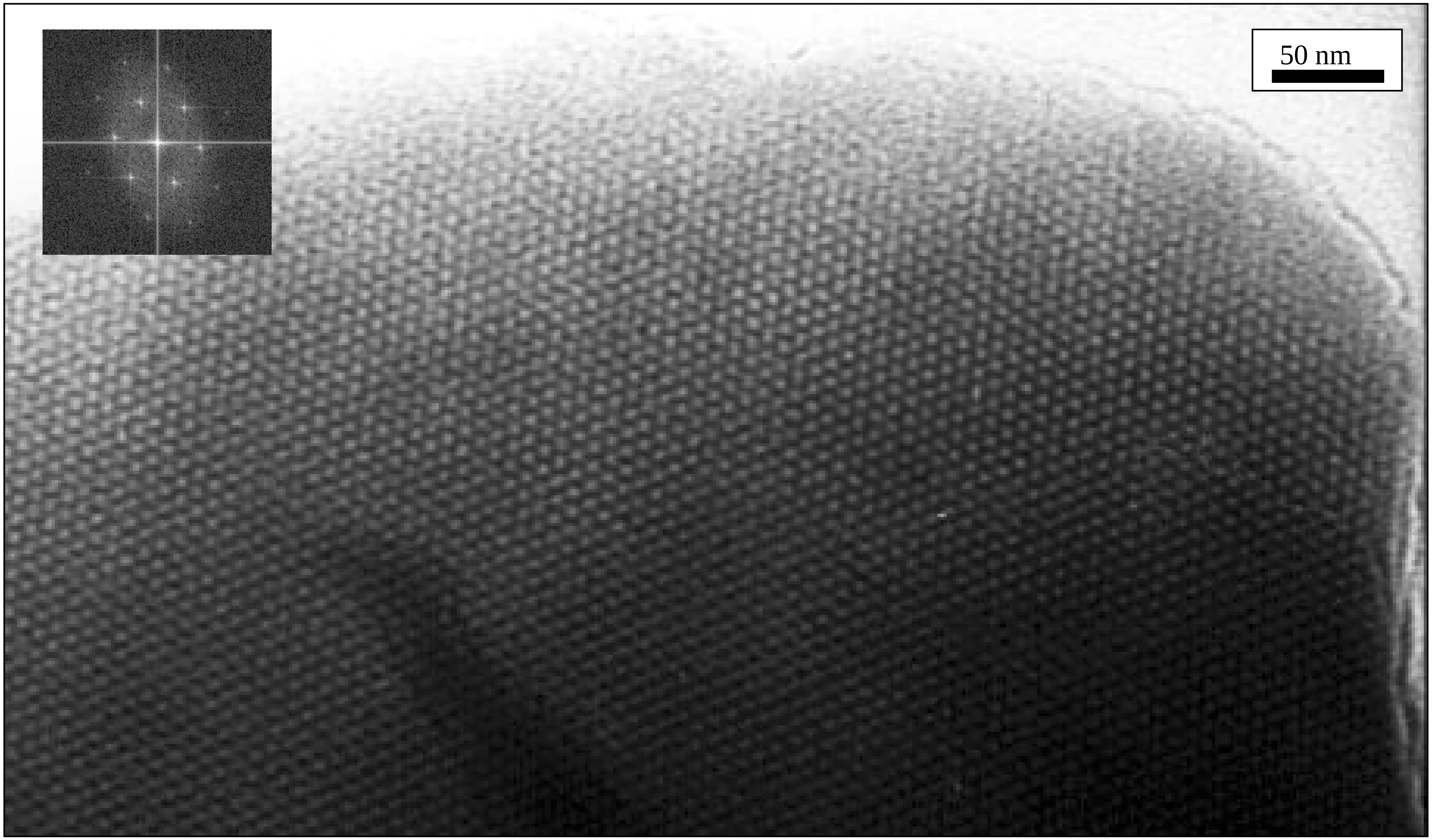
Brij Surfactants $C_nH_{2n+1}[-CH_2-CH_2-O]_m$

			Volume Fractions	
	n	m	PE	PEO
Brij 76	18	10	0.41	0.59
Brij 78	18	20	0.258	0.742

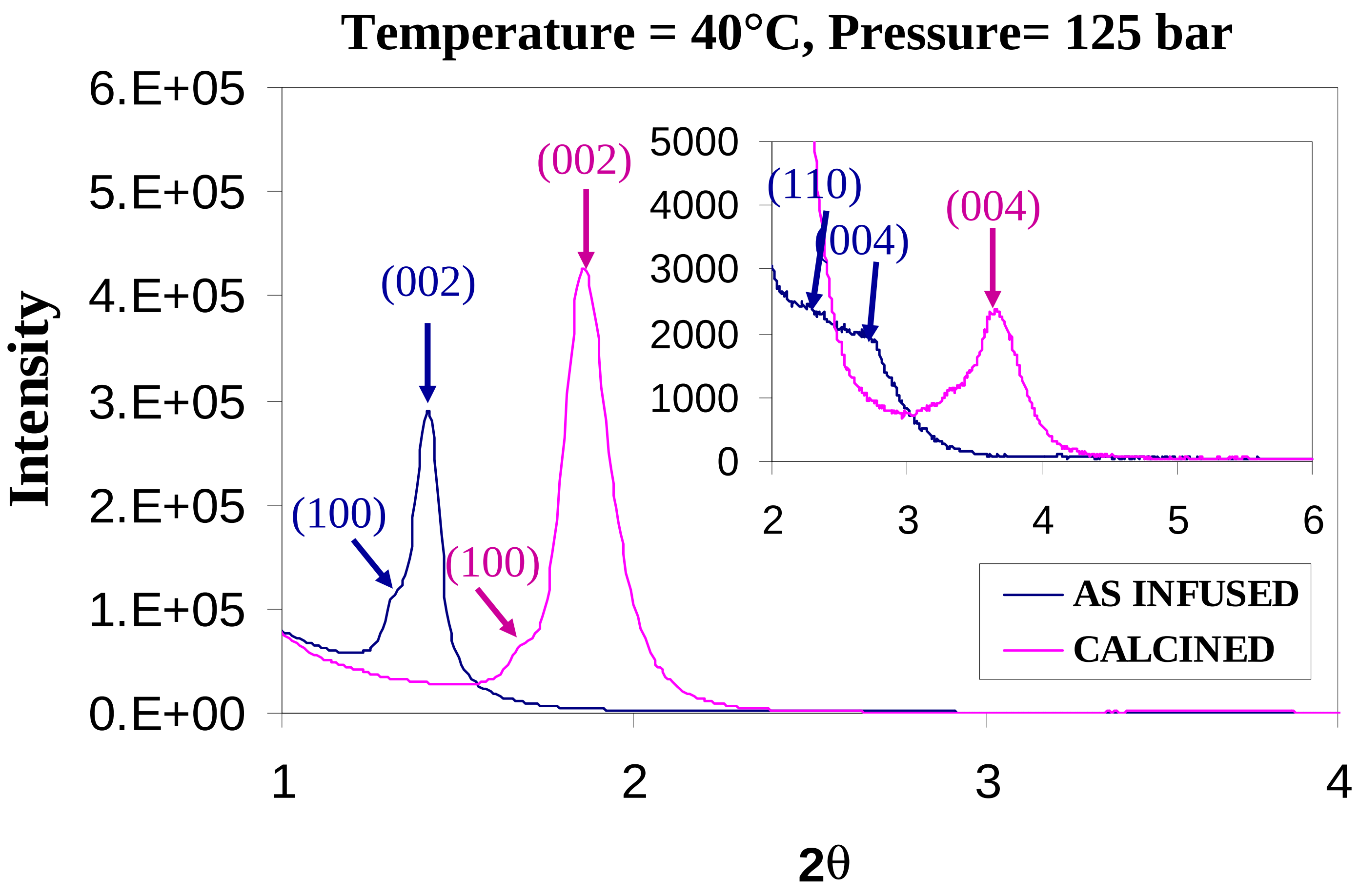
Other Hydrophilic/Hydrophobic Block Copolymers

