# Applications of SCF to Semiconductor Lithography

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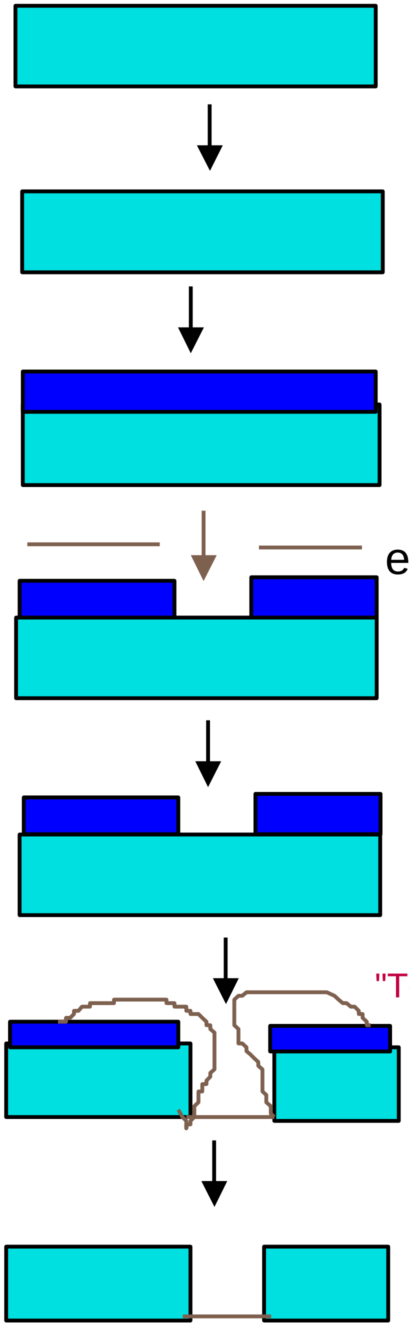
# Where and How Does a New Process Fit In

- Eliminates Present Process Steps
- Substitute Safer Liquid/Gas for Another
- Solve Process Problem
- Fit New Process to Existing Materials
- Design New Materials to Fit New Process Fluids

Reduce Costs
Improve Yields
Eliminate Waste
Recycle

→ Lower Cost

# PROCESS LIQUIDS for SC LITHO



Clean- $H_2O_2$,$NH_4OH$,Organic Solvents

Prime-HMDS or Apply Organic Arc

Apply- Organic Solvents

Develop- TMAH,Organic Solvents

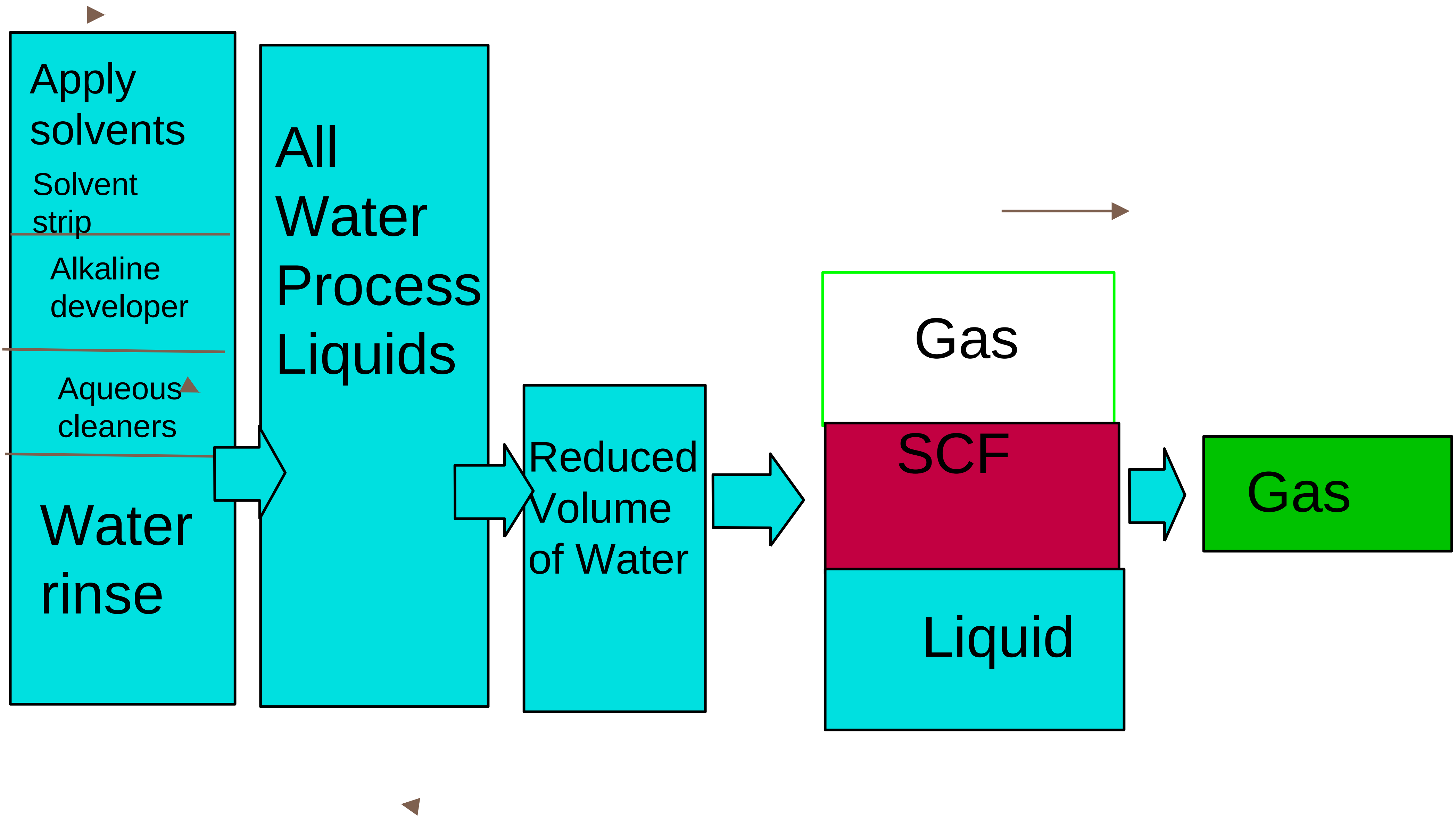
Rinse- Water,SCF,Organic Solvents

$(CF_2\text{-}CF_2)_n$

Etch(RIE)- $CF_4$ gas or HF liq

Strip- Organic Solvents

# Stages of Conversion of Green Lithography



Apply solvents

Solvent strip

Alkaline developer

Aqueous cleaners

Water rinse

All Water Process Liquids

Reduced Volume of Water

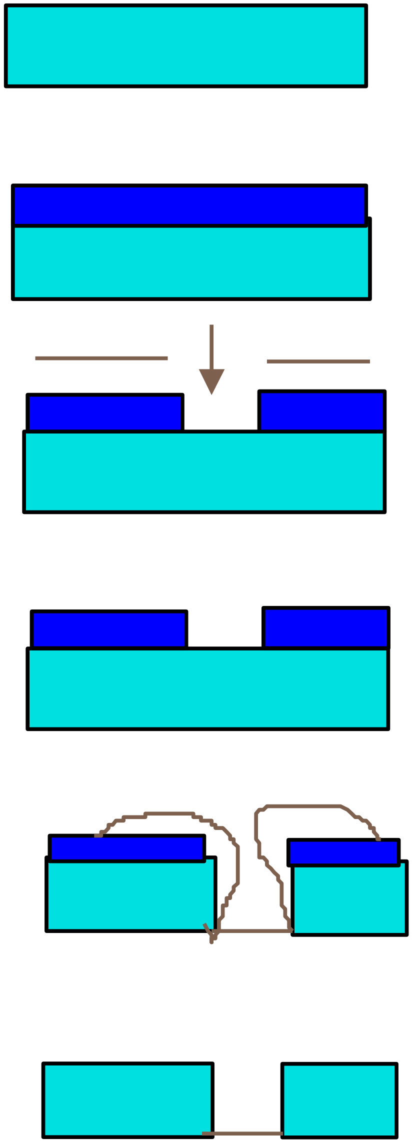
Gas

SCF

Liquid

Gas

# PROCESS LIQUIDS for SC LITHO



Clean- ~~H2O2,NH4OH~~

Apply- ~~PGMEA,Ethyl Lactate~~

Develop- ~~TMAH~~,~~Organic Solvents~~

Rinse- ~~Water~~,SCF,~~Organic Solvents~~

Etch(RIE)- CF4 gas or ~~HF~~ liq

Strip- ~~NH2OH, organic solvents~~

# Integration of SCF into Lithography

- Replace SCF anywhere water is used
- Replace SCF anywhere organic solvents used
- Reduce amt of water/solvent and waste
- Displace water/solvents
- Fit the SCF process to existing tools/mtls/process (200-300mm/1min)
- Design mtls/process/tools for SCF integration

# Properties of SCFCO2 Used in SemiConductor Proceses

- Low Toxicity
- Low Cost
- Critical Point 31C,1200 psi
- Lowest Surface Tension Fluid
- Wettability
- High Solvent Power rel Hexane
- High Diffusitivity
- Low Viscosity
- $H_2O + CO_2 \longrightarrow H_2CO_3$

$$E(coh) = E(np) + E(p) + E(hb)$$

Cyclic

Co-solvent- Good solvent dilute SCFCO2

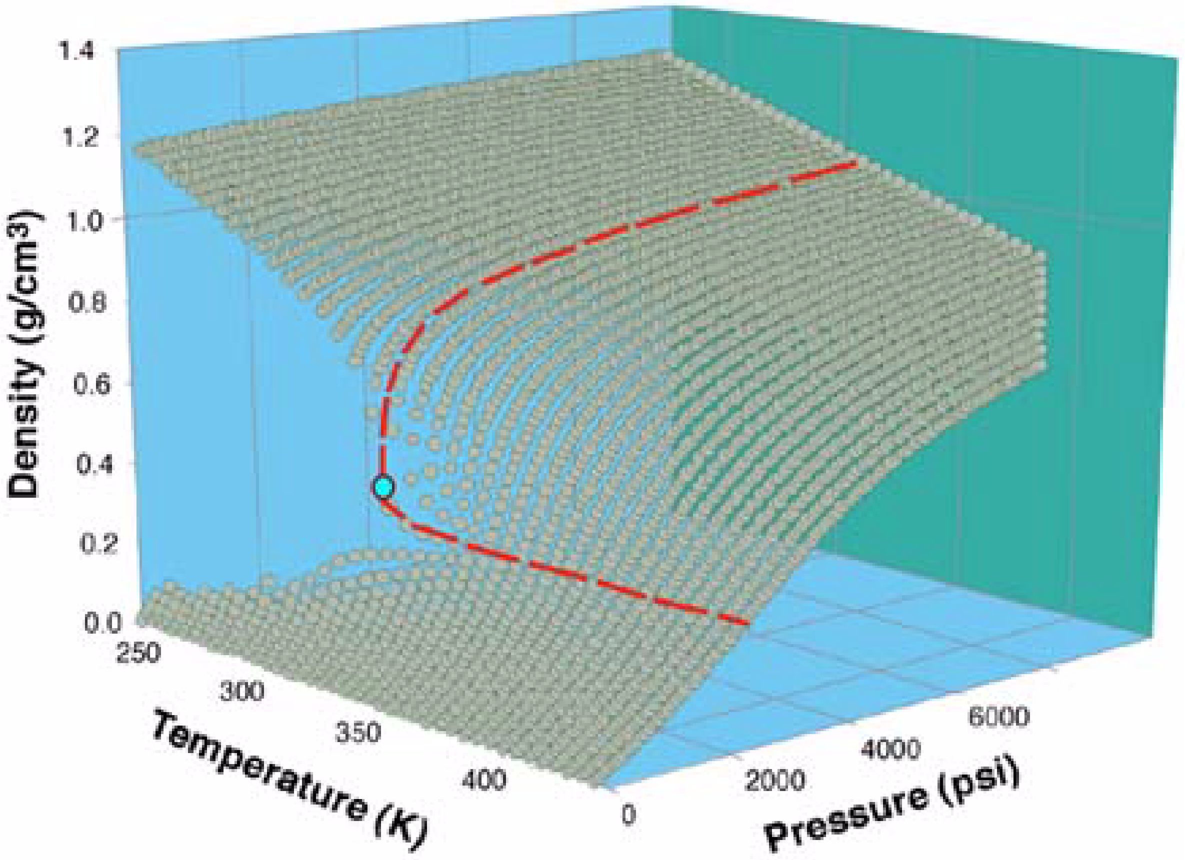
Theta solvent

Homologous Series

# Solubility Parameters

| Solvent or Polymer | Non Polar | Polar | H Bond | Sol Par |
|---|---|---|---|---|
| Methanol | 7.4 | 6.0 | 10.9 | 13.4 |
| IPA | 7.7 | 3.0 | 8.0 | 10.7 |
| Propglycol | 8.2 | 4.6 | 11.4 | 12.8 |
| Acetic acid | 7.1 | 3.9 | 4.6 | 11.0 |
| NMP | 8.8 | 6.0 | 3.5 | resist strip, 14.8 |
| Butyl acetate | 7.7 | 1.8 | 3.1 | 9.5 |
| Xylene | 8.7 | 1.0 | 1.0 | 9.7 |
| Hexane | 7.2 | 0.0 | 0.0 | 7.2 |
| $SCFCO_2$ | 7.2 | 0.0 | 0.0 | 7.2 |
| Teflon | | | | 6.6 |
| PMMA | | | | 9.3 |
| Polystyrene | | | | 8.6 |

