Methods and Kinetics of Copper Etching Using hfacH in Supercritical CO_2

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ERC/SRC TeleSeminar

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Outline

Introduction

- Definition of SCF, P-V behavior for pure fluid
- SCF density inhomogeneities

Supercritical carbon dioxide

- $scCO_2$ properties & ESH
- $scCO_2$, integrated circuits, & copper

Kinetic Investigation

- Experimental apparatus
- Sample preparation and analysis

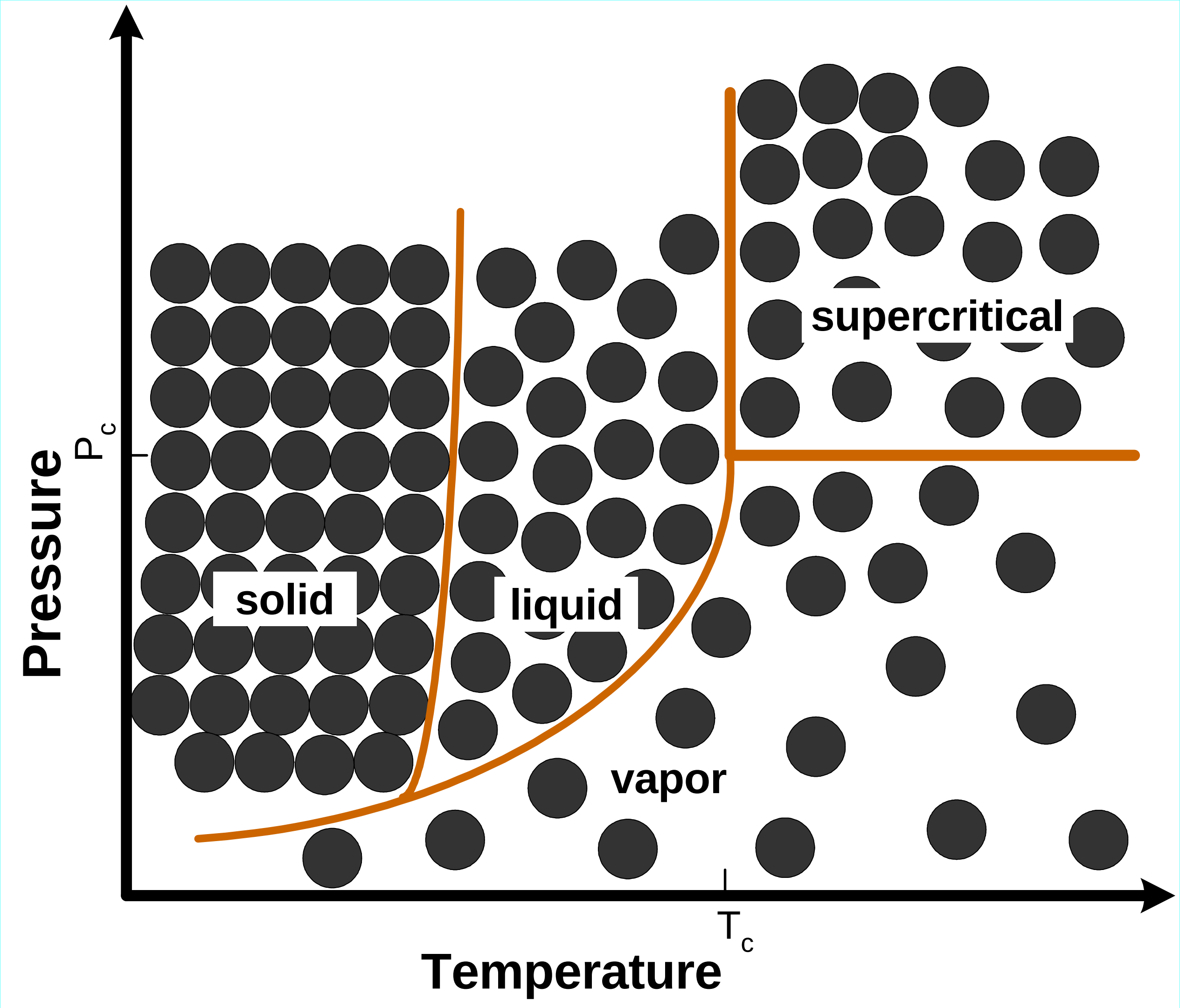
CuO Etching using hfacH

- Arrhenius Analysis
- Rate law for etching

Conclusion

Supercritical Fluids

phase diagram



P-T diagram of pure fluid

At $T > T_c$ and $P > P_c$:

fluid has properties intermediate between those of gas and liquid

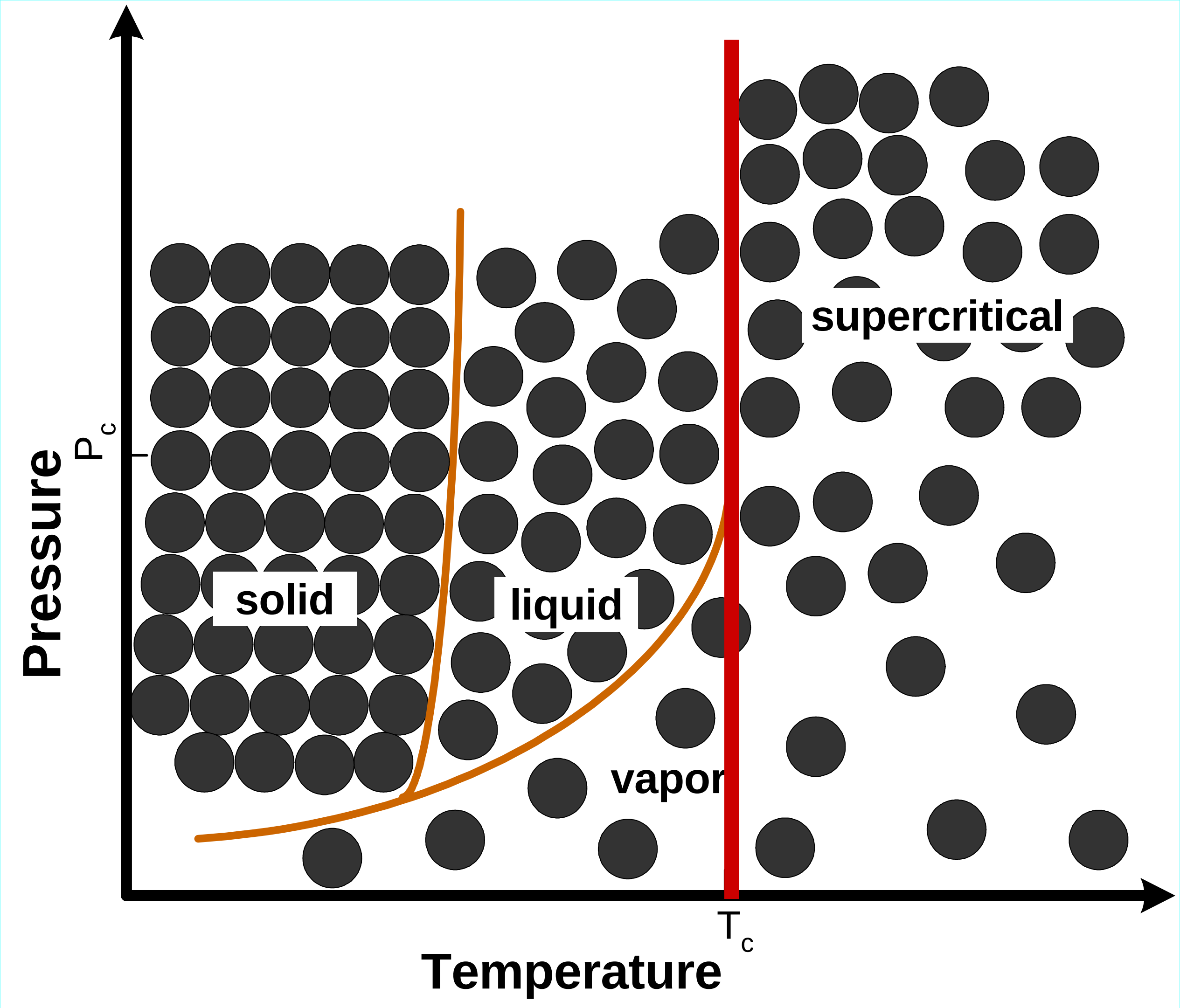
Recall reduced parameters:

$T_r = T/T_c$, $P_r = P/P_c$,

$\rho = \rho/\rho_c$

Supercritical Fluids

definition of SCF



P-T diagram of pure fluid

$SCF \equiv T > T_c$

Where $\Delta P \rightarrow$ continuous $\Delta\rho$

$\downarrow$

'tunable' density

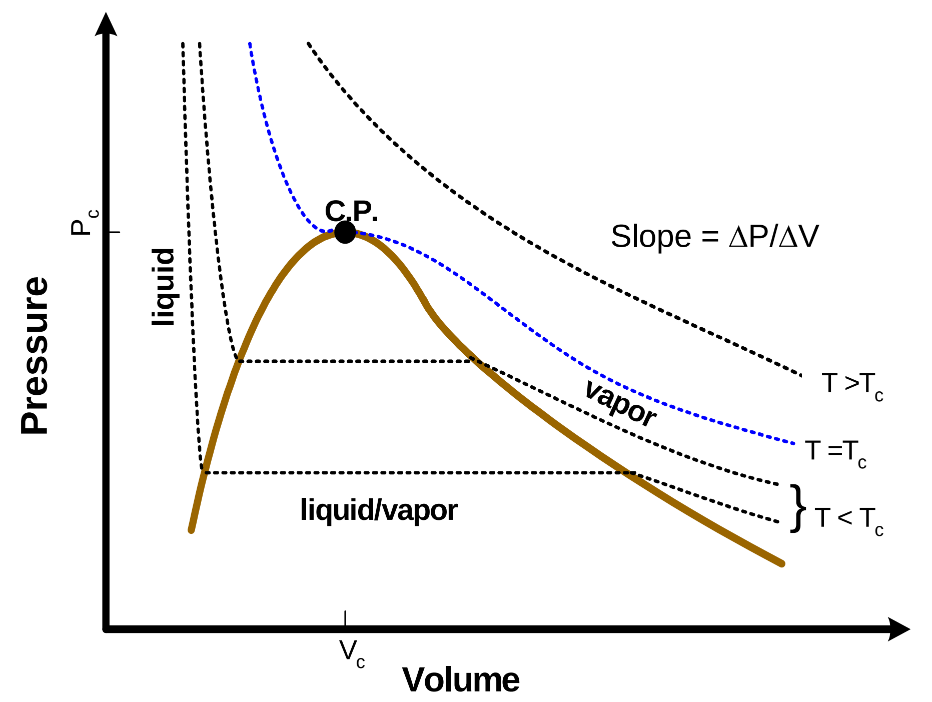
unique to region where $T > T_c$

&

fluid has properties intermediate between those of gas and liquid

P-V behavior of a pure fluid

compressibility



P-V diagram of a pure fluid

Isothermal Compressibility

$$\kappa = -(1/V)\,(\partial V/\partial P)_T$$

Compare κ at isotherms:

- $T < T_c$, $\kappa \rightarrow 0$
- $T > T_c$, $\kappa \rightarrow O(\kappa^{IG})$
- $T \rightarrow T_c^+$, $\kappa \rightarrow \infty$

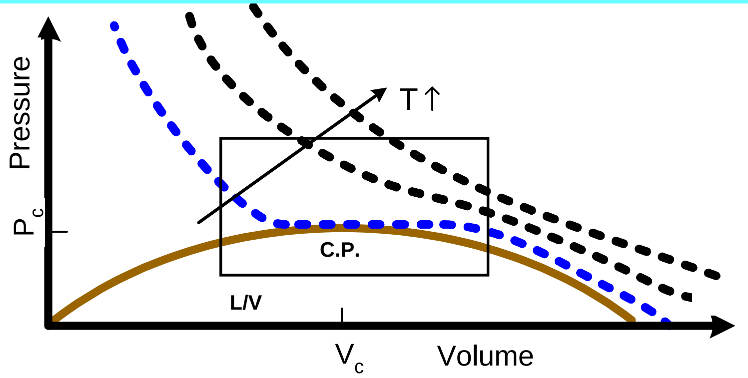
κ is discontinuous at T_c

- $\kappa \rightarrow \infty$ at critical isotherm
- Theory of Critical Fluids

Fisher. *Rev. Mod. Phys*, **70**, 653, 1998.
Fisher. *J. Math. Phys.*, **5**, 944, 1964.

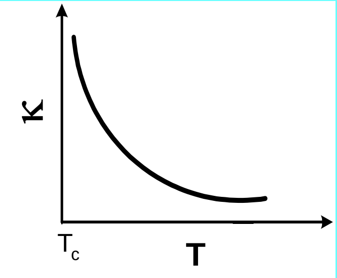
Physical Results of large κ:

- As κ ↑, fluid compression is easier
- Density varies strongly with changes in temperature and pressure
  - Macroscopic Δρ – bulk
  - Microscopic Δρ – local enhancements



Tucker. *Chem Rev.*, **99**, 391, 1999.

Macroscopic Density Variations



$$\kappa = -(1/V)\,(\partial V/\partial P)_T \rightarrow \infty$$

Bulk density variations:

- Compression (↑ ρ) requires little energy
- Large Δρ throughout entire fluid volume
- κ is large and changes rapidly with temperature as $T \rightarrow T_c^+$ so:

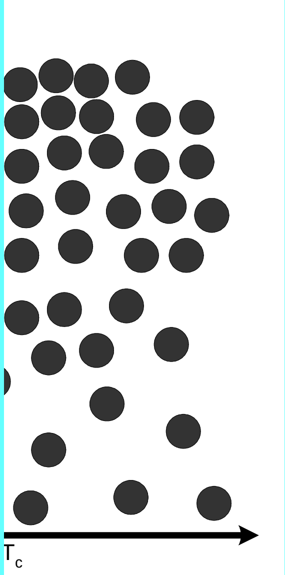
  ΔV/ΔT & ΔV/ΔP very large
- Dramatically affects solvent properties and reaction rates:
  - dielectric – ε,
  - transport – μ, $\mathcal{D}$
  - acidity, solubility

  e.g., scH_2O (T_c=374 ºC) at 380 ºC (T_r = 1.02):

  as P: 210 → 270 bar:

  ρ: 0.15 → 0.54 g/mL

  ε: 2 (nonpolar) → 10 (polar)
- Readily detectable as f(T, P)



Bulk density variations

Tucker. *J. Phys. Chem. B*, **102**, 2437, 1998.

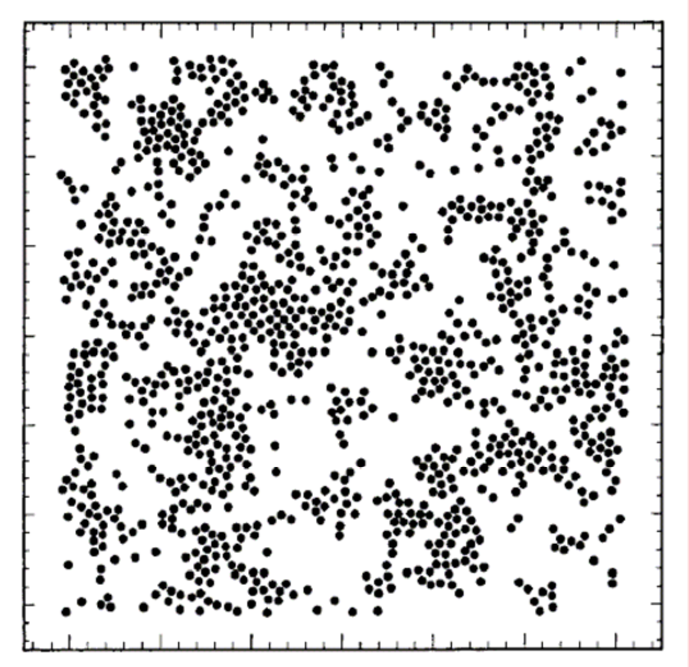
Microscopic Density Variations

High $\kappa = -(1/V)(\partial V/\partial P)_T$

Variations in local density:

- Localized to small regions within the bulk fluid
- For localized compression (molecular coalescence):

  Entropy↓ ≈ Energetic↑
- Molecules may coalesce (disperse) in small regions of increased density → localized density augmentations (depletions)
- Affect same bulk properties
  - dielectric
  - transport
  - solvation
  - diffusion & reaction rates
- Affected by T, P, & solute concentration
- Localized density enhancement or depletions
- Pure fluids or mixtures



Configurational 2-D ‘snapshot’ of a pure fluid, w/ T_r=1.1, P_r = 0.86

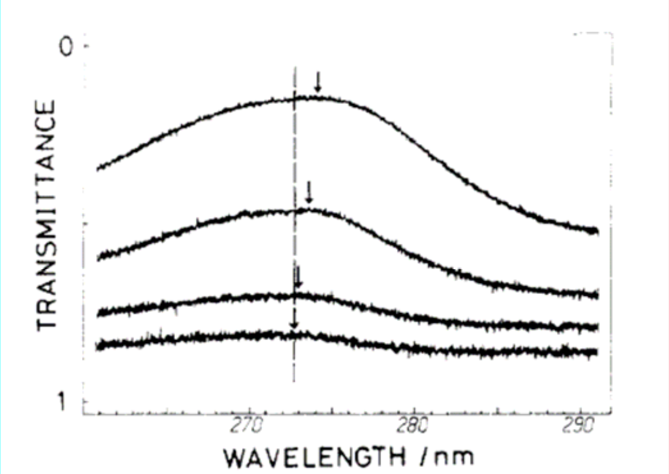
Tucker. *J. Phys. Chem. B*, **102**, 2437, 1998.

Microscopic Density Variations

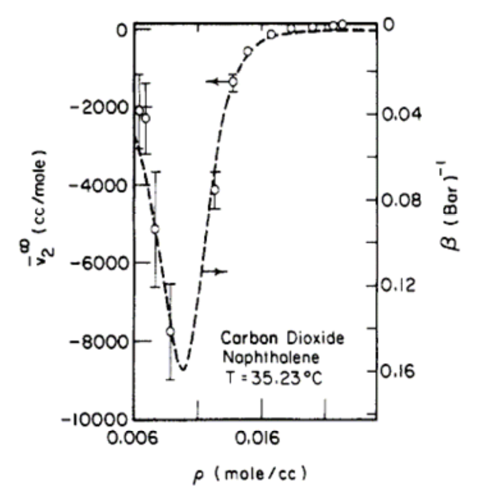
Experimental Evidence

Spectroscopic Methods:

- Solvatochromic shift: changes in UV absorption maxima of a solute due to changes in polarity or density of the solvent.
- Correlate solvatochromic shifts at known solute conc to localized density enhancements, as total density remains ~ constant.
- Shorter-range enhancements – "direct"
- Centralized: - extend to range of solute-solvent intermolecular potential



UV absorbance for peak shifts for DMABN in sc ethane



Estimated partial volume as a function of compressibility as a function of reduced density

Partial Molar Volume Data:

- Correlate density measurements with conc. of solute at infinite dilution

$$v_2^{\infty} = (\partial V / \partial n_2)_{T,P}\,\infty$$

- Negative v_1^{∞} corresponds to positive density enhancements
- Longer-range enhancements – "indirect"
- Long-range:
  - Outside of range solute-solvent intermolecular potential
  - As T → T_c^+, divergent

Eckert et al. *J. Phys. Chem*, **90**, 2738, 1986.
Morita et al. *J. Phys. Chem*, **94**, 6420, 1990.