Brij 76 Template / TEOS Infusion
40 ^{0}C, 125 bar

TEM Microscopy – Post Calcination



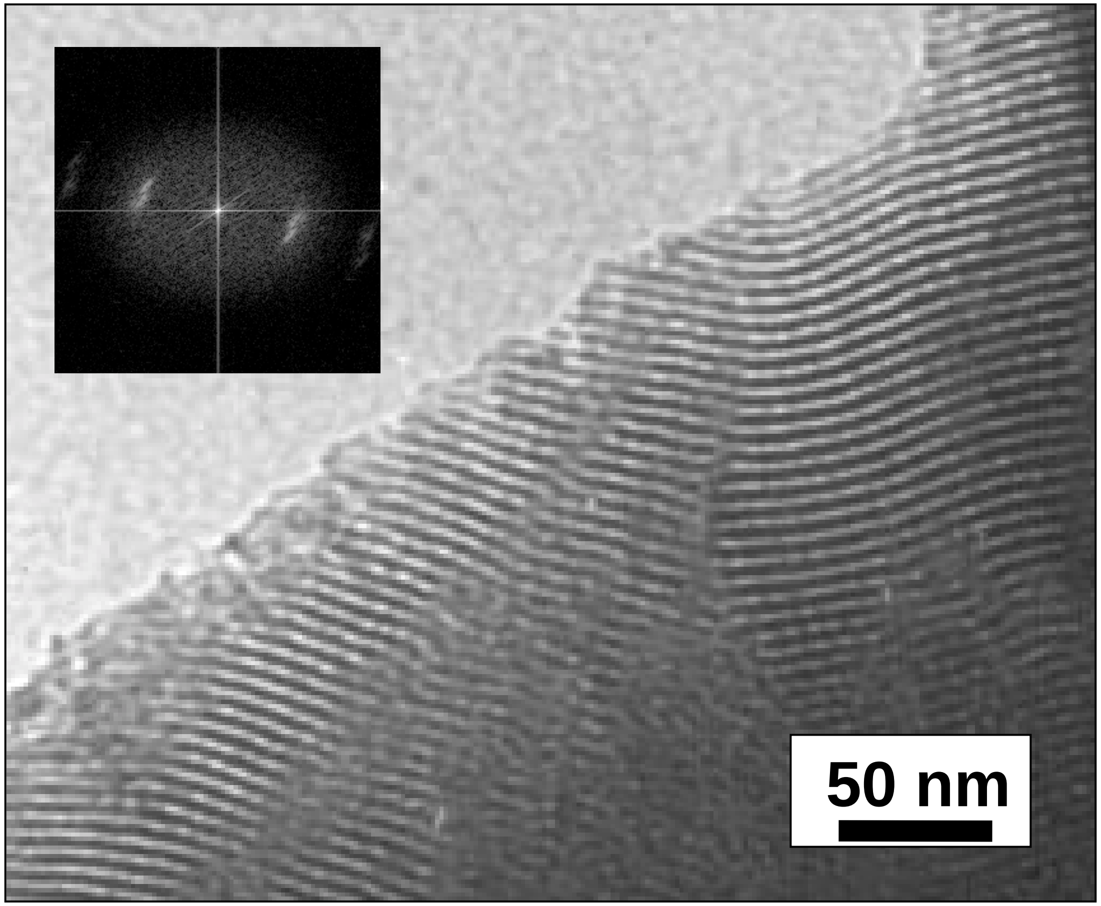
X-Ray Diffraction: TEOS Infusion into Brij 76 films



3-D Hexagonal Spheres

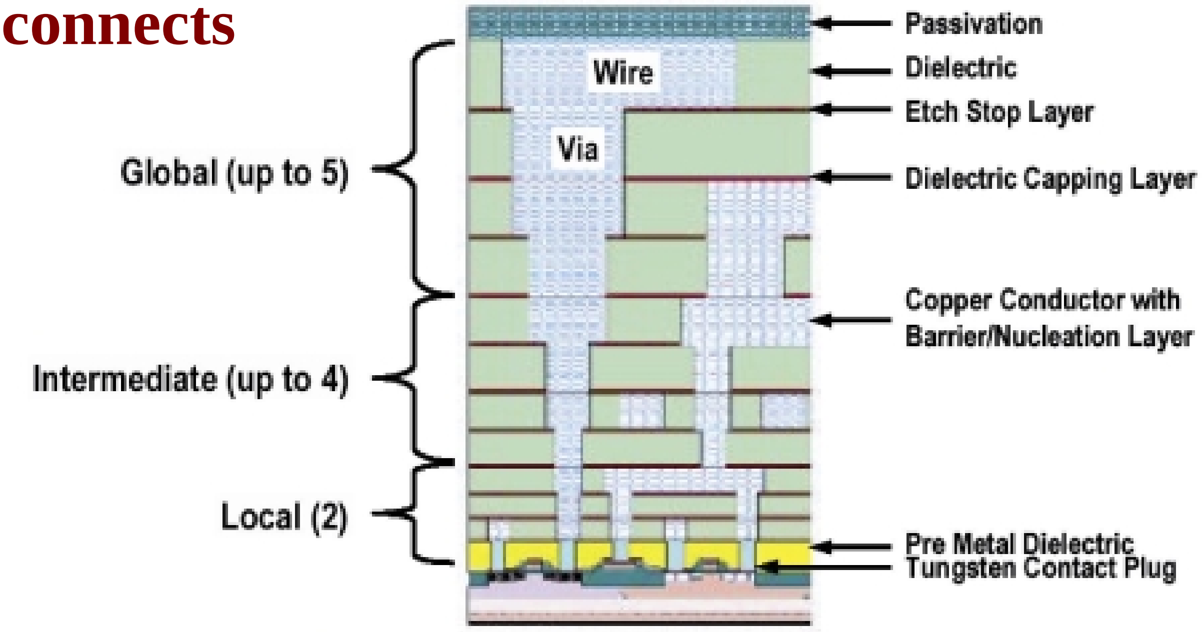
Brij 76 Template / TEOS Infusion
60 ^{0}C, 123 bar