# p - $\rho$ -T Surface of Pure $CO_2$



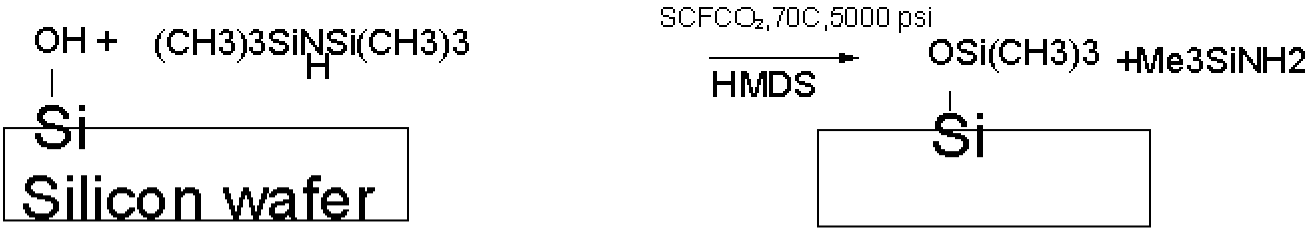
# Surface Tension of Process Liquids

| Liquid | Density,g/ml | Viscosity,cps | Surface Tension, mN/m |
|---|---|---|---|
| Water | 0.99 | 0.91 | 72 |
| Water/surfactants | | | 20-40 |
| Ethanol | 0.85 | 1.08 | 22 |
| t- butyl alcohol(TBA) | 0.81 | 3.5 | 20 |
| 50/50 TBA/H2O | | | 24 |
| Fluoroalkane | | | 5-14 |
| Liquid CO2 | 0.87 | 0.08 | 1.5 |
| SCF CO2 | 0.35-0.85 | 0.03 | 0 |
| | | | |

# Interfacial Tension

| Interface | Surface Tension , mN/m |
|---|---|
| Water/SCF CO2 | 15 |
| Water/SCF CO2/Silicone surfactant | 2 |

# EXAMPLE - Silylation in SCF



OH + (CH3)3SiNSi(CH3)3
H
Si
Silicon wafer

$SCFCO_2$,70C,5000 psi
HMDS

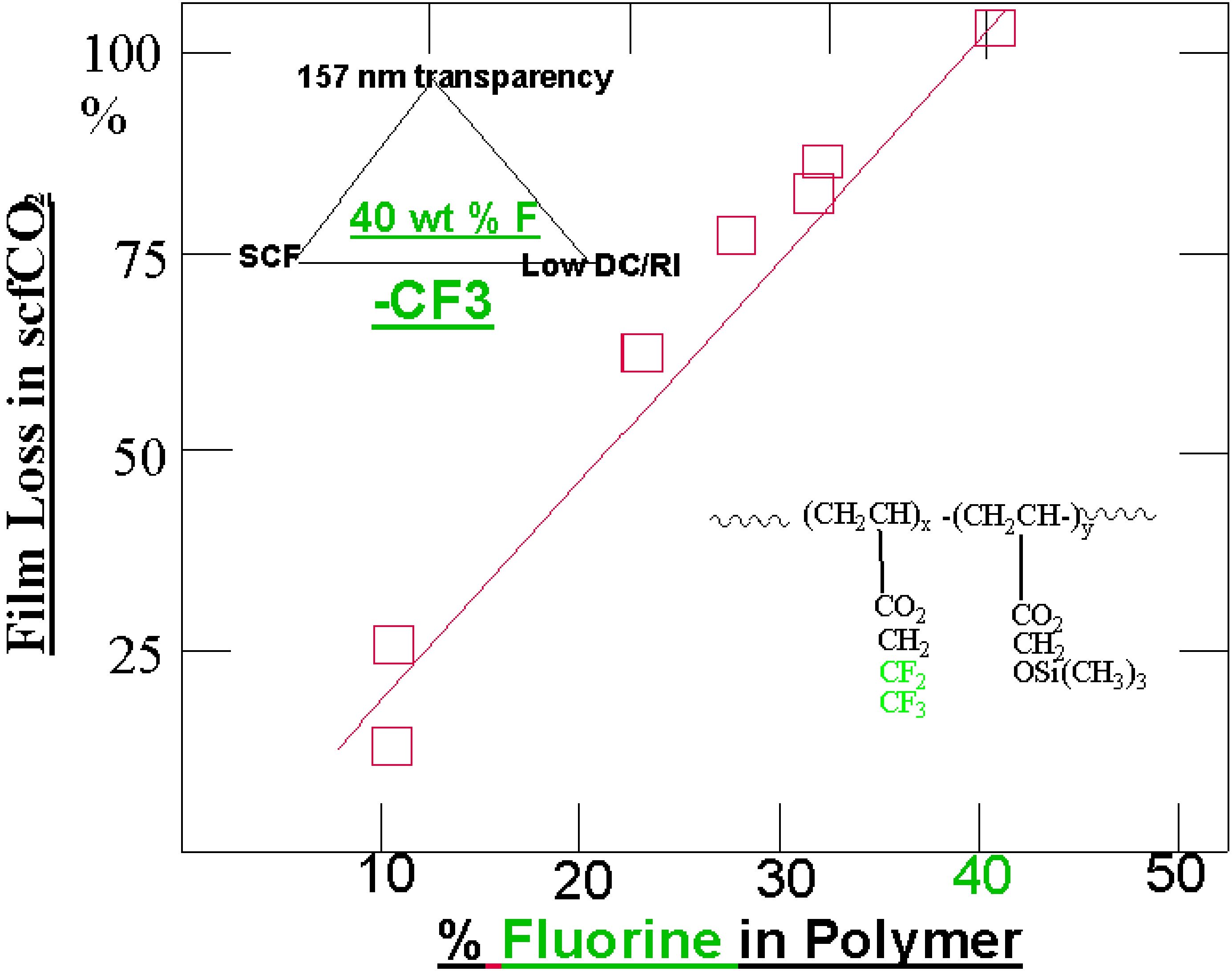
OSi(CH3)3 +Me3SiNH2
Si

| Sample | CONTACT ANGLE(water drop)deg |
|---|---|
| Bare silicon wafer | 26 |
| Silicon wafer silylated by HMDS in Gas Phase YES oven | 78 |
| Silicon Wafer silylated by HMDS in SCFCO2 | 87 |
| Glass slide | 21 |
| After silylation | 59 |

# REPLACE Aq BASE/water with SCF as DEVELOPER

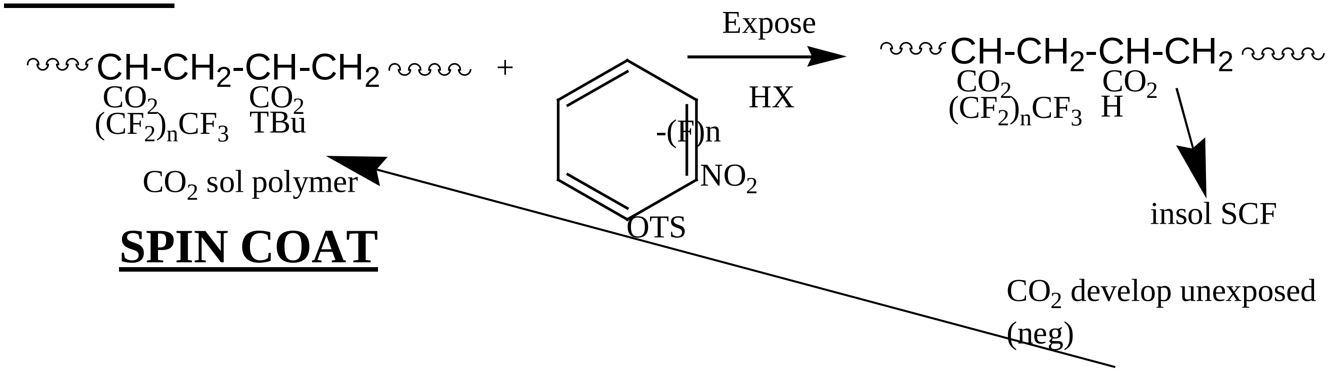
Reason- avoid image collapse with Low ST SCFCO2 and reduce volumes of dev/water for processing

Challenge-Few Polymers Soluble in SCFCO2
mainly low ST polarity(ST) Fluorocarbons/siloxanes/
ethers solubilty parameter < 8
⇨ May require co-solvent to boost polarity of SCFCO2
Positive resist most difficult
Polar to non polar
Chain Scission


Film Loss in scfCO$_2$
%
100
75
50
25
10
20
30
40
50
% Fluorine in Polymer
157 nm transparency
SCF
Low DC/RI
40 wt % F
-CF3
(CH$_2$CH)$_x$ -(CH$_2$CH-)$_y$
CO$_2$
CH$_2$
CF$_2$
CF$_3$
CO$_2$
CH$_2$
OSi(CH$_3$)$_3$

# Deposit Resist from by Spin Coating in Liquid $CO_2$

## DEVELOP UNEXPOSED SCF $CO_2$ SOLUBLE as NEGATIVE RESIST



~~~ CH-$CH_2$-CH-$CH_2$ ~~~ +

$CO_2$ $(CF_2)_nCF_3$ $CO_2$ TBu

-(F)n $NO_2$ OTS

Expose HX