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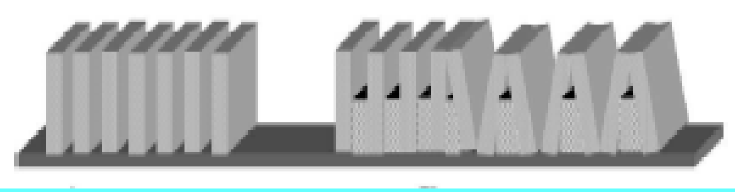
scCO$_2$ Physical Properties

thermodynamic/kinematic properties

Solvent	**Viscosity** (cP)	**Surface Tension** (mN/m)	**Density** (kg/m^3)	**Tc** (˚C)	**Pc** (bar)
scCO2	0.03	~ 0	~ 300-800	31.1	73.8
IPA (liq)	2.86	20.9	785	235.1	47.2
water (liq)	1.0	72.0	1000	373.9	220.1
methanol (liq)	0.55	22.1	791	239.5	80.9
TCE (liq)	0.57	25.2	1462	271.1	50.2

- Gas-like mass transfer properties (diffusivity, viscosity)
- Liquid-like solvating capability (density)
- Diffusivity comparable to gases
- Low surface tension
  - nanoscale penetration
  - structure integrity



pattern maintenance vs. pattern collapse

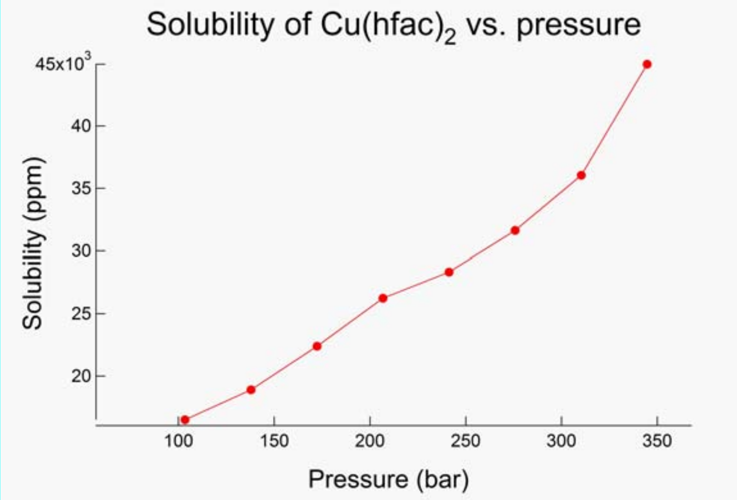
J. Phys. Chem. Ref. Data. **1**, 841, 1972
Ind. Eng. Chem. Res., **39**, 12, 2000
Microelec. Engin., **65,** 145, 2003

$scCO_2$ Physical Properties

tunability / general

Tunability

- Control density & solvent properties with variations in pressure
  - solubility
  - viscosity
  - dielectric properties
- Explore special behavior in near-critical region
  - solubilities
  - diffusivities
  - reaction rates



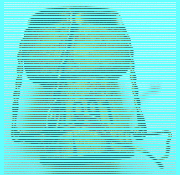
General CO_2 properties

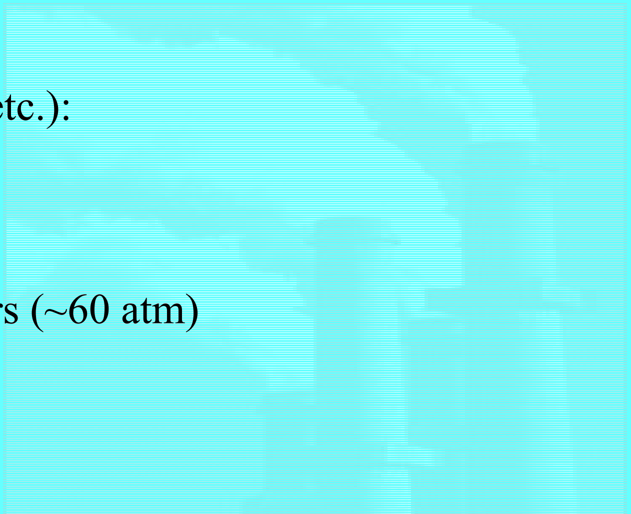
- Molecules with low vapor pressures are soluble
- Dielectric properties similar to organic solvents
- Unreactive under most conditions
- Inexpensive and reusable
- Nonflammable, nontoxic, nonaqueous

Inorganic Chemistry, **34,** 23, 1995
Agnew. Chem. Res., **40**, 518, 2001
Ann. Rev. Energy. **8**, 275-306, 2001

scCO$_2$ ESH

- Health
  - accumulates in confined areas because it is heavier than air, work space must be well-ventilated
  - may cause asphyxiation at concentrations > 5%
  - large quantities of CO$_2$ compressed into small volumes
    - 1 liter scCO$_2$ at 3000 psi and 50 ºC generates roughly 440 liters gas in atmosphere conditions
- Safety
  - pressure hazards:
    - - champagne bottle ≈ 6 bar
    - - scCO$_2$ ≥ 74 bar





  - special equipment (seals, pumps, fittings, valves, etc.):
    - - must be rated to accommodate high pressures
    - - must be inert to dissolution capabilities of scCO$_2$
    - - must have safety pressure release mechanisms
  - liquid CO$_2$ is stored on-site in pressurized cylinders (~60 atm)
- Environment
  - CO$_2$ is a green house gas
  - high-volume manufacturing should recycle CO$_2$ streams
  - 82% of commercially used CO$_2$ is a by-product from other industries
  - Additives must be separated from CO$_2$ streams
  - CO$_2$ must be transported onsite in trucks

www.vinoinrete.it

$scCO_2$ Applications

industrial applications

- Food processing:
  - Non-toxicity of solvent
  - Extraction of caffeine, oils, cholesterol, and spices

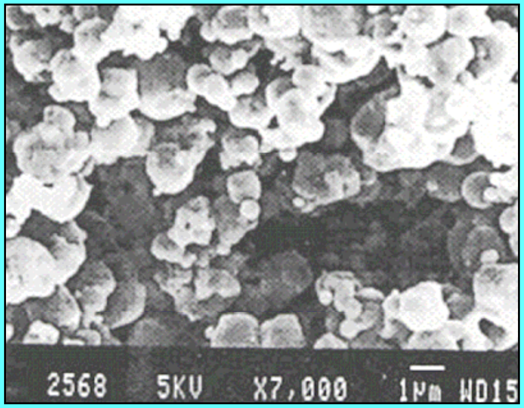
    Food Chem, **52**, 345, 1995, *Chem. Ind.*, **21**, 831, 1996,
    J. Supercrit. Fluids **9**, 3, 1996.

- Pharmaceutical synthesis/separation:
  - Low T_c amenable to processing biomolecules
  - Particle size control

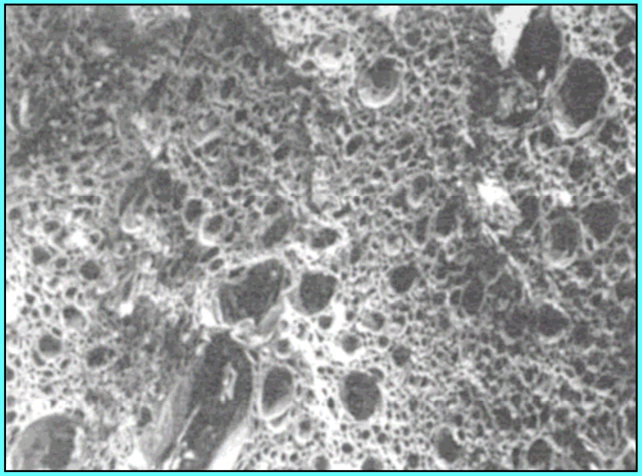
    J. Pharm. Sci., **86**, 8, 1997[a], *Int. J. Pharm.*, **292**, 1, 2005.

- Polymer and particle design:
  - Ease of separation through depressurization
  - Particle size control
  - Inertness of solvent

    J. Mat. Sci., **10**, 207, 2000, *Chem. Rev.*, **99**, 543, 1999,
    J. Mat. Chem. **10**, 207, 2000[b].



[a] Lysozyme particles formed in $scCO_2$



[b] Porous polyurethane foam formed in $scCO_2$

$scCO_2$ Applications

integrated circuit fabrication – water & energy

- 200 mm wafer production:
  - A fab producing 40,000 200 mm wafers/month consumes ~ 2-3 million total gallons water/day[a]
  - One 8-inch wafer requires ~ 250 gallons UPW[b]
- 300 mm wafer production: [c]
  - One 300 mm wafer requires ~ 53 L UPW in wet-bench processing
  - Requires 5-7 L UPW/cm^2 of Si → ~ 900-1200 total gal UPW/wafer
- 1 cm^2 of fabricated wafer: [d]

Requires:	Produces:
- 20 L water	- 17 kg wastewater
- 45 g chemicals	- 7.8 kg solid waste
- 1.5 kWh/cm^2 electricity	
- 1 MJ/cm^2 fossil fuels	

a. *Semicond. Intern.* **21**, 2, 71, 1998
b. *Electrochem. Soc. Proc.* **99**, 193, 1999.
c. *Semicond. Intern.* **27**, 4, 55, 2004
d. *Environ. Sci. Technol.*, **36**, 5504, 2002

- Intel uses 112 million gal of fresh water each week for all manufacturing operations worldwide.[e]
- *The New York Times* requires over 200 million gal of water/week to print the Sunday edition.[e]

e. *Environ. Sci. Technol.*, **38**, 1915, 2004

$scCO_2$ Applications

semiconductor industry processes

- Photoresist development – U. of Cornell/MIT

  Chem. Mater., **15**, 4893, 2003, *Chem. Vap, Dep.* **7**, 195, 2001.

- Photoresist drying – U. of Wisconsin/IBM

  JVST B, **18**, 3313, 2000.

- Spin coating – U. of North Carolina

  Ind. Eng. Chem. Res., **43**, 2113, 2004.

- Metal and low-*k* film deposition – U. of Mass Amherst, U of Idaho

  Chem. Mater., **15**, 83, 2003., *Chem. Mater.* **16**, 2028, 2004, *Science*, **294**, 141, 2001, *Science*, **303**, 507, 2004.

- Low-*k* film damage repair – U. N. Texas/TI, U. of Missouri/TEL/SSI, U. of Arizona

  J. Vac. Sci. Technol. B, **22**, 1210, 2004.

- Low-*k* film pore capping – U. of N. Texas/TI, U. of Arizona

  Microelec. Engin., **80**, 17, 349, 2005.

- SiGe surface preparation – U. of Arizona

  Mat. Sci. Semi. Proc., **8**, 1-3, 231, 2005.