Transmission Electron Microscopy
Post-Calcination



Device Fabrication Requires Robust Films

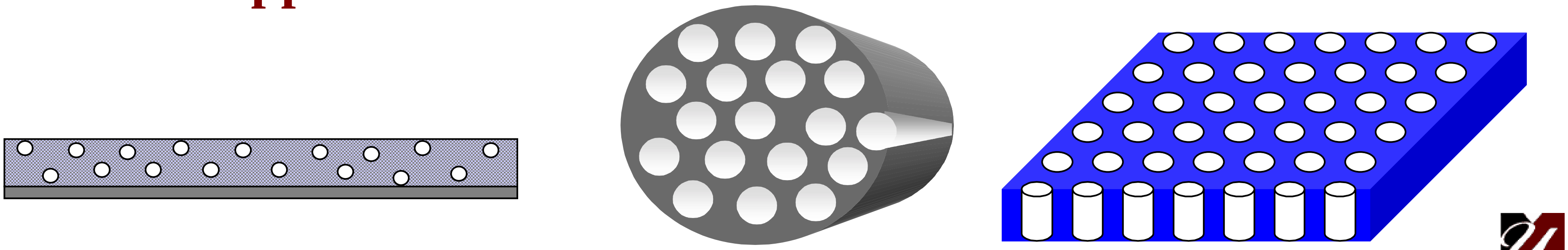
Cu Interconnects



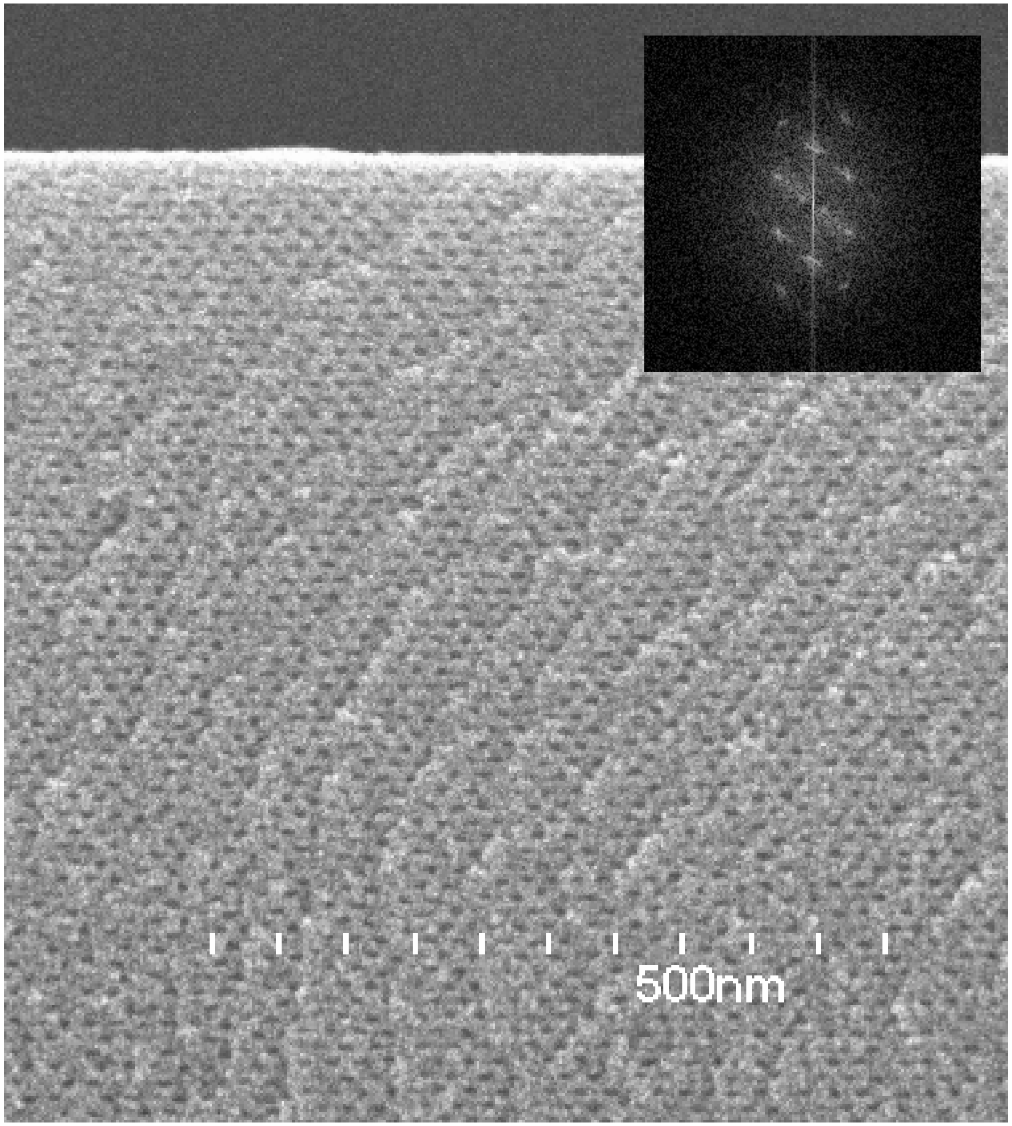
Cross-section of Hierarchical Scaling