~~~ CH-$CH_2$-CH-$CH_2$ ~~~

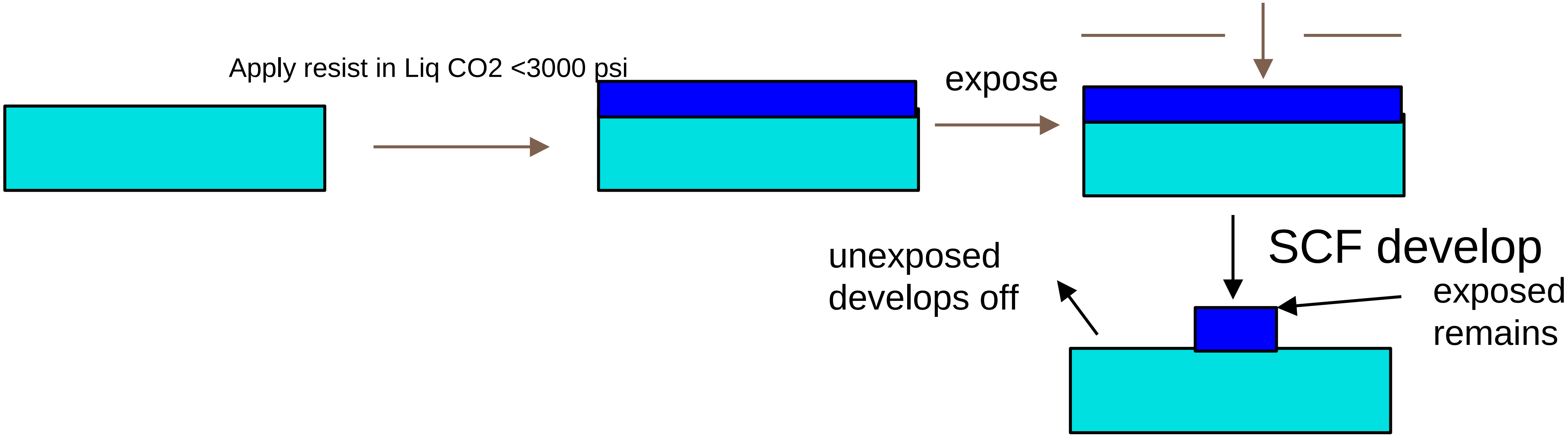
$CO_2$ $(CF_2)_nCF_3$ $CO_2$ H

insol SCF

$CO_2$ sol polymer

$CO_2$ develop unexposed (neg)

**SPIN COAT**



Apply resist in Liq CO2 <3000 psi

expose

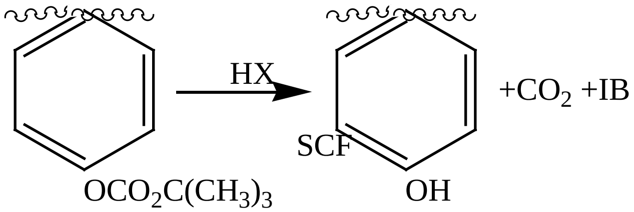
SCF develop

unexposed develops off

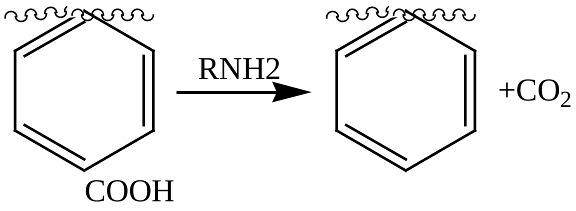
exposed remains

# EXAMPLE

# POLARITY CHANGE POSITIVE RESIST

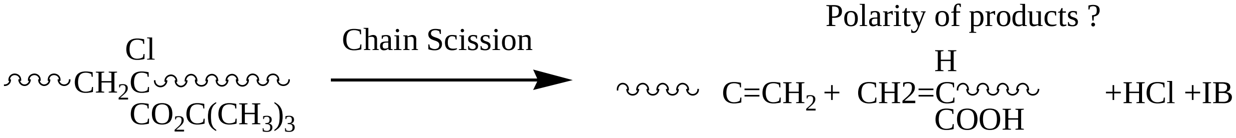


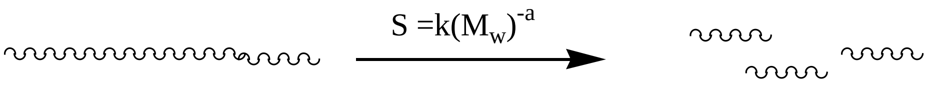
Non polar $\xrightarrow{\text{TMAH}}$ polar



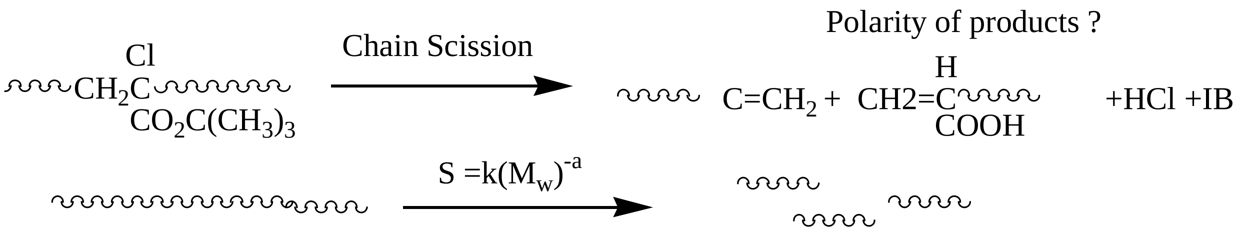
Polar $\xrightarrow{\text{SCF}}$ Non polar

Polarity of products ?





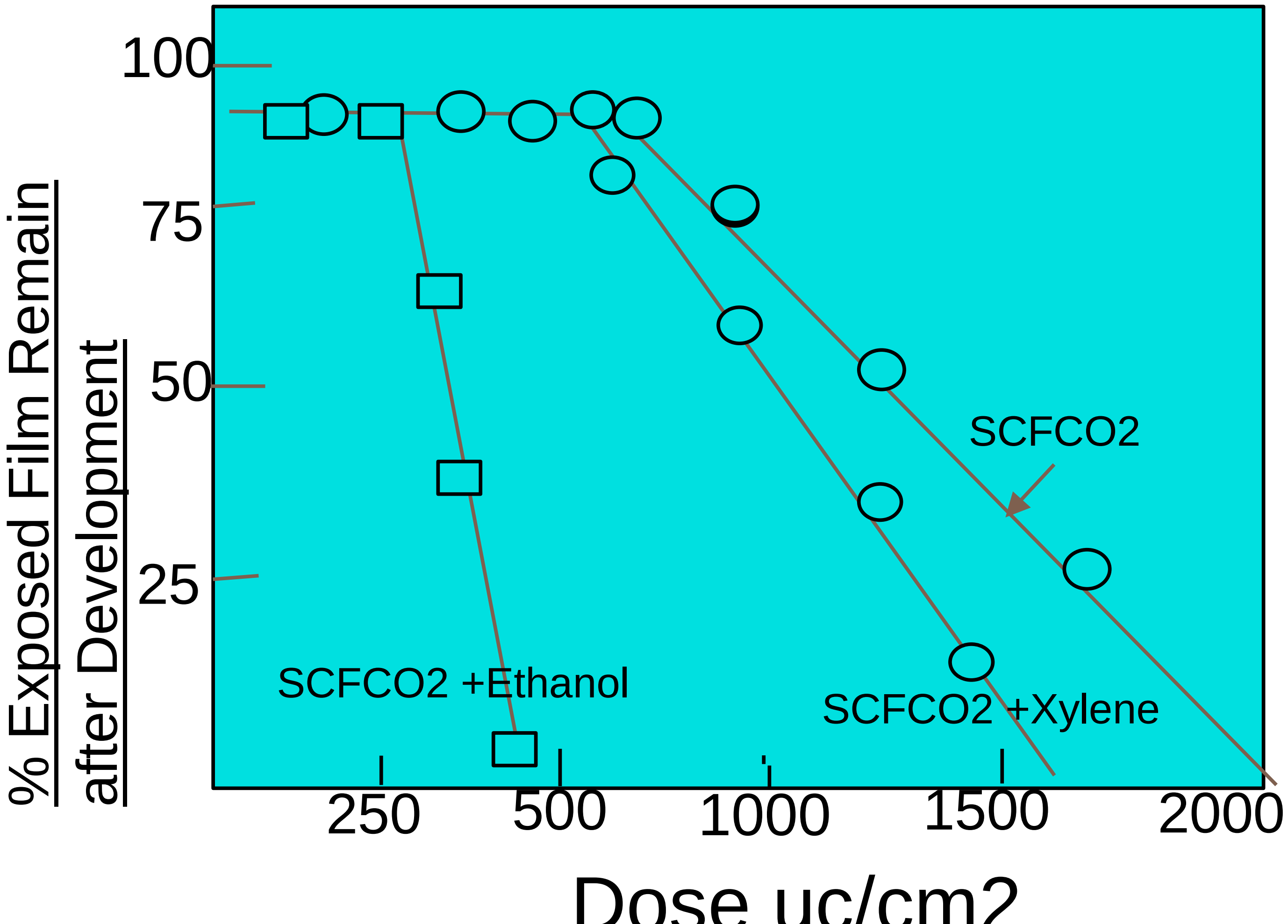
# Example of SCF/Co-solvent Developed EB resist



Polarity of products ?

$$\sim\sim CH_2\overset{Cl}{\underset{CO_2C(CH_3)_3}{C}}\sim\sim\sim \xrightarrow{\text{Chain Scission}} \sim\sim\ C{=}CH_2 + CH2{=}\overset{H}{\underset{COOH}{C}}\sim\sim \quad +HCl +IB$$

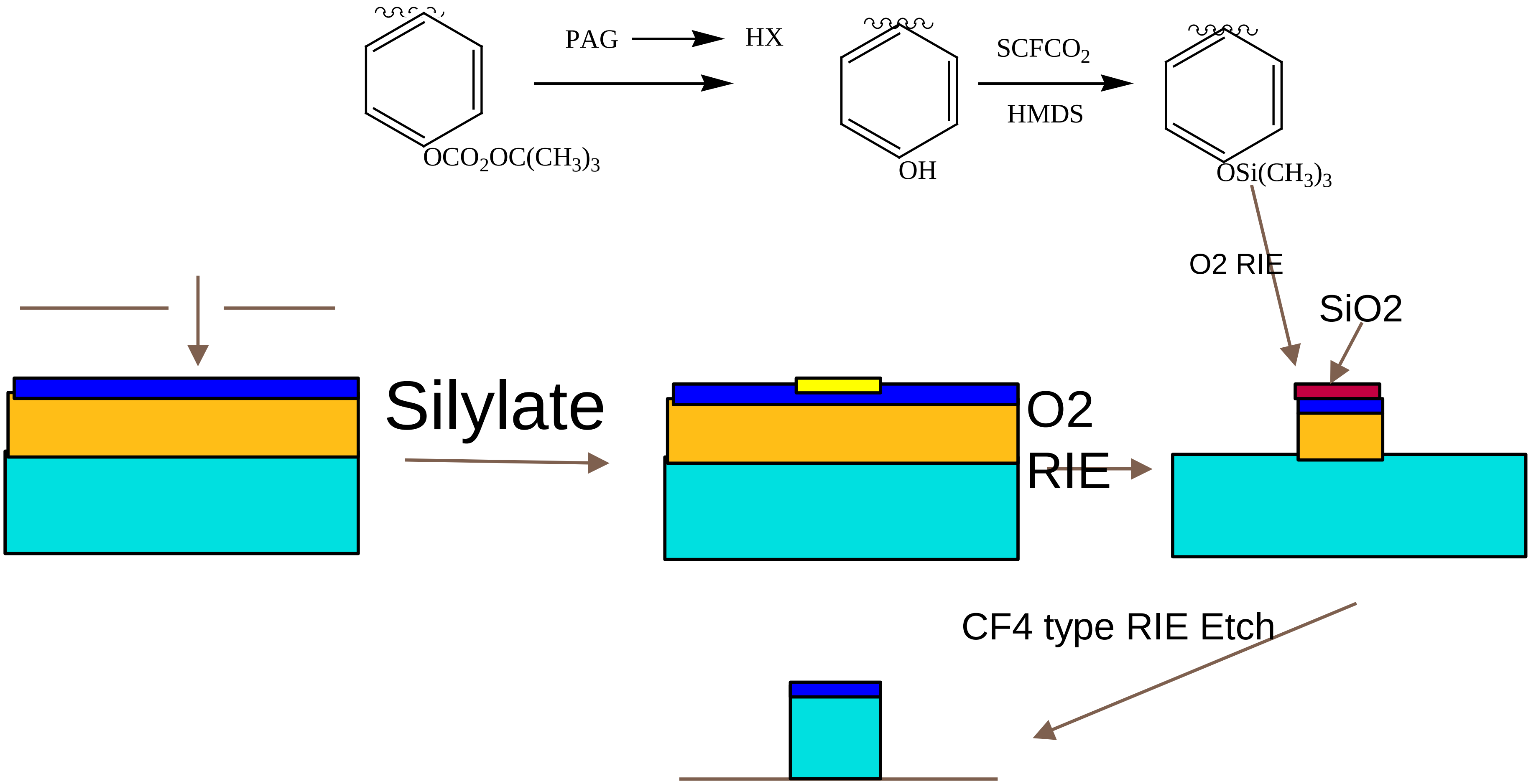
$$\sim\sim\sim\sim\sim\sim \xrightarrow{S = k(M_w)^{-a}} \sim\sim \quad \sim\sim \quad \sim\sim$$