- **Cu etching – U. of North Carolina, U. of Arizona**

  J. Am. Chem. Soc. **125**, 4980, 2003, *Chem. Mat.*, **17**, 1753, 2005

scCO_2 & Integrated Circuits

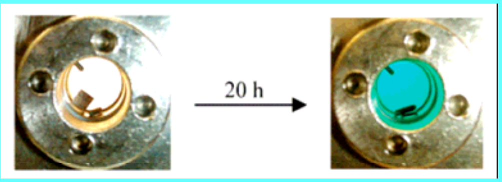
copper etching using scCO_2

Copper Etching in scCO_2 has been demonstrated

Etchant Solutions for the Removal of Cu(0) in a Supercritical CO2-Based “Dry” Chemical Mechanical Planarization Process for Device Fabrication

“Both liquid and supercritical (sc) CO_2 have significant potential for replacing current aqueous and organic CMP solvents.”

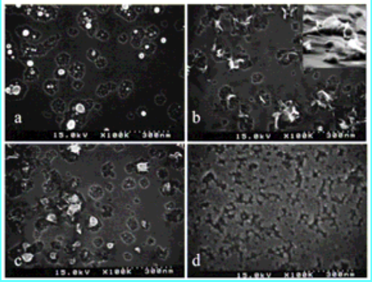
- *JACS*, **125**, 4980, 2003



Removal of Copper from Silicon Surfaces Using Hexafluoroacetylacetone (hfacH) Dissolved in Supercritical Carbon Dioxide

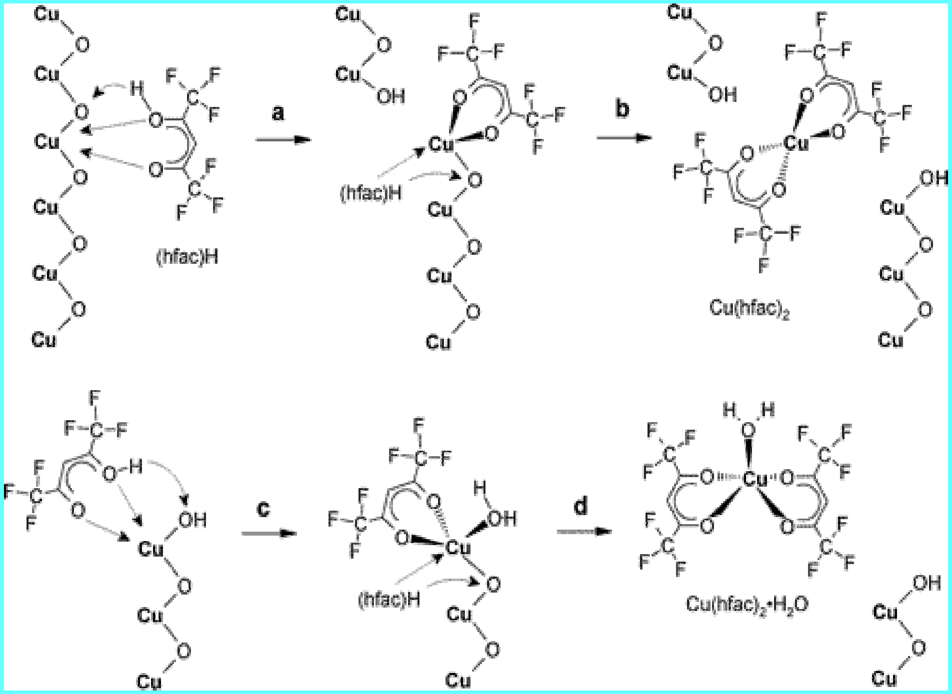
“ . . . scCO_2 processing is industrially viable for cleaning Cu from surfaces and perhaps for etching Cu.”

- *Chem. Mat.*, **17**, 1753, 2005



Copper etching in $scCO_2$

project significance



Chem Mat., **17**, 1753, 2005

$$CuO + hfacH \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Cu\text{-}hfac + {}^*OH$$

$$Cu\text{-}hfac + hfacH + {}^*OH \xrightarrow{k_2} Cu(hfacH)_2 + HOH$$

$$r_{etching} = r_{Cu(hfac)_2}$$

$$r_{etching} = k_2 \frac{k_1}{k_{-1}} [CuO][hfacH]^2$$

I. Demonstrate viability of copper etching/removal in $scCO_2$.

II. Characterize the kinetics and mechanism of a surface reaction for the first time in a supercritical fluid.

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Kinetic Investigation

experimental apparatus

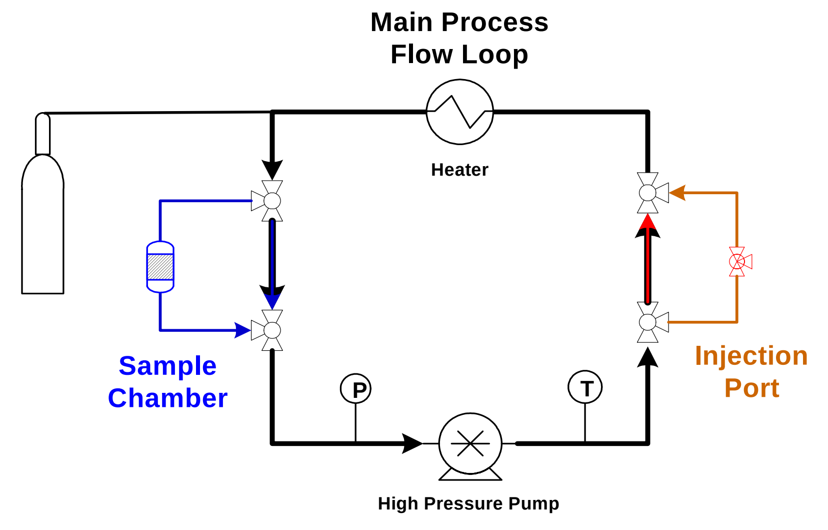
$$r_{(hfac)H} = \frac{-dc_{(hfac)H}}{dt} = Ae^{\frac{-E_{act}}{RT}} c^{\alpha}_{(hfac)H}$$

Parameters:

- E_{act} = Activation energy
- α = Reaction order
- A = Pre-exponential factor

Precision Requirements:

- Temperature
- Pressure
- Concentration/purity/mixing
- Exposure time



Three loops: mixing, injection, sample exposure

Kinetic Investigation

experimental apparatus

Specifications:

- Total Volume ≈ 246 mL
- ~ 90% volume within oven
- Max P ≈ 300 bar (4000 psi)
- Online P & T control

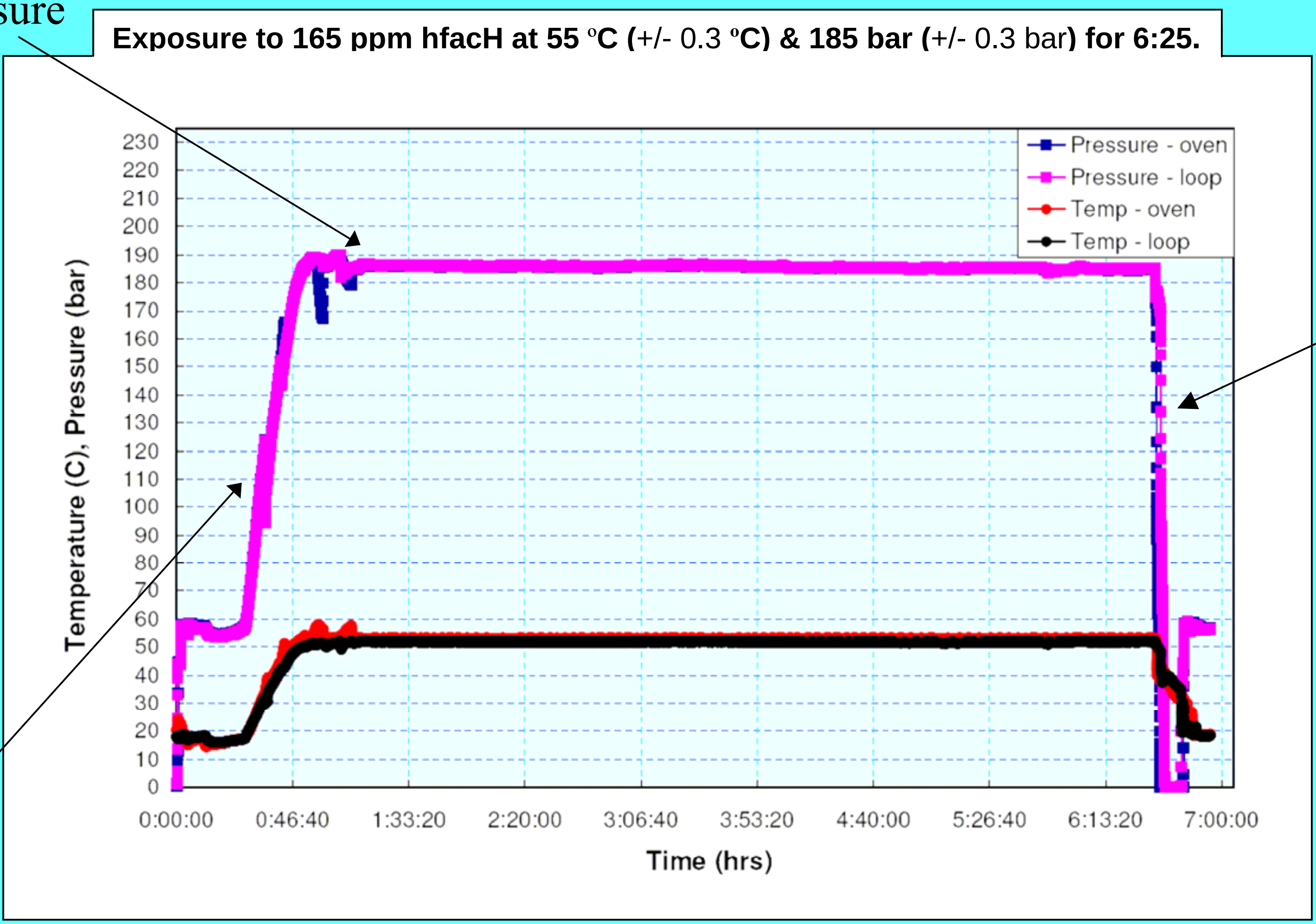
Precision achieved:

- Temperature (+/- 0.2 ºC)
- Pressure (+/- 0.5 bar)
- Concentration/purity/mixing
  (~3 mL N_2)
- Exposure time
  (~1 min to s.s., 30 sec to vent)

Experimental Apparatus

precise P & T control

Open to sample,
begin exposure



Exposure to 165 ppm hfacH at 55 °C (+/- 0.3 **°C) & 185 bar (**+/- 0.3 bar**) for 6:25.**

vent
chamber

Ramp-up to
s.s.