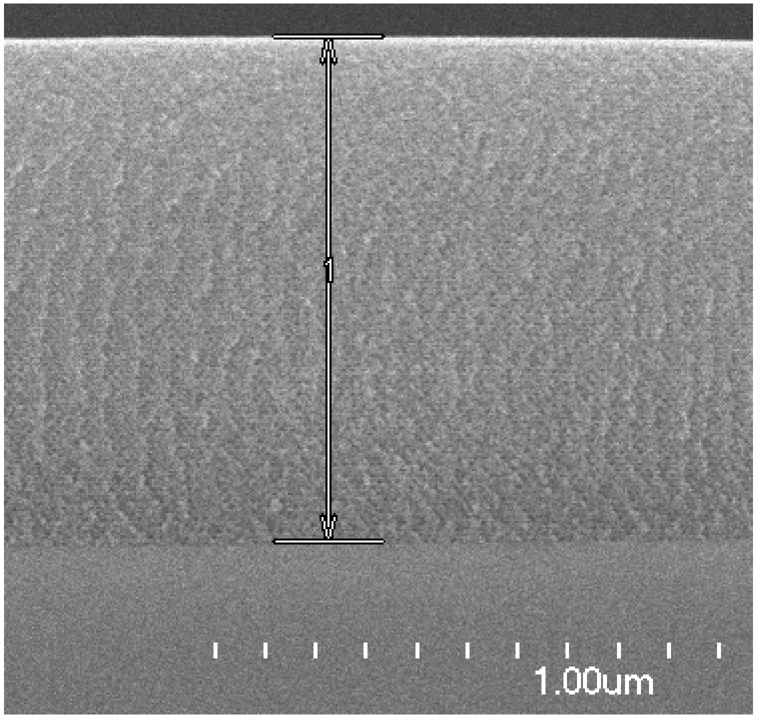
(2001 ITRS Roadmap)

Other Applications



Fabrication of Thick Films – TEOS/ F108 Template, 60 ^{0}C, 123 bar

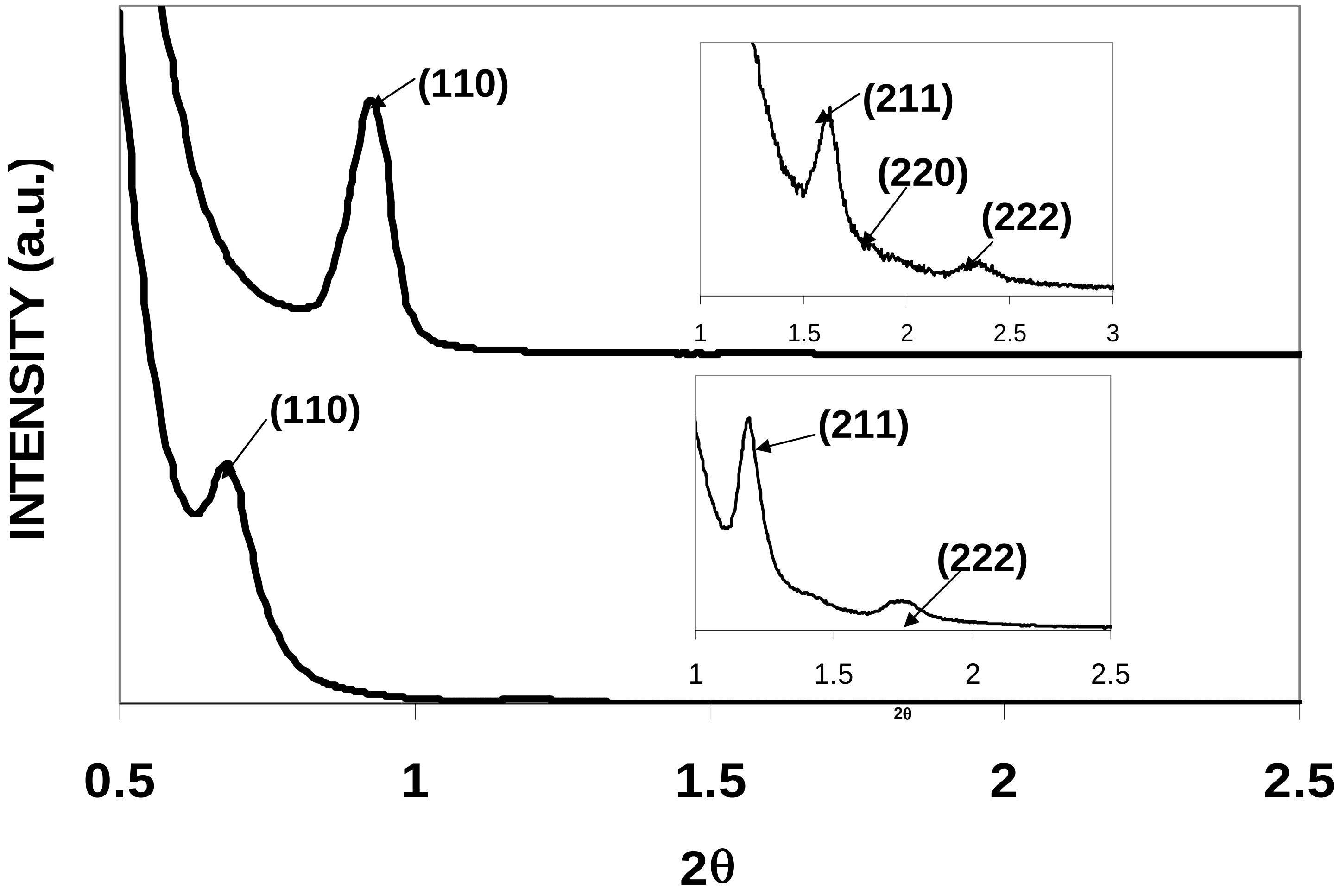




(Pai et al., Science, 303, 507, 2004)