# SILYLATION with SCF - BILAYER (TOP SURFACE IMAGING

for High Resolution Imaging over Reflective Substrates or Topography

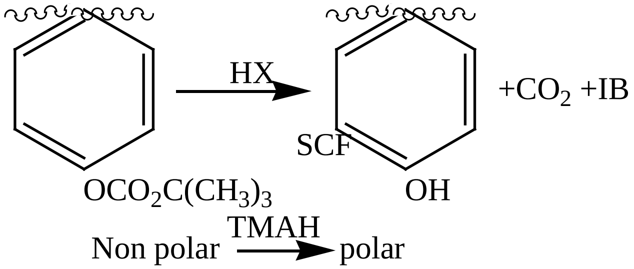
Provide Uniform Silyation over 300 mm diameter wafers



# Present Chem Amplified Resist

# Aqueous base Developer/water rinse

## Example



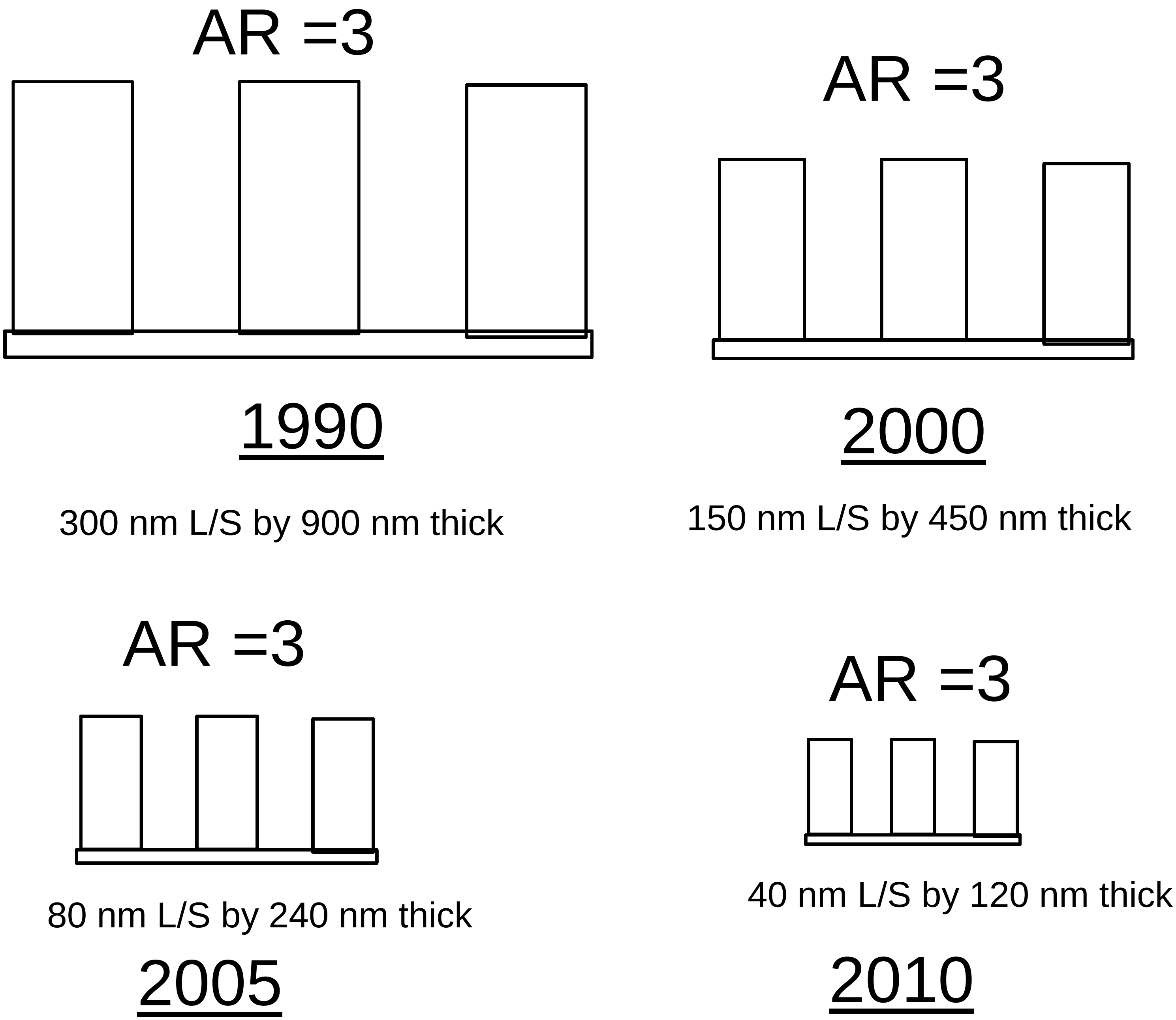
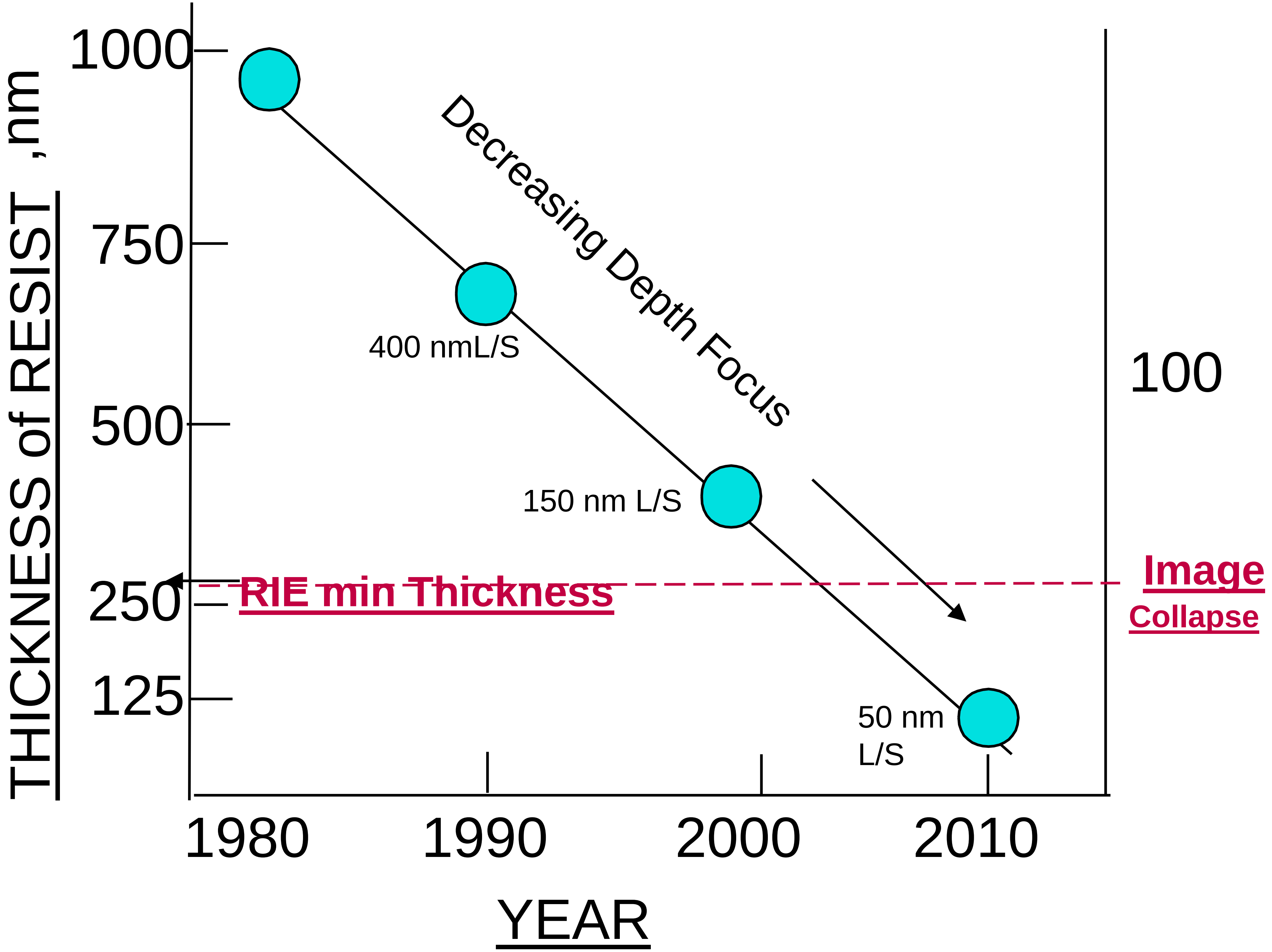
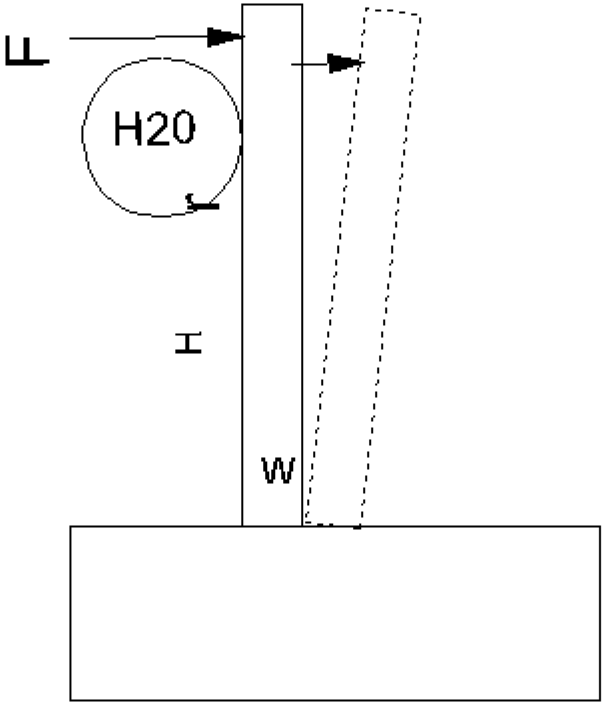
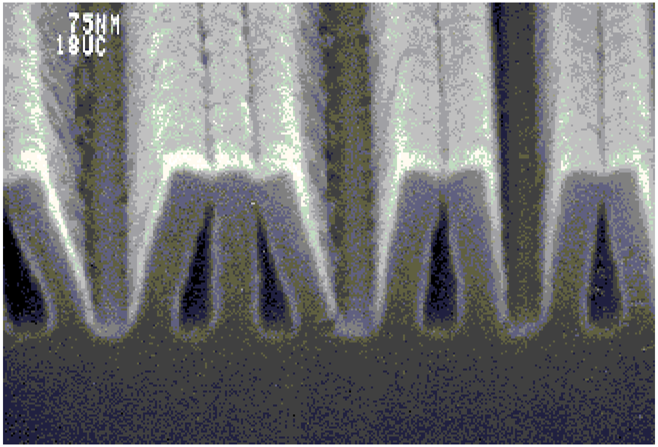


Figure 1 - Trends in Resist Feature Sizes

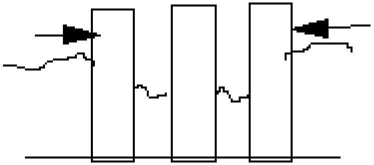
# Where Has all The Resist Gone ?