Example of temperature and pressure recordings for the duration of an extended experiment in $scCO_2$.

Kinetic Investigation

sample preparation/processing

8” p-doped silicon wafer

Copper metal deposition on Cr

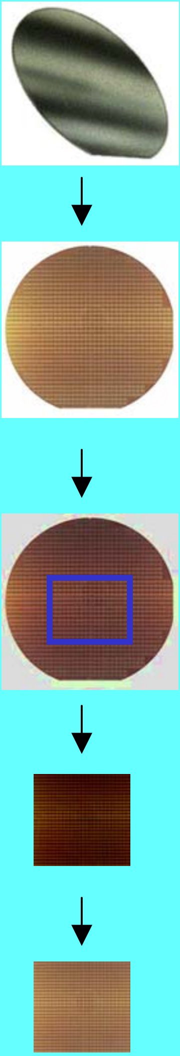
Liquid H_2O_2 oxidation of copper metal[a]

Cleave into 1 cm^2 samples

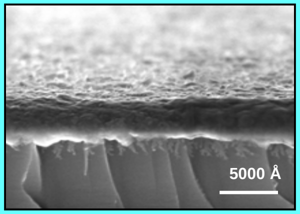
XPS & SEM analysis

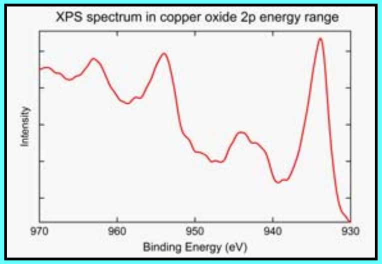
$scCO_2$ processing with hfacH

XPS & SEM analysis



500 Å CuO
on Cu metal





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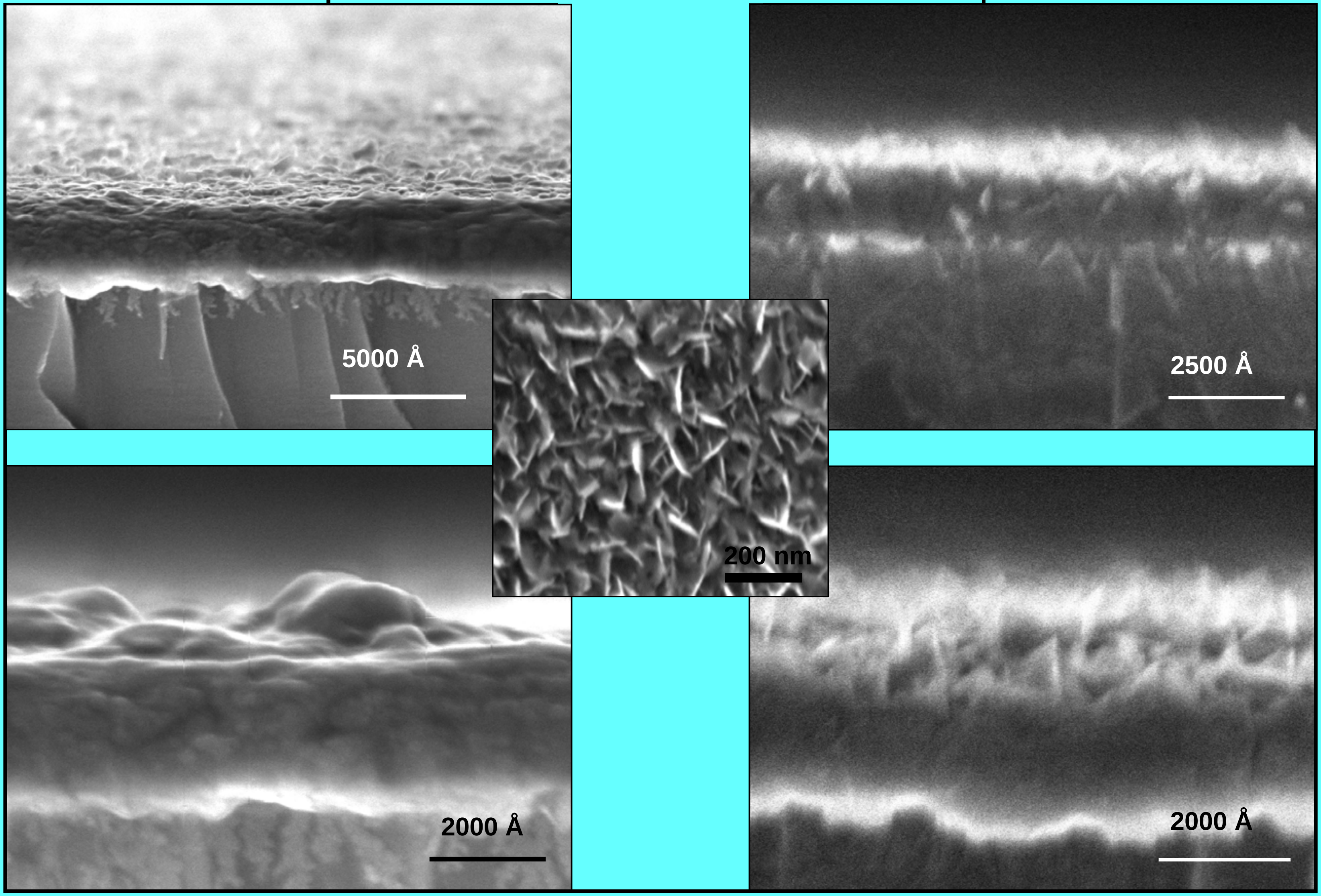
[a] *Thin Sol. Films.*, **455**, 491, 2004