Fabrication of Films – TEOS/ F108 Template, 60 ^{0}C, 123 bar

XRD Data

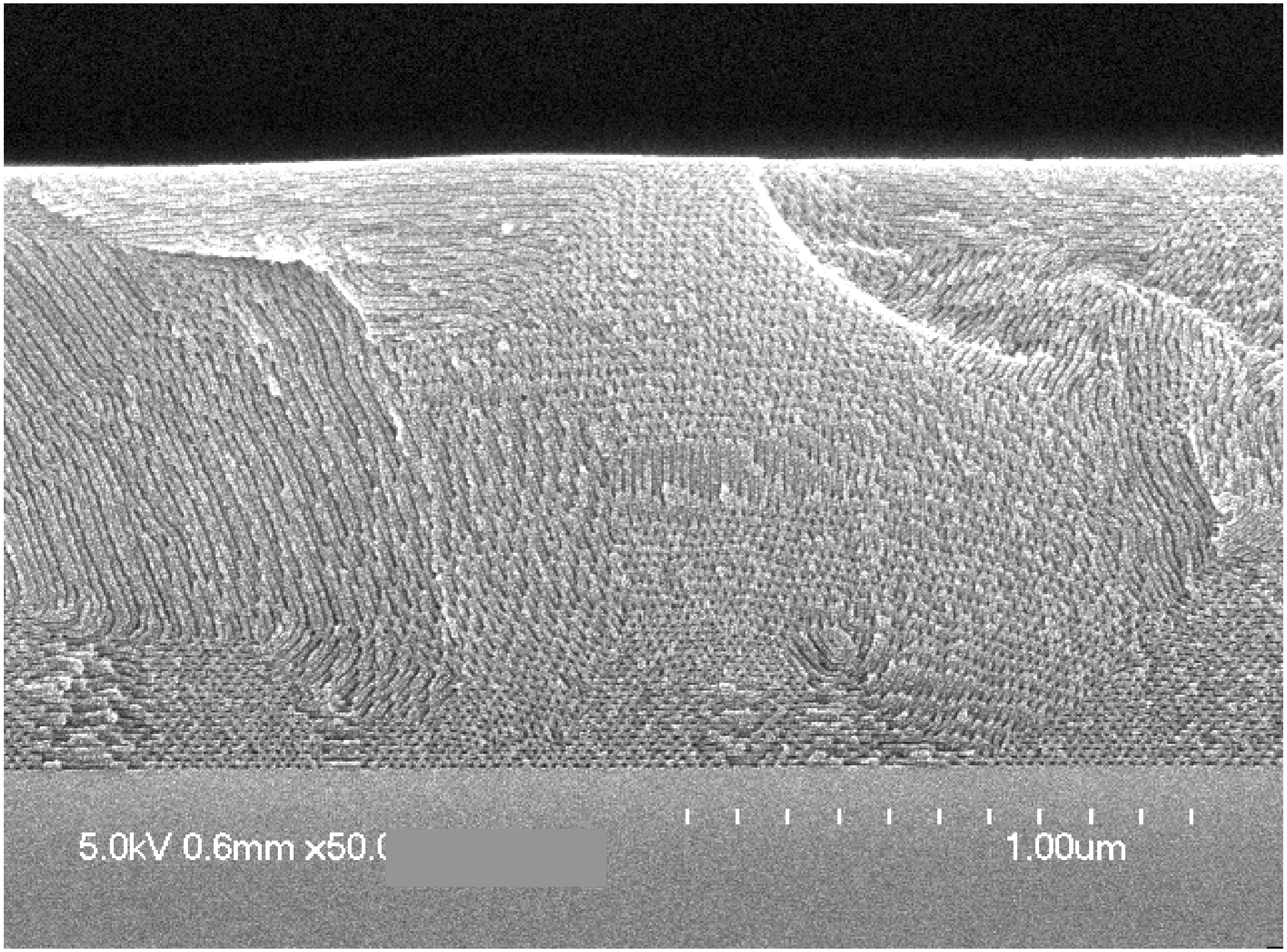


Calcined

As Infused

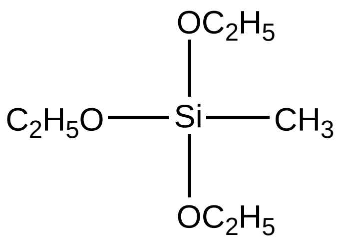
Fabrication of Thick Films – TEOS/ F127 Template

Cylindrical Morphology – Random Grains



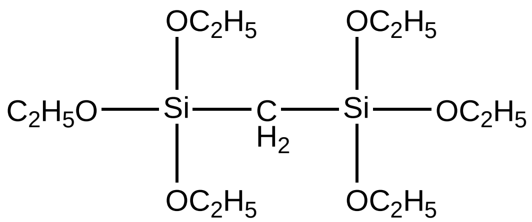
(Pai et al., Science, 303, 507, 2004)

Organosilicates for Low k - TEOS Derivatives



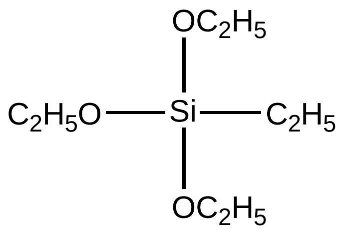
$C_2H_5O{-}\overset{OC_2H_5}{\underset{OC_2H_5}{Si}}{-}CH_3$

Methyltriethoxysilane (MTES)



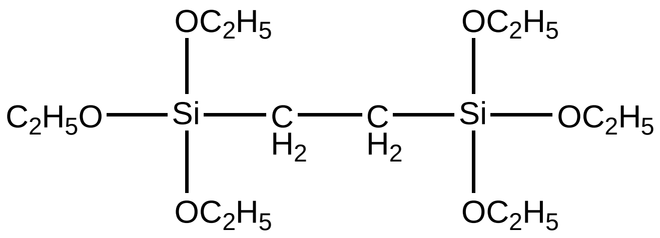
$C_2H_5O{-}\overset{OC_2H_5}{\underset{OC_2H_5}{Si}}{-}CH_2{-}\overset{OC_2H_5}{\underset{OC_2H_5}{Si}}{-}OC_2H_5$

Bis(triethoxysilyl)methane (BTESM)