**75nm x 75nm , 3500Å**



$$F=(St)/r$$

$$W(o)=4A(exp+3)F/E$$

$$W(o)=4A(exp+3)(St)/Er$$

$A_r=H/w >3$

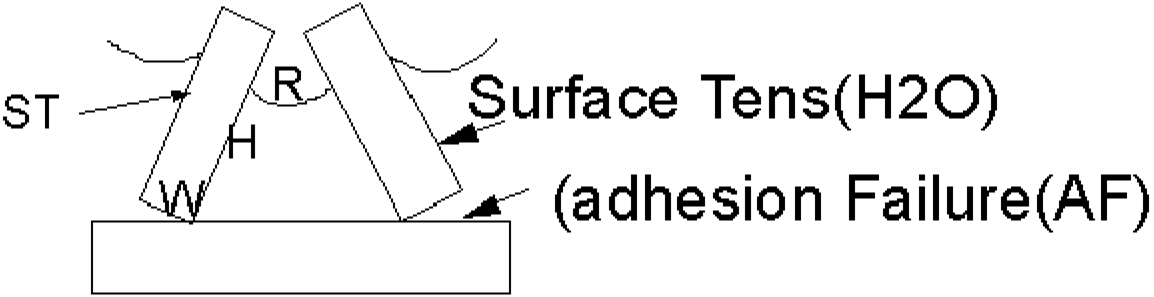
Tanaka,J.Elec. Soc.,141,1169(1994)

E = Youngs Modulus(GP(a))

Lower (ST) or raise E

- Example of Image Collapse and Early Model

# IMAGE COLLAPSE in DRYING DUV RESIST



$$\text{Collapse} = (\text{Pressure})(\text{Aspect Ratio}(H/W)$$

$$= 2\left(\frac{ST}{R}\right)\left(\frac{H}{W}\right) = \frac{(144\text{d/cm})(500\text{nm})}{(1000\text{ nm})\ (100\text{nm})}$$

**Collapse Force** = 7 x 10(exp+7)dynes/cm

ADHESIVE BOND STRENGTH = < 1 X 10(exp+7) d/cm

USE LOW ST to DRY LIQUID as SC CO2 <1 d/cm

USE STIFFEST RESIST ( High Shear modulus)

Shear Modulus general increase with T(g)

Highest in X linked mtls( neg resist ?)

# Young's Modulus of Resist Films

| SAMPLE | E (GPa)+/- 0.2 |
|---|---|
| KRS-XE (PHS) | 5.3 |
| ESCAP KrF resist | 5.1 |
| APEX-KrF PHS | 5.1 |
| Neg(exp) PHS KrF | 4.2 |
| Acrylate ArF | 3.9 |
| COMA ArF | 2.6 |
| CO ArF | 2.6 |
| ZEP e beam | 2.2 |

PHS -Polyhydroxystyrene,ESCAP-PHS-co-tbutylacrylate ,COMA -Cyclic olefin/maleic anhydride ,EB-ele
beam,ZEP-Nippon Zeon -Poly co-chloroacrylate/methylstyrene,APEX Shipley PHS type ;SAW by Dr.T
Schuelke, Fraunhofer USA, Bradley Univ, Peoria, Illinois.

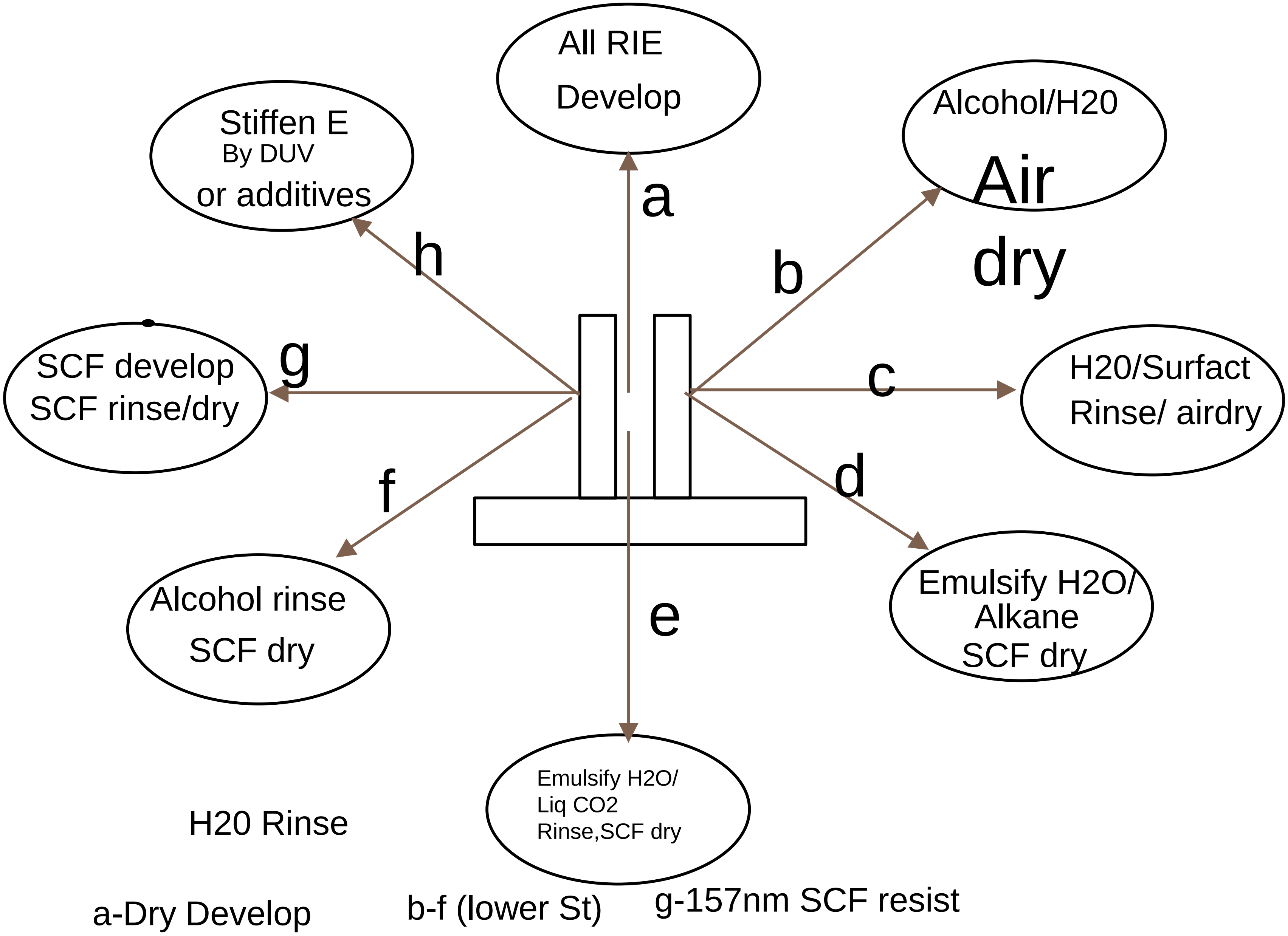
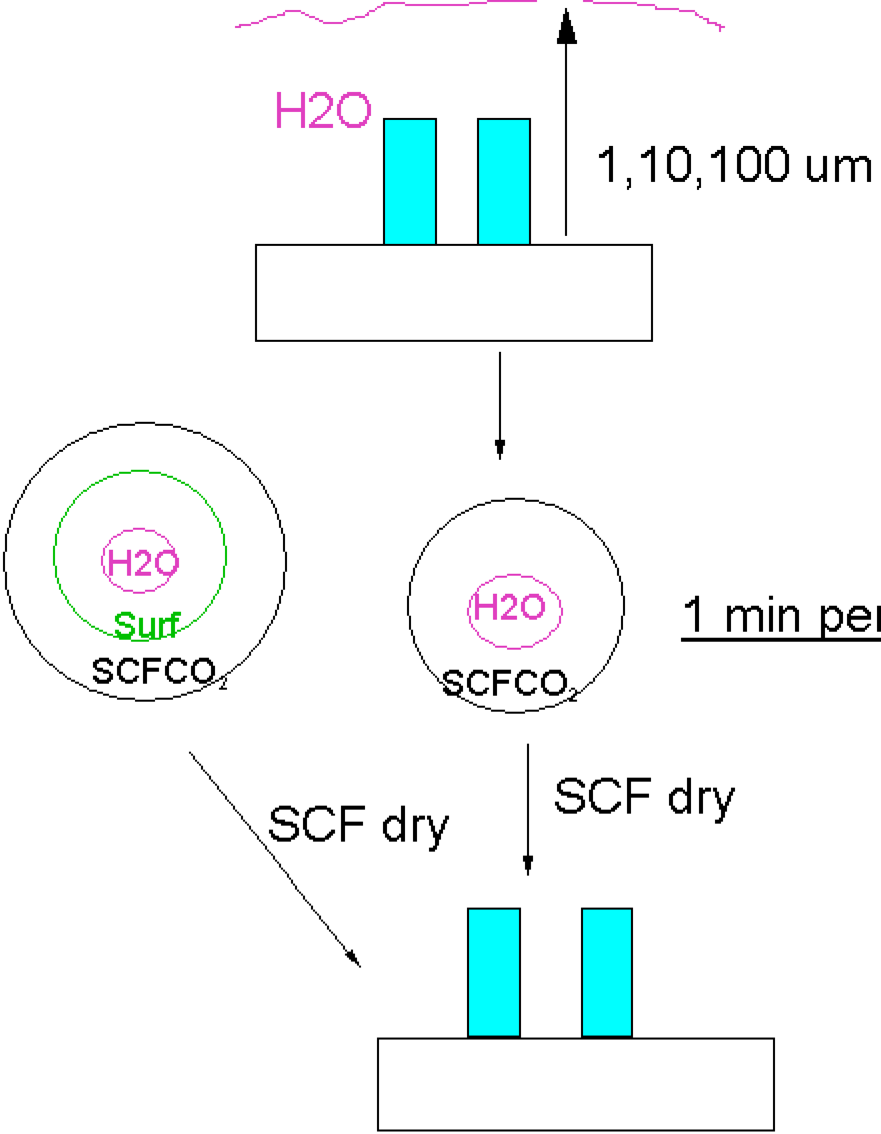


Fig. 2- Methods of Image Collapse Reduction

# Super Critical Fluid for Prevention of Image Collapse

- **_Solvents Highly miscible in scCO2_**
    - **_Acetic Acid_**
    - **_Methanol_**
    - **_IPA_**
    - **_Toluene_**
    - **_Ethanol_**
    - **_Fluorinated Solvents and polymers > 40 % F by wt and fluorosurfactants_**
    - **_Polysiloxane_**
    - **_cyclic cpds such as ethers,lactones_**
- **_Not miscible in scCO2 - < 0.1 grams/100 grams_**
    - **_Water_**