Kinetic Investigation

SEM analysis

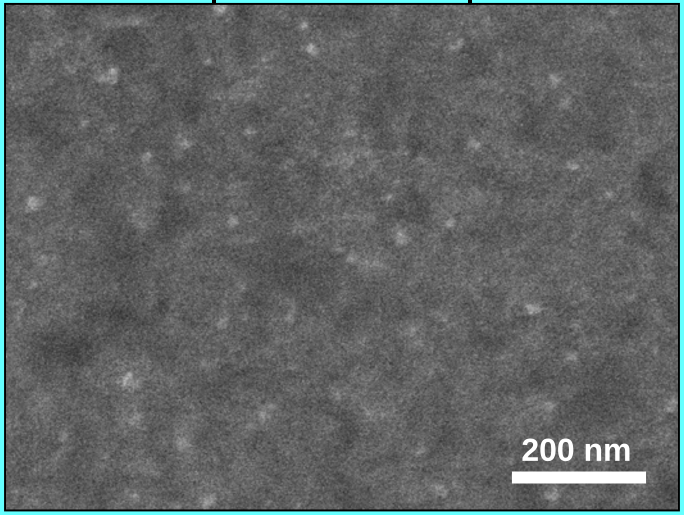
500 Å CuO on 2000Å Cu metal



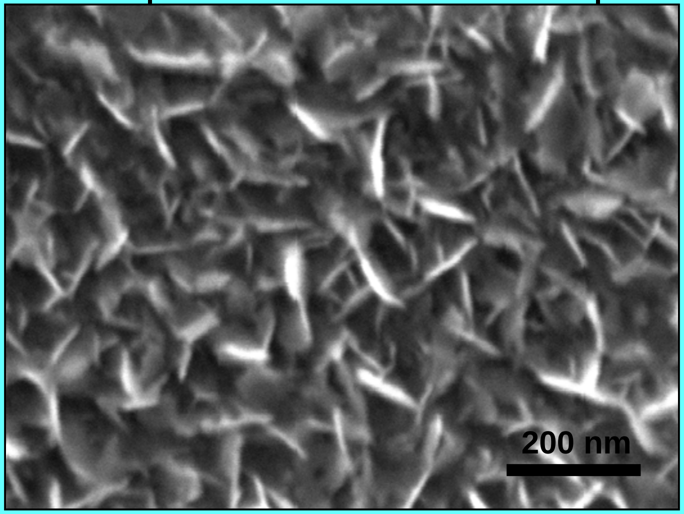
Kinetic Investigation

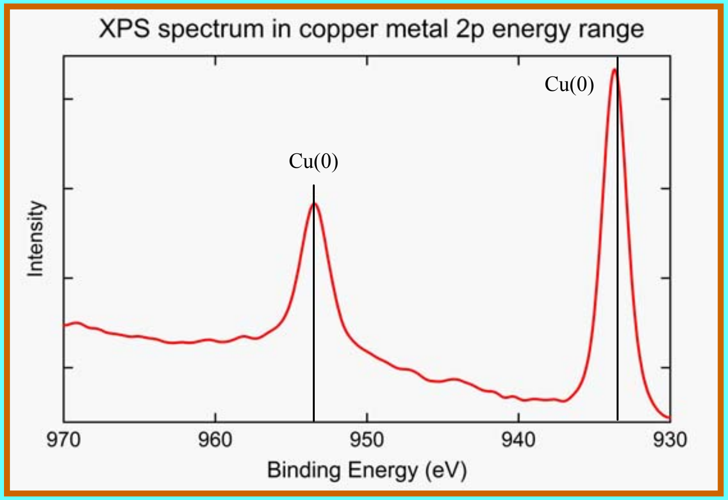
XPS analysis - spectra

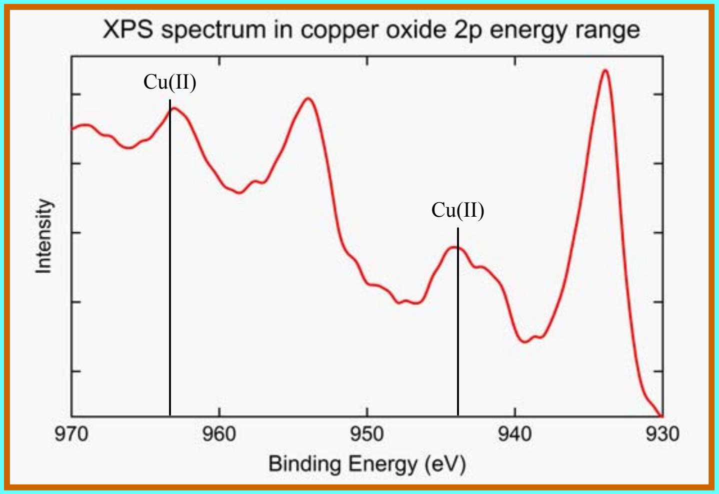
Cu metal



500 Å CuO on Cu metal




XPS spectrum in copper metal 2p energy range


XPS spectrum in copper oxide 2p energy range

XPS and SEM indicate presence or absence of superficial CuO

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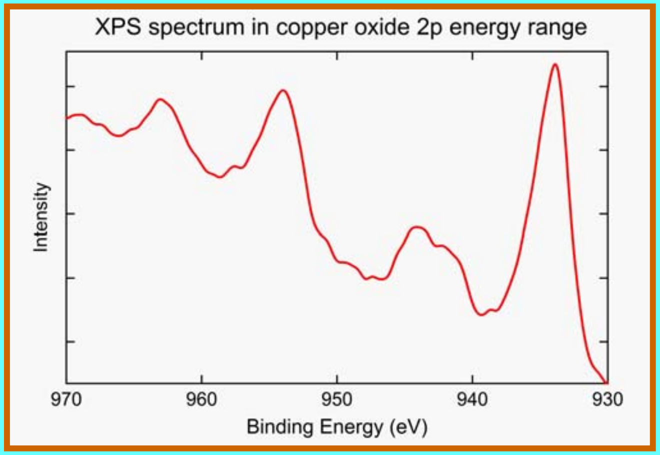
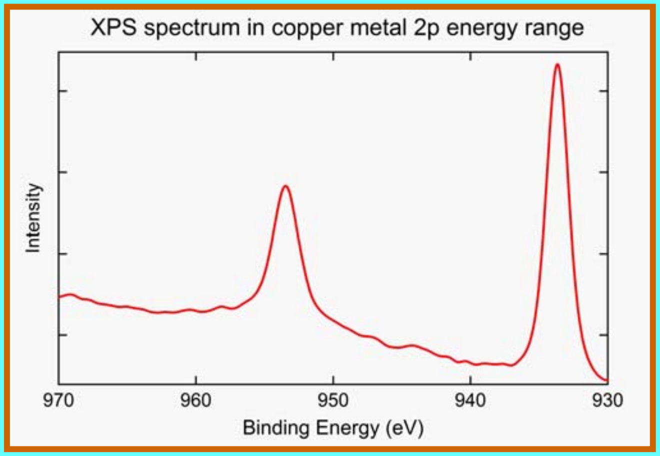
XPS analysis – etching rates





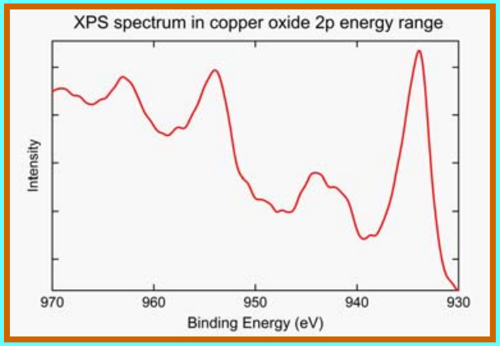
Complete removal of CuO

- Samples of characterized CuO thickness
- At one temperature, find time to remove CuO
- Repeat for different temperatures at same concentration
- Δ(moles CuO)/Δt = etching rate

$$\frac{dCu(hfac)_2}{dt} = A_{app} e^{\frac{-E_{app}}{RT}} c_{CuO} c_{hfacH}^2$$

Experimental Results

XPS analysis - CuO removal



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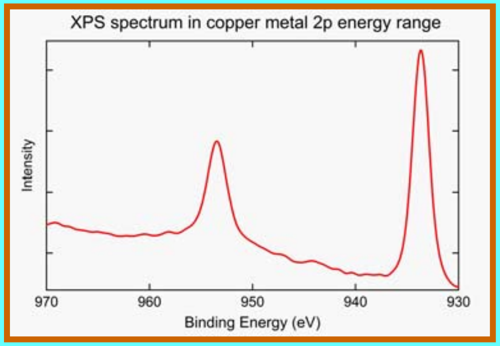
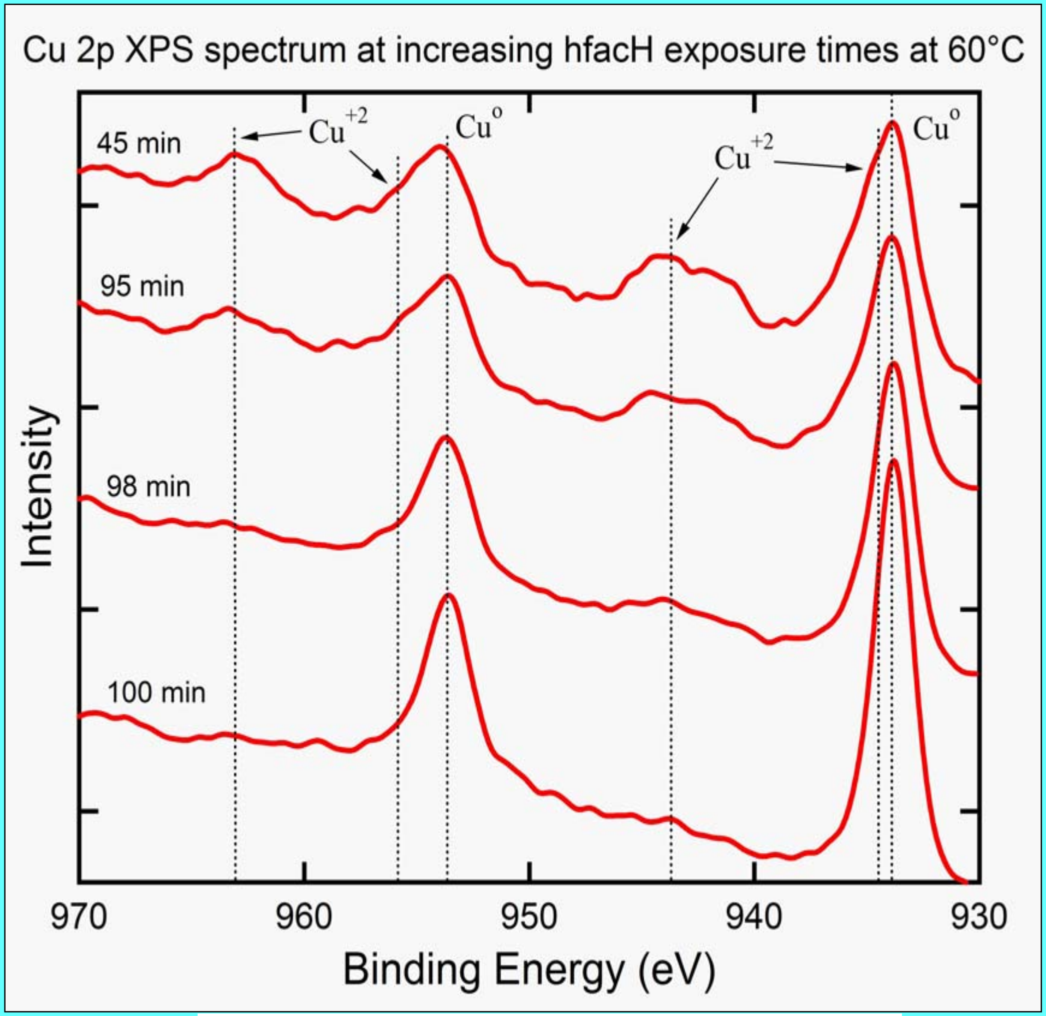


At 60º C (+/-0.2º) & 180 bar, 1000 ppm hfacH:

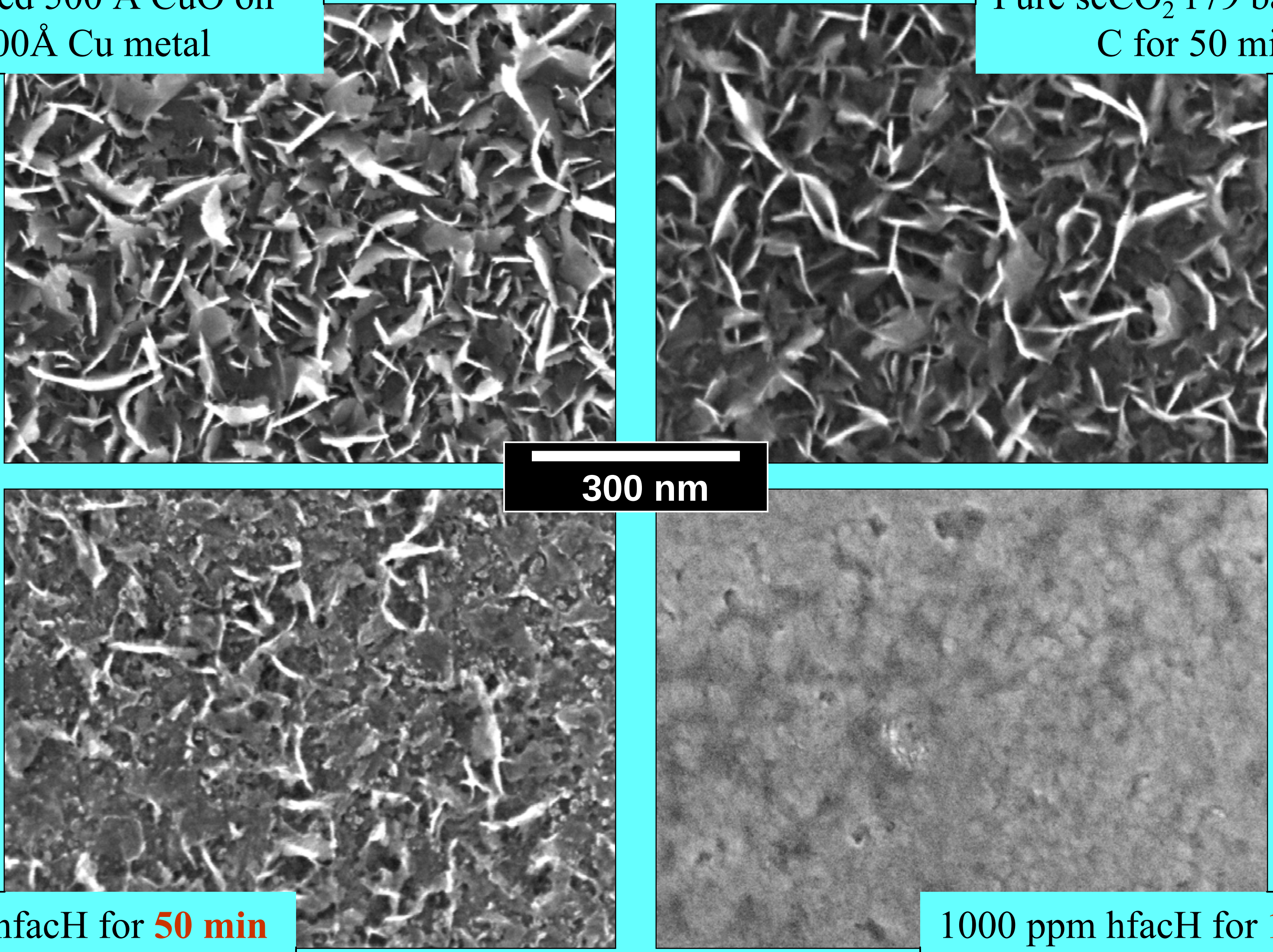
etching rate = **7.21x10^{-9}** mol/min



hfacH conc. = 1000ppm, P = 180 bar (+/- 5)