$C_2H_5O{-}\overset{OC_2H_5}{\underset{OC_2H_5}{Si}}{-}C_2H_5$

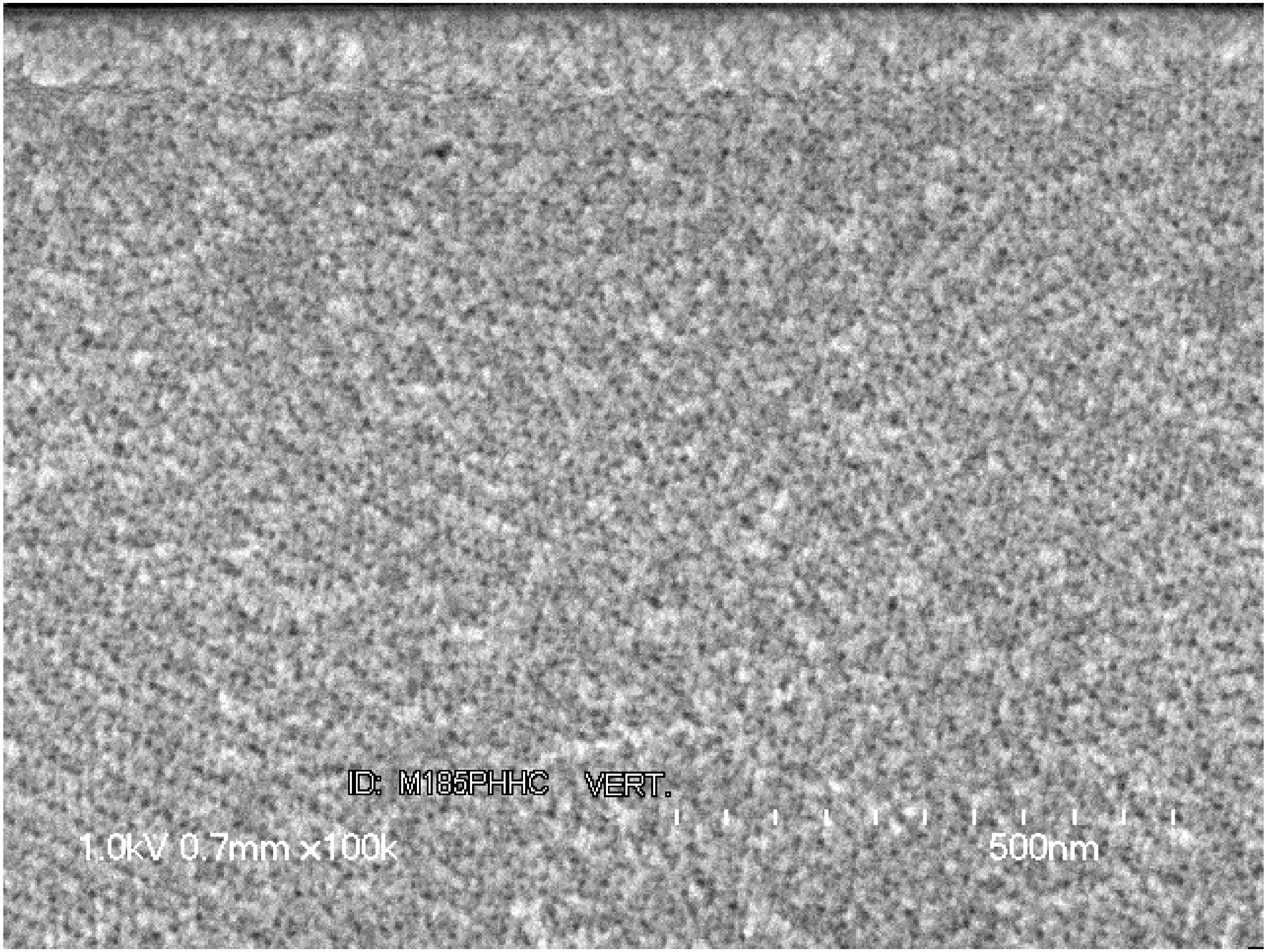
Ethyltriethoxysilane (ETES)



$C_2H_5O{-}\overset{OC_2H_5}{\underset{OC_2H_5}{Si}}{-}CH_2{-}CH_2{-}\overset{OC_2H_5}{\underset{OC_2H_5}{Si}}{-}OC_2H_5$

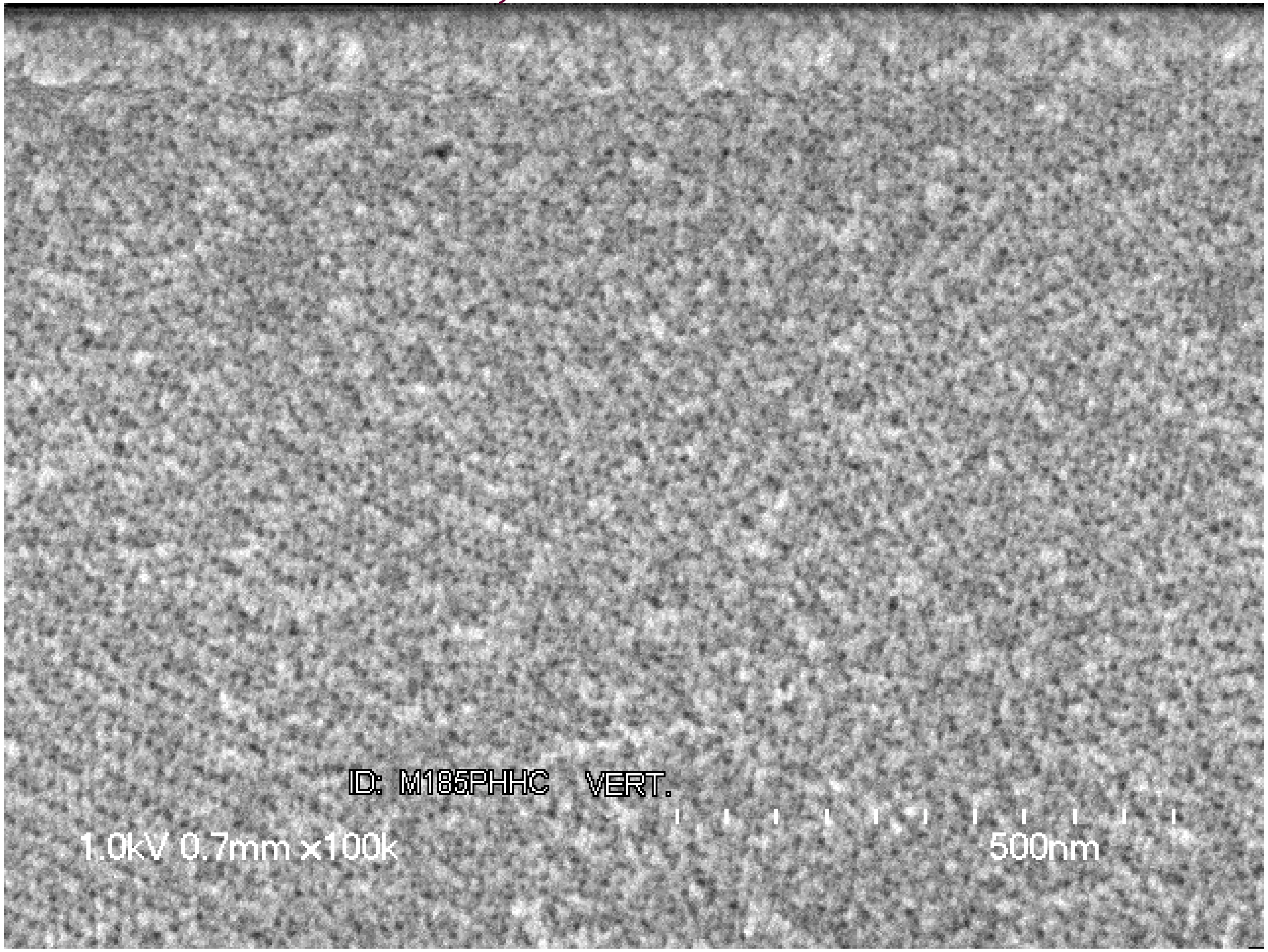
Bis(triethoxysilyl)ethane (BTESE)