H2O

1,10,100 um

H2O

Surf

$SCFCO_2$

H2O

$SCFCO_2$

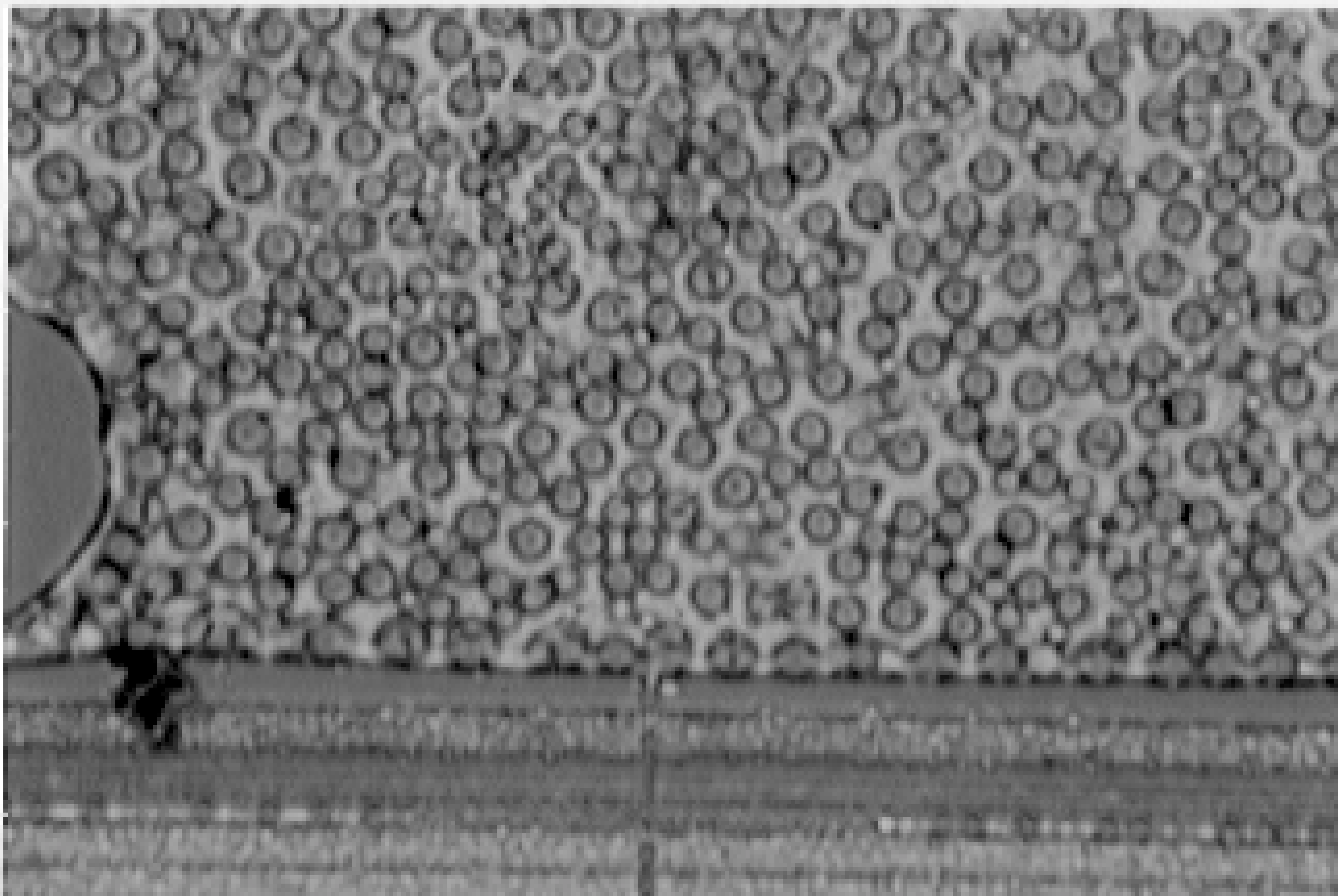
1 min per wafer ?

SCF dry

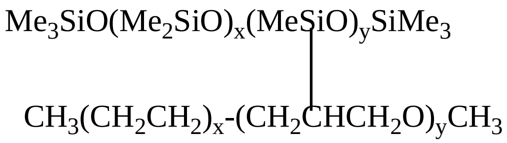
SCF dry

# Water Removal Directly on 193 nm Resist

Under SCF 65C, 4500 psi

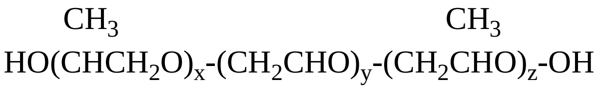


# EXAMPLES of $CO_2$ Phillic SURFACTANTS

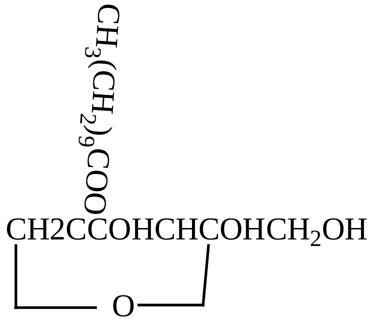


$$Me_3SiO(Me_2SiO)_x(MeSiO)_ySiMe_3$$
$$CH_3(CH_2CH_2)_x\text{-}(CH_2CHCH_2O)_yCH_3$$

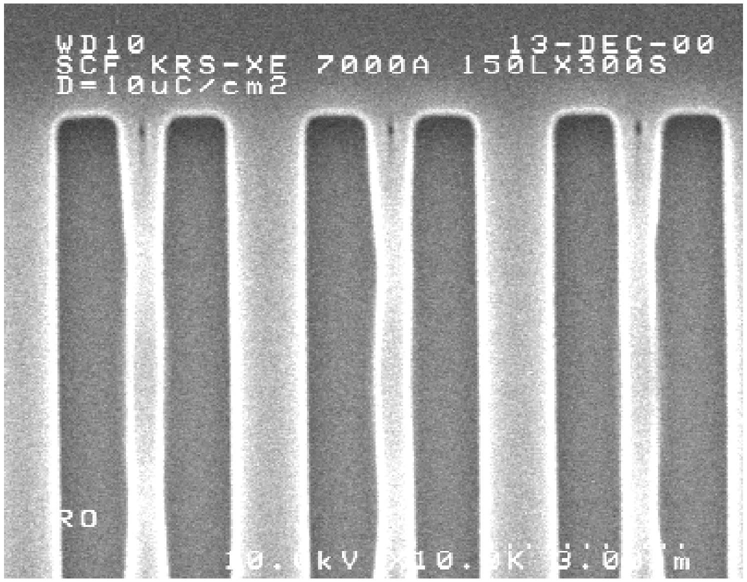
$CF_3(CF_2CF_2))_nCF_2CF_2COOH$



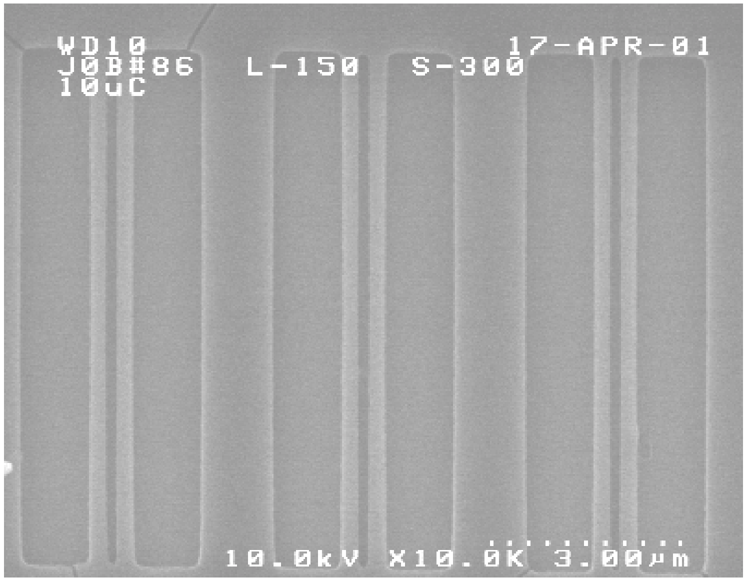
$$HO(\overset{CH_3}{CH}CH_2O)_x\text{-}(CH_2CHO)_y\text{-}(CH_2\overset{CH_3}{CH}O)_z\text{-}OH$$



# SCF CO2 Drying of Resist to Prevent Image Collapse

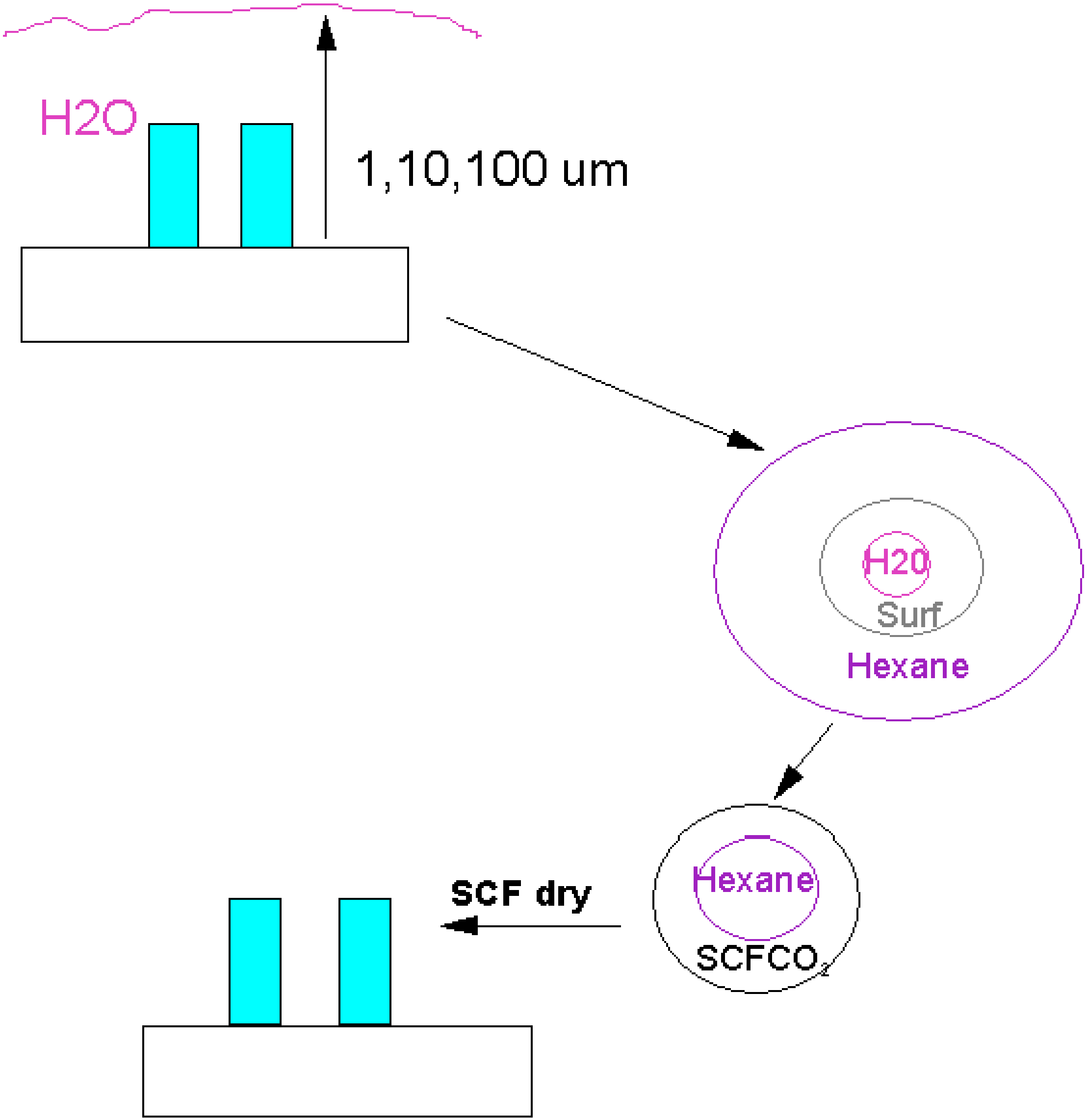


control



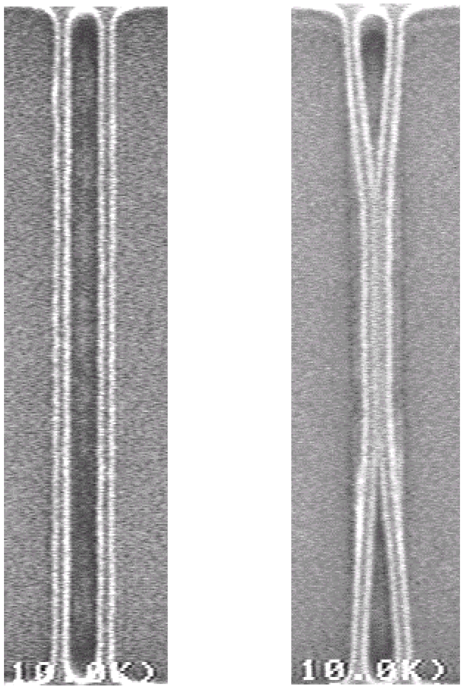
SCF dry

Positive CA Resist TMAH Dev,H2O rinse
800 nm thick 150 nm images , Aspect ratio =5