Experimental Results

SEM images - CuO removal



untreated 500 Å CuO on
2000Å Cu metal

Pure $scCO_2$ 179 bar & 60º
C for 50 min

1000 ppm hfacH for **50 min**
at 180 bar 60º C

1000 ppm hfacH for **100 min**
at 179 bar & 60º C

Kinetic Investigation

Arrhenius analysis

Data taken at 185 (±0.5 bar) & 164 ppm hfacH:

	Etching Rate	
Temperature (^{o}C) ($^{+/-}$0.15^{o})	**(Å/min)**	**(mol/min)**
53.5^{o} C	**1.6**	**2.35×10^{-9}**
60.8^{o} C	**3.0**	**4.28×10^{-9}**
68.0^{o} C	**5.4**	**7.76×10^{-9}**
74.8^{o} C	**7.8**	**1.13×10^{-8}**
82.4^{o} C	**13.9**	**2.00×10^{-8}**
88.4^{o} C	**20.1**	**2.88×10^{-8}**

Literature reported data for CuO etching using hfacH in gas phase.

Chemistry	**Phase / Temp.** (^{o} C)	**Etching rate** (Å/min)
0.25 Torr (hfac)H + 50 Torr O_2	Gas / 250	100 [a]
4 Torr (hfac)H + 50 Torr O_2	Gas / 250	1000 [a]
0.04 Torr (hfac)H + 0.86 Torr O_2	Gas / 125	190 [b]

a. *Thin Sol. Films*, **342**, 221, 1999

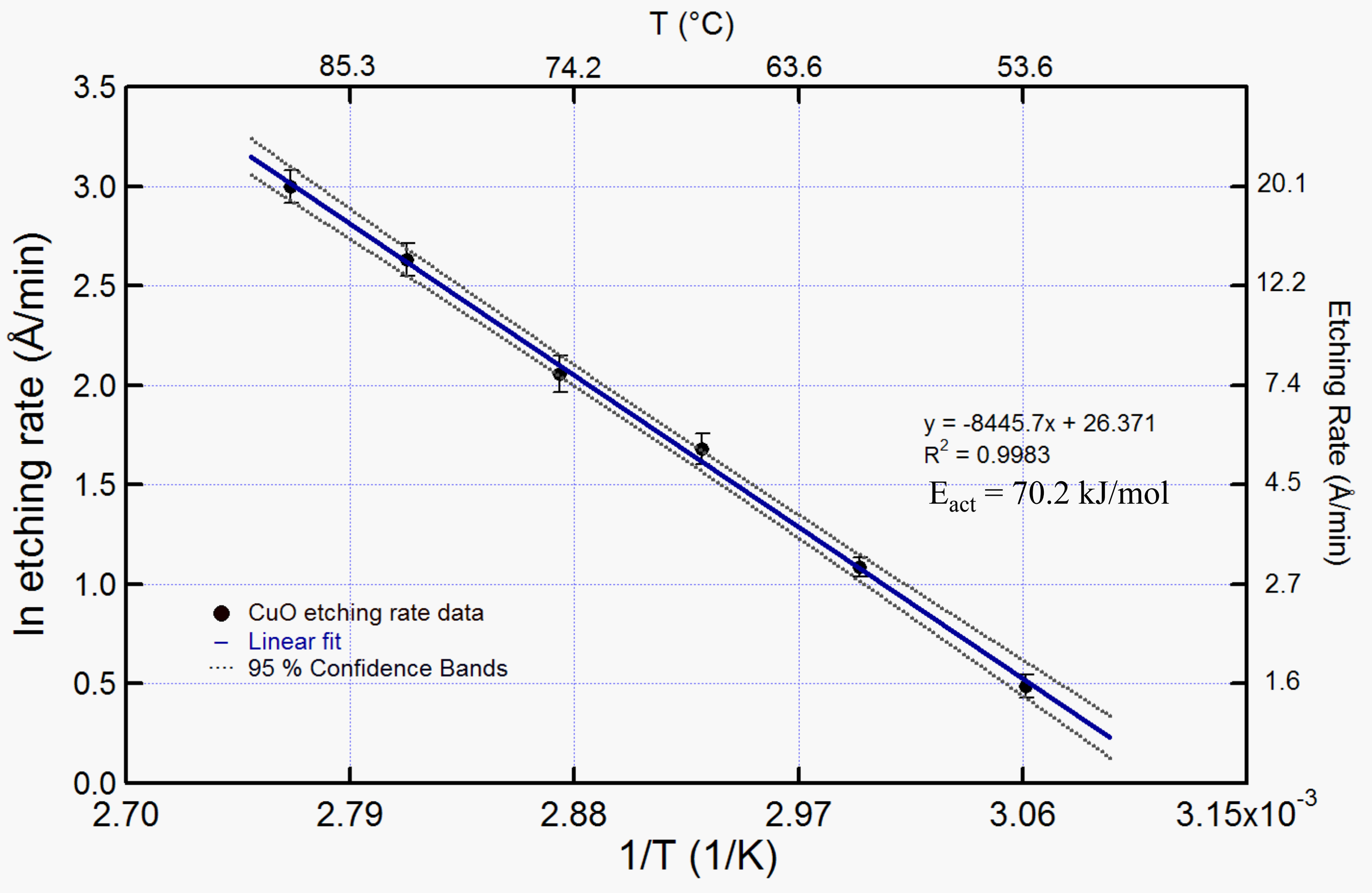
b. *J. Vac. Sci. Tech. B*, **17**, 154, 1999

Kinetic Investigation

Arrhenius analysis

$$r_{Cu(hfac)_2} = A_{app} e^{\frac{-E_{app}}{RT}} c_{CuO} c^{\alpha}_{hfacH}$$

$$\ln r_{Cu(hfac)_2} = -\frac{E_{app}}{R}\frac{1}{T} + \ln(A_{app} c_{CuO} c^{\alpha}_{hfacH})$$



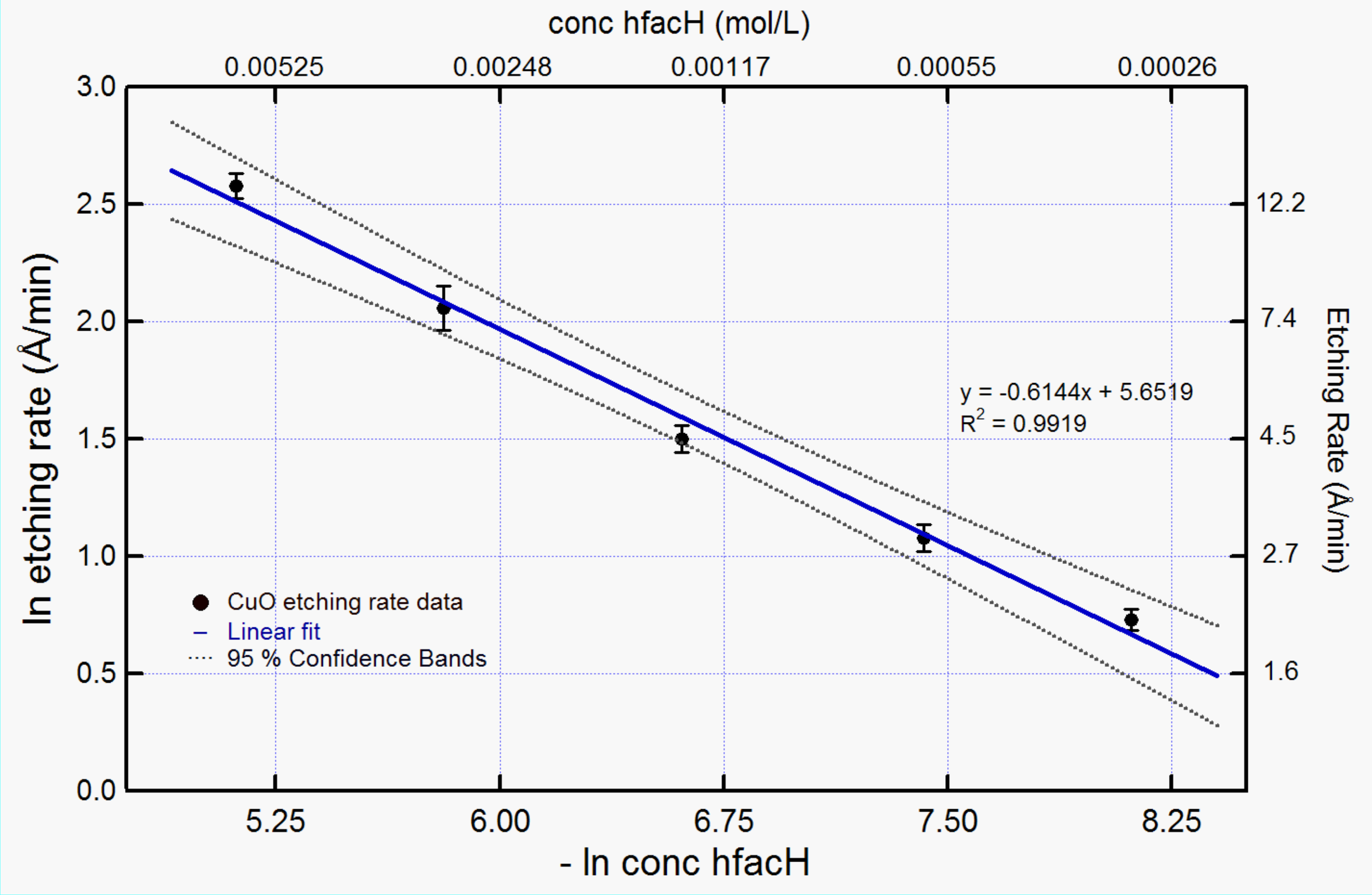
Arrhenius plot for CuO etching using 164 ppm hfacH dissolved in scCO$_2$ at 185 +/- 0.5 bar in temperature range 53.5-88.4 ºC (+/- 0.25 C).