F127 Template 40% MTES, 60% TEOS

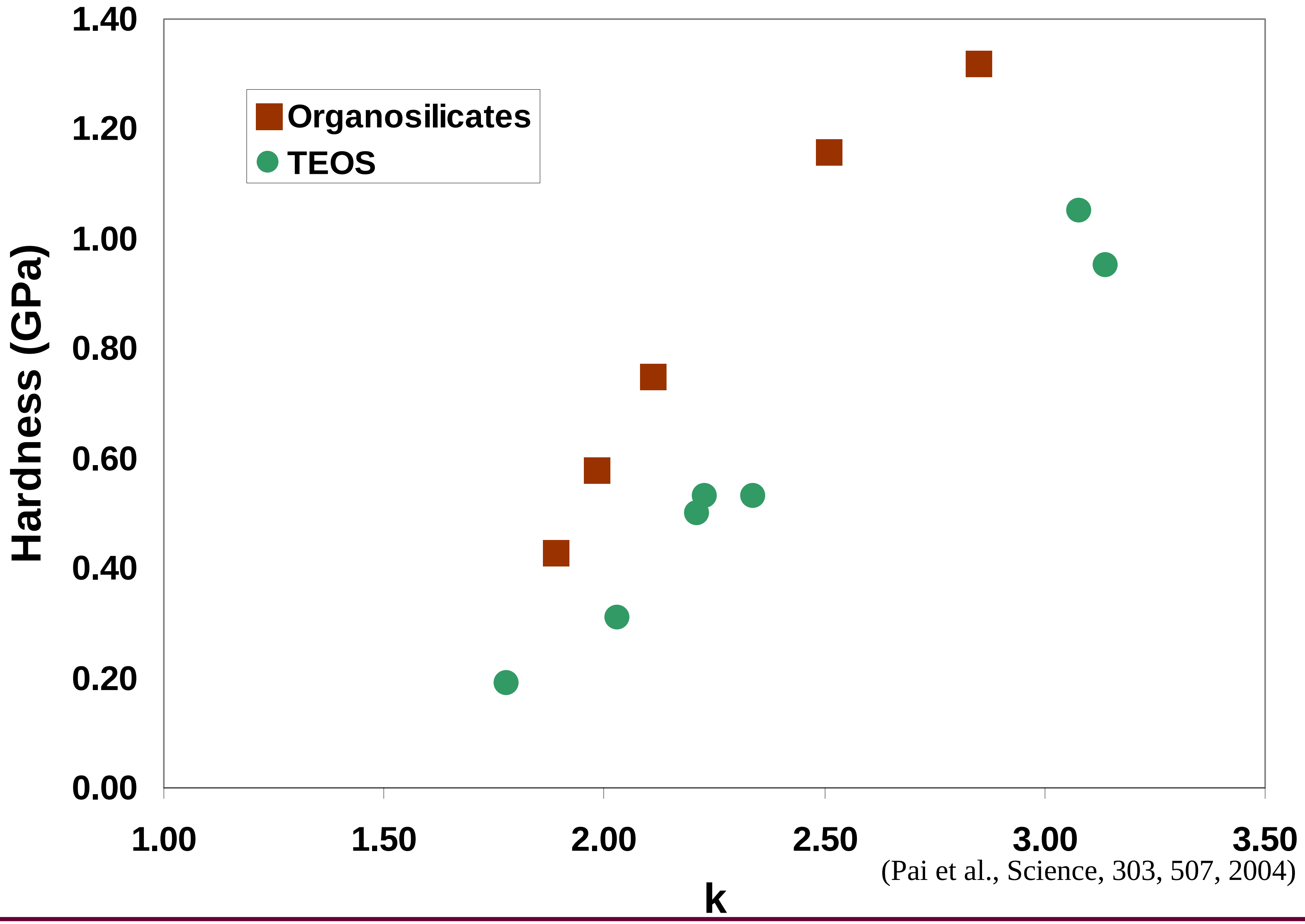


F127 Template 40% MTES, 60% TEOS Post – Processed at Novellus

k = 2.11, Hardness = 0.75 GPa

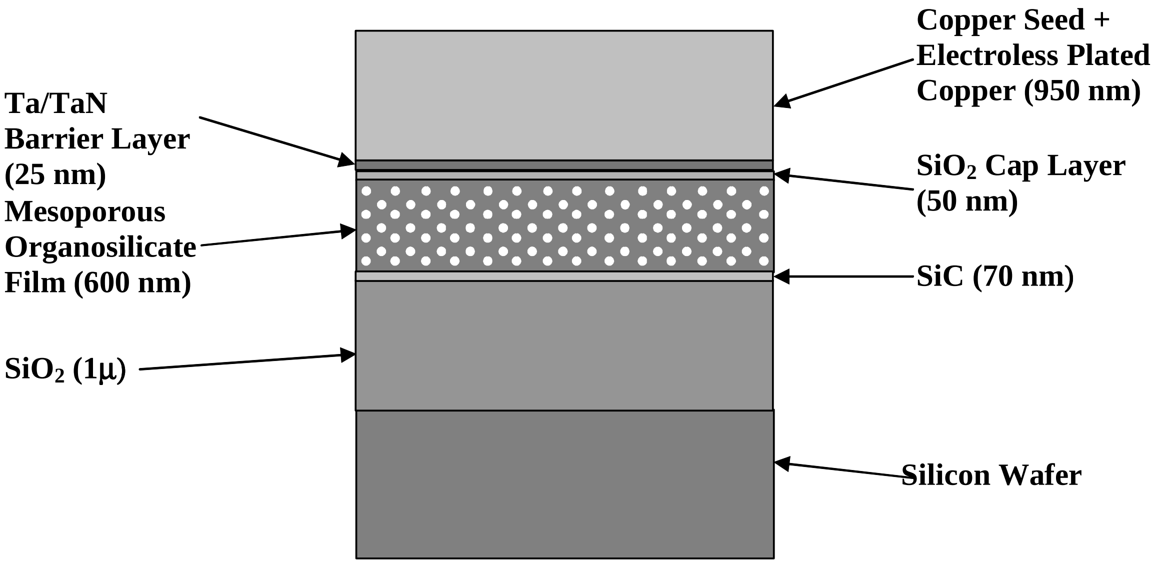


Mesoporous ULK Films Post-Processed at Novellus – Initial Results



(Pai et al., Science, 303, 507, 2004)