H2O
1,10,100 um
H20
Surf
Hexane
Hexane
SCFCO$_2$
SCF dry

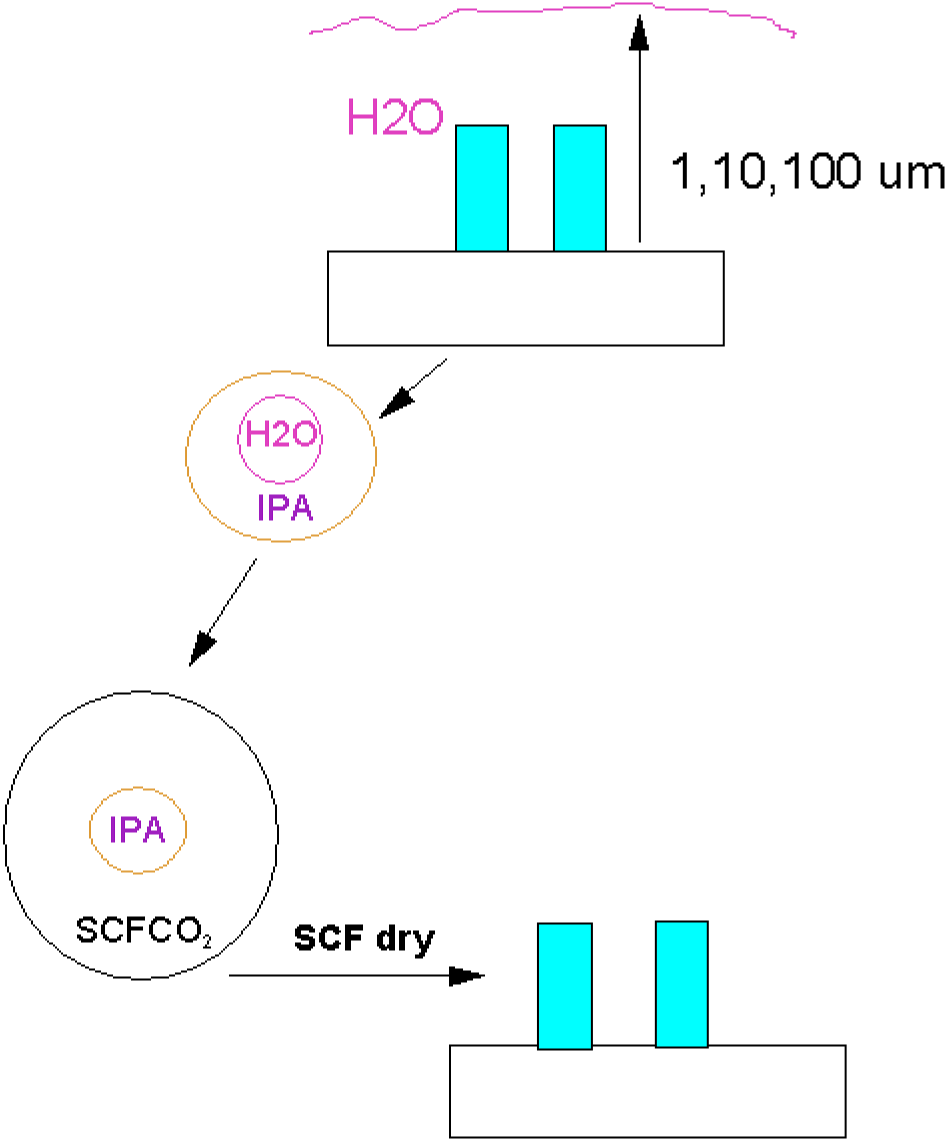
## Sets of pairs of Apex-E lines were written using a Leica Cambridge EBMF 10.5 ebeam

**APEX-E line** processed
using **scCO$_2$**
**and surfactant AOT**
linewidth = 130 nm
spacing = 370 nm
Aspect ratio = 7.3
L/S = 1 : 2.8
magnification = 20K



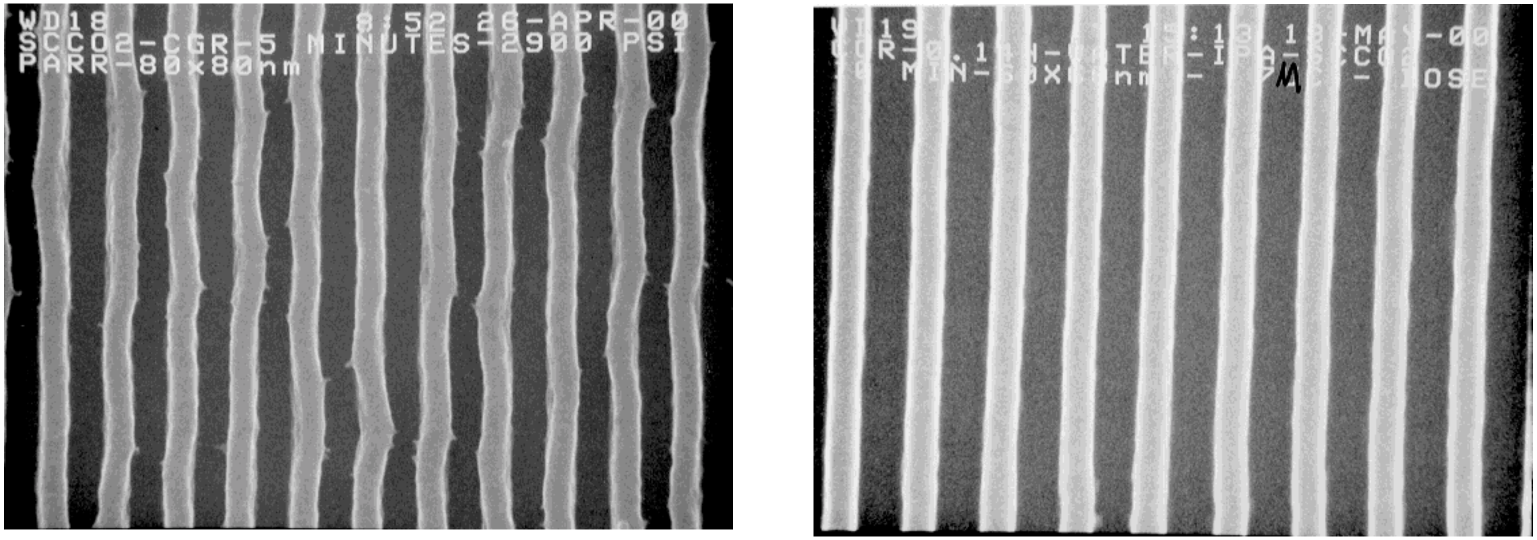
Same sample after
rewetting in **hexane**
and normal dried

Figure 6-APEX- E ,AR =7, AOT/Hexane Rinse,SCF CO2 dry


H2O
1,10,100 um
H2O
IPA
IPA
SCFCO$_2$
SCF dry

# Solvent Resistance of NEG CAR RESIST

| SOLVENT | ATTACK |
|---|---|
| Methanol | Severe- 20 % film loss |
| Ethanol | Severe |
| Isopropyl alcohol IPA | Slight- 2 % film loss |
| Butanol | moderate |
| Acetone | Severe |
| Methoxyproponal | Stripped |
| Ethyl lactate | Severe |
| Glacial acetic acid | Moderate |



a

b

Figure 7-a, 90 nm lines CGR AR=5, Water/SCF CO2 dry
b,90 nm lines,CGR AR=5,Water/IPA/SCF CO2 dry

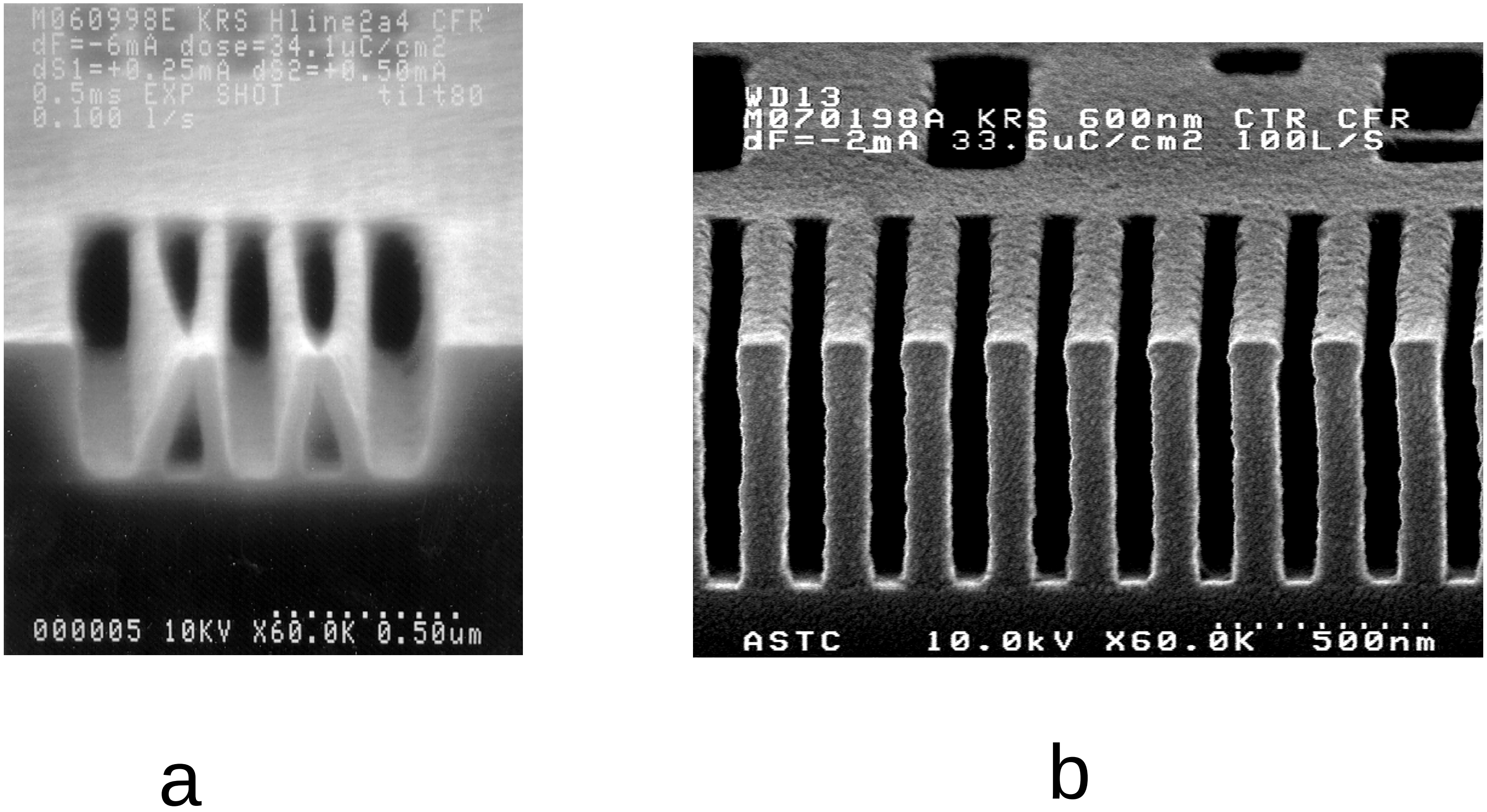


Figure 4-a,100nm,AR=4, KRS-XE, Water rinse ,air dry
b, 100 nm,AR=6, KRS-XE,Surf Rinse, air dry