Kinetic Investigation

reaction order

$$r_{Cu(hfac)_2} = A_{app} e^{\frac{-E_{app}}{RT}} c_{CuO} c_{hfacH}^{\alpha}$$

$$\ln r_{Cu(hfac)_2} = \alpha \ln(c_{hfacH}) + (\ln A_{app} c_{CuO} - \frac{E_{app}}{RT})$$



Plot of etching rate of CuO vs. concentration over an hfacH concentration range 16-328 ppm hfacH in $scCO_2$ at 74.8 ºC and 82.4 ºC 185 (+/- 0.5) bar.

Kinetic Investigation

summary of results

Reaction Order	**Temperature** (ºC) (+/-0.15º)
0.61	74.8

Activation Energy (164 ppm hfacH, 53.5-88.4 º C)

70.2 kJ/mol

$$r_{Cu(hfac)_2} = \frac{dCu(hfac)_2}{dt} = A_{app} e^{\frac{-E_{app}}{RT}} c_{CuO} c^{\alpha}_{hfacH}$$

Highest Etching Rate (82.4 º C, 185 bar, 328 ppm hfacH)

27.0 Å/min

Chemistry	**Phase / Temp.** (º C)	**Etching rate** (Å/min)	$\mathbf{E_{act}}$ (kJ/mol)
0.25 Torr (hfac)H + 50 Torr O_2	Gas / 250	100	54.4 [a]
4 Torr (hfac)H + 50 Torr O_2	Gas / 250	1000	33.4 [a]
0.04 Torr (hfac)H + 0.86 Torr O_2	Gas / 125	190	28.5 [b]

a. *Thin Sol. Films*, **342**, 221, 1999;b. *J. Vac. Sci. Tech.*, **17**, 154, 1999

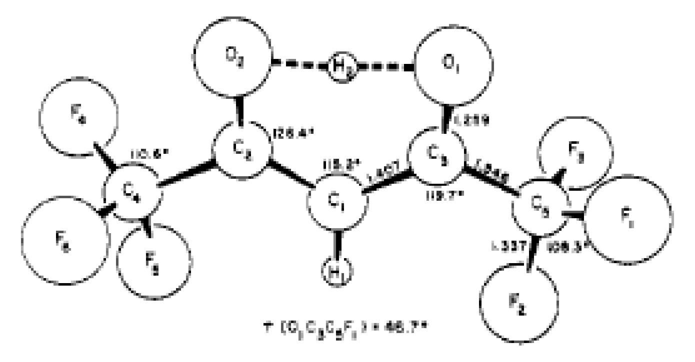
Estimated Etching Rates (185 bar, 164 ppm hfacH)	Temperature (ºC)
42.0 Å/min	100
174.0 Å/min	125
609.0 Å/min	150

Experimental Results

future work

Concentration variation

- 1000 ppm ~ 3 μmol hfacH/L
  - - ~ 700,000 monolayers (hfac)H
  - - (hfac)H soluble up to 30,000 ppm
- reaction order for (hfac)H at more temperatures



minimum energy conformation
with C=O facing Cu metal[a,b],
estimated molecular area ~ **17 Å²**

Additives/catalysts

- acid catalysts
- in situ oxidants
- reaction inhibitors
- different chelators

Explore near-critical region

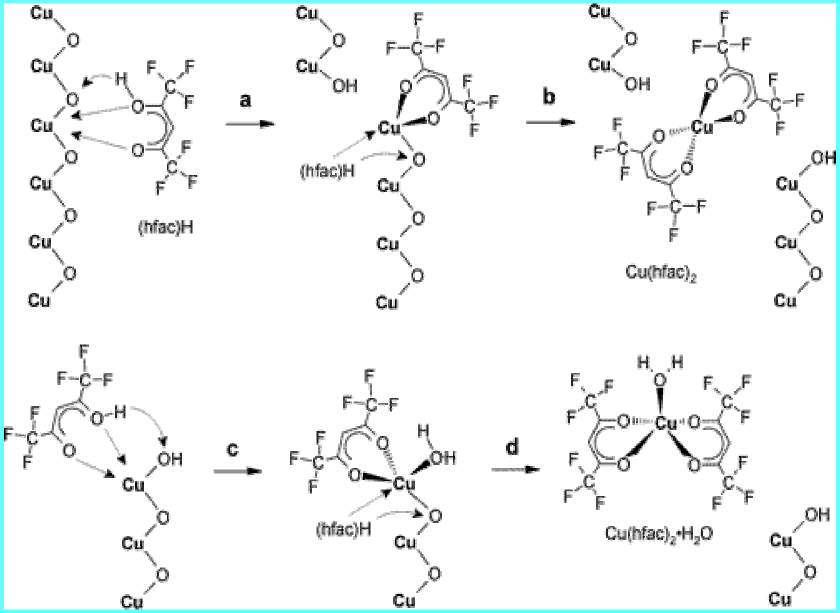
- density inhomogeneities
- variation in solvent properties

$$r_{Cu(hfac)_2} = \frac{dCu(hfac)_2}{dt} = A_{app} e^{\frac{-E_{app}}{RT}} c_{CuO} c_{hfacH}^{\alpha}$$

a. *JACS.*, **93**, 1148, 1971
b. *Surf. Sci.*, **409**, 428, 1998

Experimental Results

future work – mechanism/rate



$$r_{Cu(hfac)_2} = \frac{dCu(hfac)_2}{dt} = A_{app} e^{\frac{-E_{app}}{RT}} c_{CuO} c^{\alpha}_{hfacH}$$

$$\mathbf{CuO + hfacH} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathbf{Cu\text{-}hfac + {}^*OH}$$

$$\mathbf{Cu\text{-}hfac + hfacH + {}^*OH} \xrightarrow{k_2} \mathbf{Cu(hfacH)_2 + HOH}$$

$$r_{etching} = k_2 \frac{k_1}{k_{-1}} [CuO][hfacH]^2$$

$$r_{etching} = A' e^{\frac{-E_{act2} - E_{act1} + E_{act-1}}{RT}} c^{\alpha}_{(hfac)H}$$

$$r_{etching} = A' e^{\frac{-E_{app}}{RT}} c^{\alpha}_{(hfac)H}$$

For CuO etching reaction:

- Fully develop rate equation
- Elucidate mechanism
- Explore energy barriers or individual steps

Outline

Introduction

- Definition of SCF, P-V behavior for pure fluid
- SCF density inhomogeneities

Supercritical carbon dioxide

- $scCO_2$ properties & ESH
- $scCO_2$, integrated circuits, & copper

Kinetic Investigation

- Experimental apparatus
- Sample preparation and analysis

CuO Etching using hfacH

- Arrhenius Analysis
- Rate law for etching

Conclusion

Conclusion

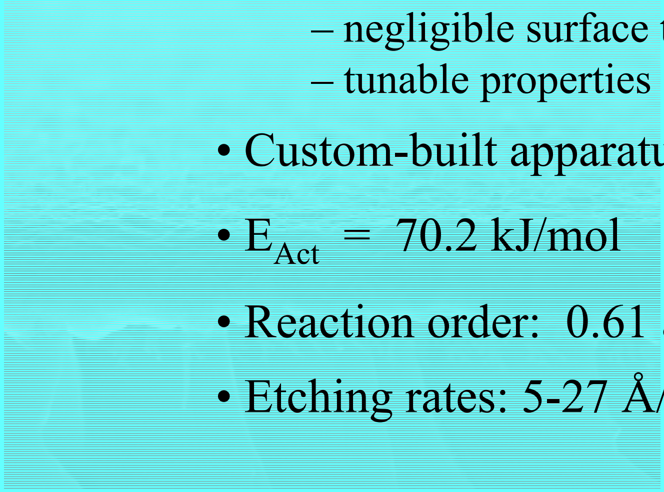
supercritical fluids and copper etching in $scCO_2$

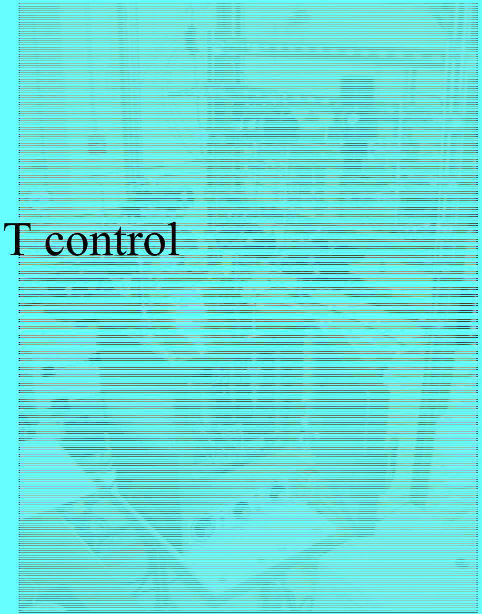
Supercritical fluids:

- SCF ≡ $T > T_c$, where $\Delta P \rightarrow$ continuous $\Delta\rho$
- Divergent compressibility as $T \rightarrow T_c+$ leads to microscopic and macroscopic density inhomogeneities that affect fluid properties

Copper etching in supercritical carbon dioxide

- $scCO_2$ as a solvent
  - – favorable critical parameters
  - – negligible surface tension
  - – tunable properties
- Custom-built apparatus allows for precise P & T control
- $E_{Act} = 70.2$ kJ/mol
- Reaction order: 0.61 at 74.8 º C
- Etching rates: 5-27 Å/min at T < 100 ºC





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