CMP on Planar 200 mm Wafers at Novellus



Ta/TaN Barrier Layer (25 nm)

Mesoporous Organosilicate Film (600 nm)

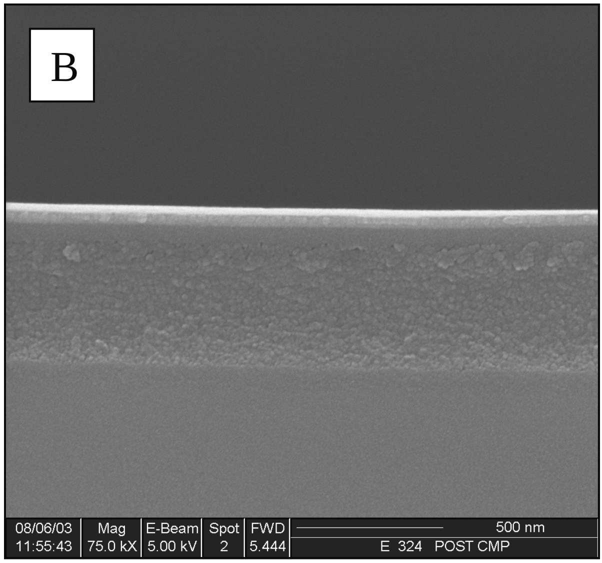
SiO_2 (1μ)

Copper Seed + Electroless Plated Copper (950 nm)

SiO_2 Cap Layer (50 nm)

SiC (70 nm)

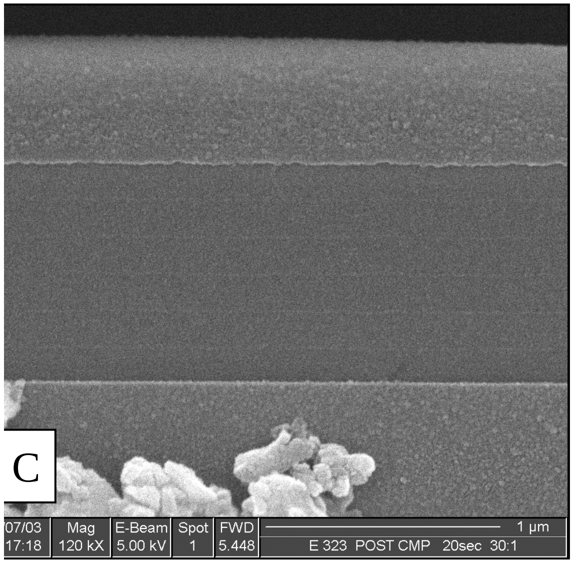
Silicon Wafer



Ta/TaN barrier layer

SiO_2 cap layer

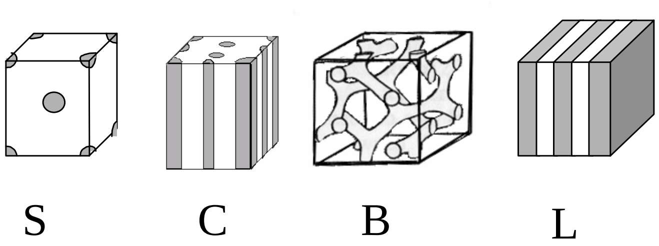
Mesoporous Film

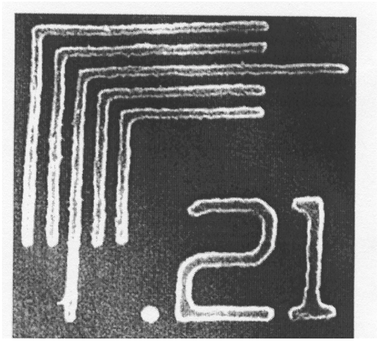


(Pai et al., Science, 303, 507, 2004)

What’s Next? - Direct Preparation of Hierarchical Structures

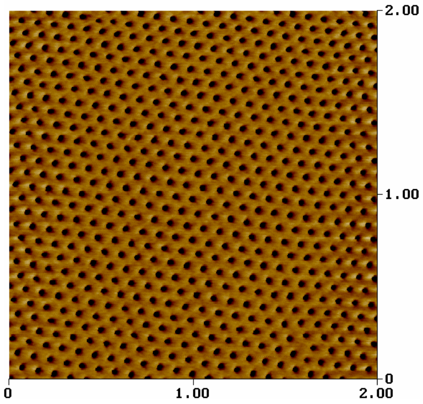
Structural Control at the Local and Device Level is Relatively Easy in Block Copolymer Films / Melts - But Difficult in Metal Oxides





Lithography

193 nm BCP Resist Developed in CO_2
(Ober, 2000)

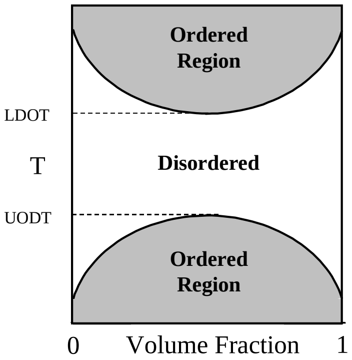


Domain Alignment

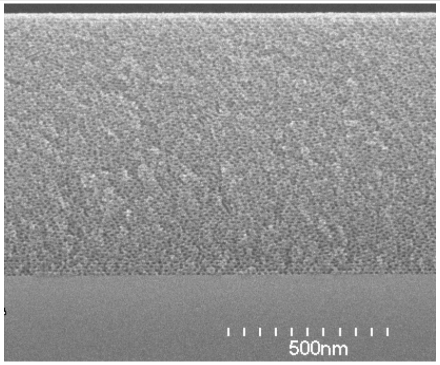
Aligned PS-PEO Cylinders
(Russell Group - UMass, 2003)

Ideally: Impart Structure to BCP Melt – Replicate in Oxide

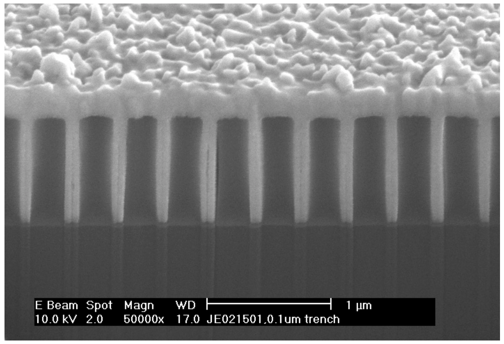
Acknowledgments



(*Macromolecules*, 2002)



(*Science, 2004*)



(*Science*, 2001)

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