# ASPECT RATIO ACHIEVEMENTS in Solving Image Collapse

| Line/space, | Aspect Ratio | AR/LS | Resist | Process | Reference |
|---|---|---|---|---|---|
| 20/20 nm | 7 | 0.35 | ZEP (PO) | SCF dry | Namatsu |
| 50/120 nm | 6 | 0.12 | NEB-31(NA) | Surf/Liq/SCF | Namatsu |
| 80/80nm | 5 | 0.07 | ZEP (PO) | Perflhex dry | Yamashita |
| 50 nm/50 nm | 6 | 0.06 | 157 nm (PS) | SCFdev/dry | someday |
| 100/100 nm | 6 | 0.06 | KRS-XE (PA) | Surf/H20Rin | This work |
| 140/370 nm | 7 | 0.05 | APEX (PA) | Surf/Hex,SCF | Goldfarb |
| 150/250 nm | 6 | 0.04 | KRS-XE(PA) | H20/SCF dry | This work |
| 200/200 nm | 5 | 0.03 | PN 100 (NA) | TBA/H20 Rin | Tanaka |
| 130/130 nm | 3.5 | 0.03 | COMA (PA) | H20 Rinse | Cao |

PO-Pos organic dev resist

NA-Negative Aqueous based resist

PA- Positive Aqueous Based Resists

PS- Positive SCF develop

# SCFCO2 CONSIDERATIONS/Water Removal

- ➡ Surfactant Required and Is it Inert to Resist
- ➡ Remove Water Prior to SCF Dry ?
- ➡ Time to Dissolve Rinse Solvent in SCF
- ➡ Press/Temp of SCF Reactor
- ➡ Rate of Depressurization

# IMAGE COLLAPSE

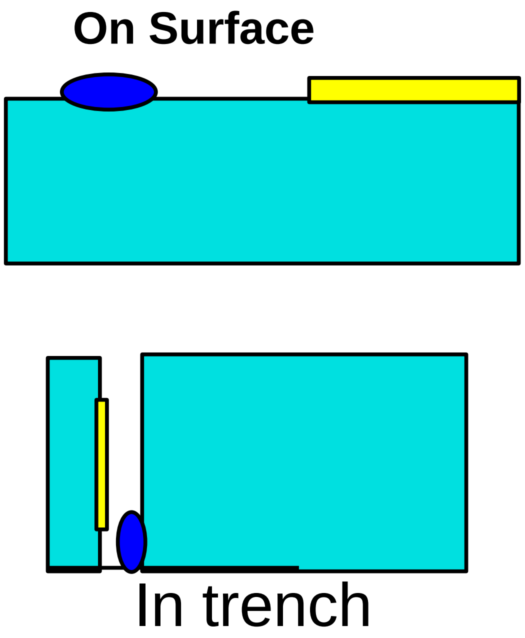
- Aspect Ratio > 3 < 150 nm L/S =IC
- Lower ST of Rinse/DRY Effective
- Removal Of Rinse Water Challenge in PR
- Remove Water by Inert Liquids followed by SCFCO2 Dry Shows Promise
- Future Challenges in Overcoming IC

➡ Positive Resists "Insolubility"

➡ Tool Design/Process Throughput

➡ SCF Developable Resist

# Cleaning Applicatons for SCF



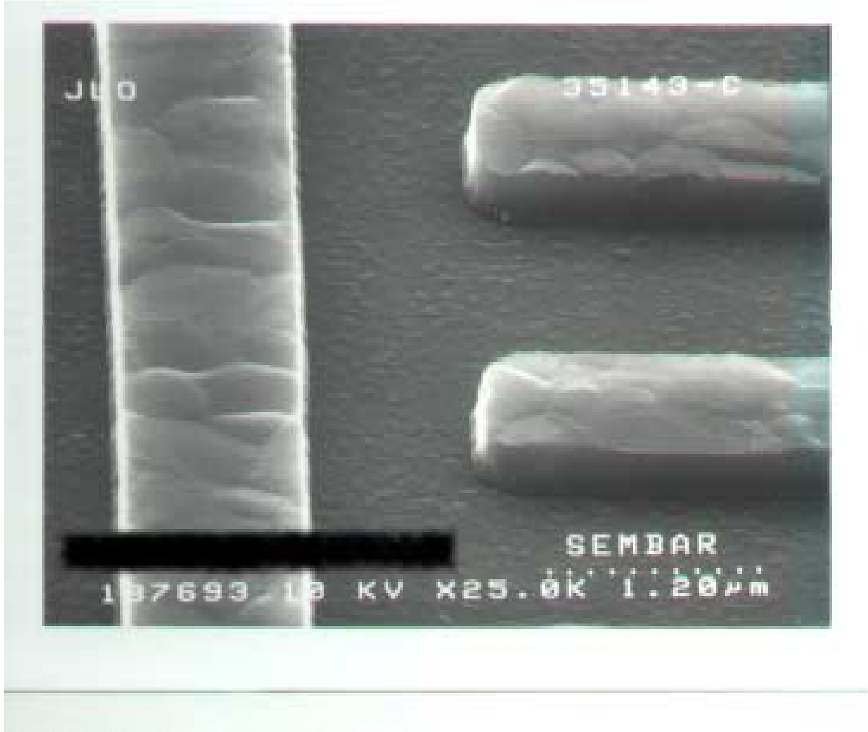
DISSOLVE OFF
DISPLACE
DISLODGE
SWELL
EMULSIFY
UNDERCUT
CHEMICAL CONVERSION

Strip vs Etch vs Clean

Residue or Film
Type- Polymeric
Organic/inorganic/Metallic/mixed

- RIE Residue Removal.

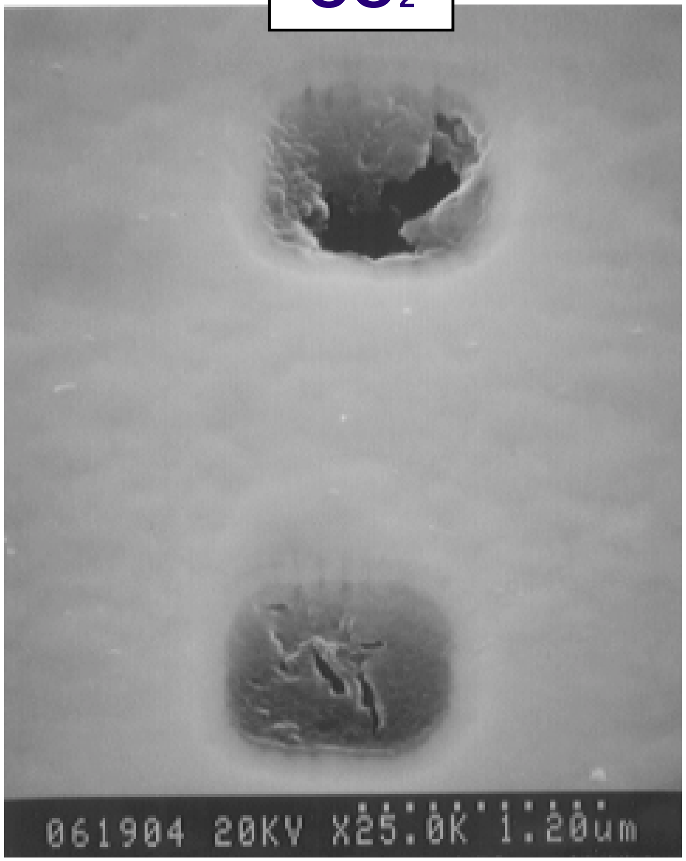
**Al structure post RIE**



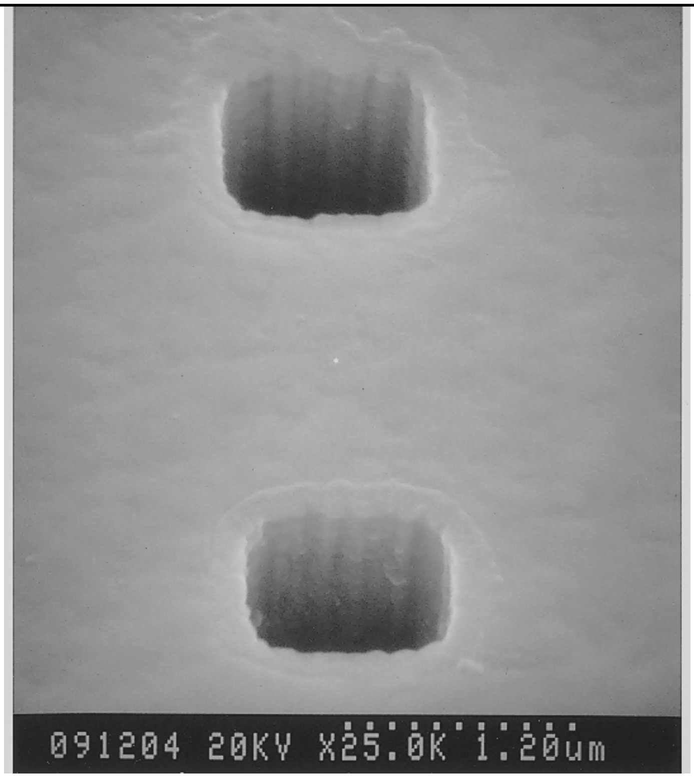
**After clean w/$CO_2$**

- Post CMP Residue Removal.

**$CO_2$**

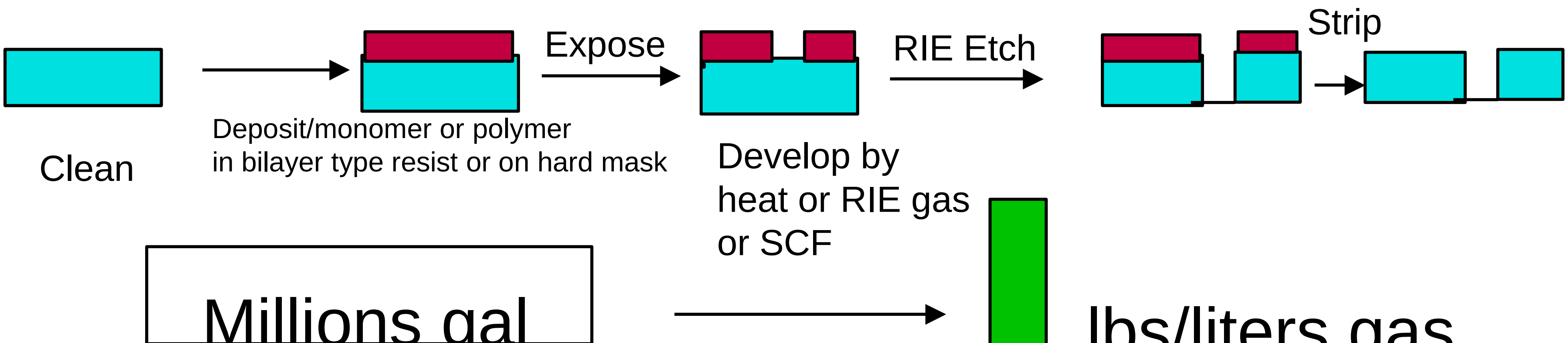


**$CO_2$ + CoSolvent C**



# TOWARD ALL GAS PHASE LITHO

- Stage1-Eliminate/Reduce Organic Solvents- by Aqueous Strip
- Stage 2- Eliminate/Reduce Aqueous Liquids by SCF Process in Clean/strip and Deposit and develop/dry
- Stage 3- All Gas Phase Lithography monomer example octavinylsilsesquioxane .



Clean

Deposit/monomer or polymer
in bilayer type resist or on hard mask

Expose

Develop by
heat or RIE gas
or SCF

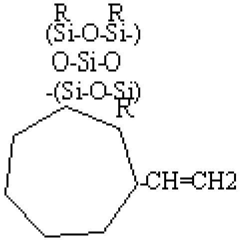
RIE Etch

Strip

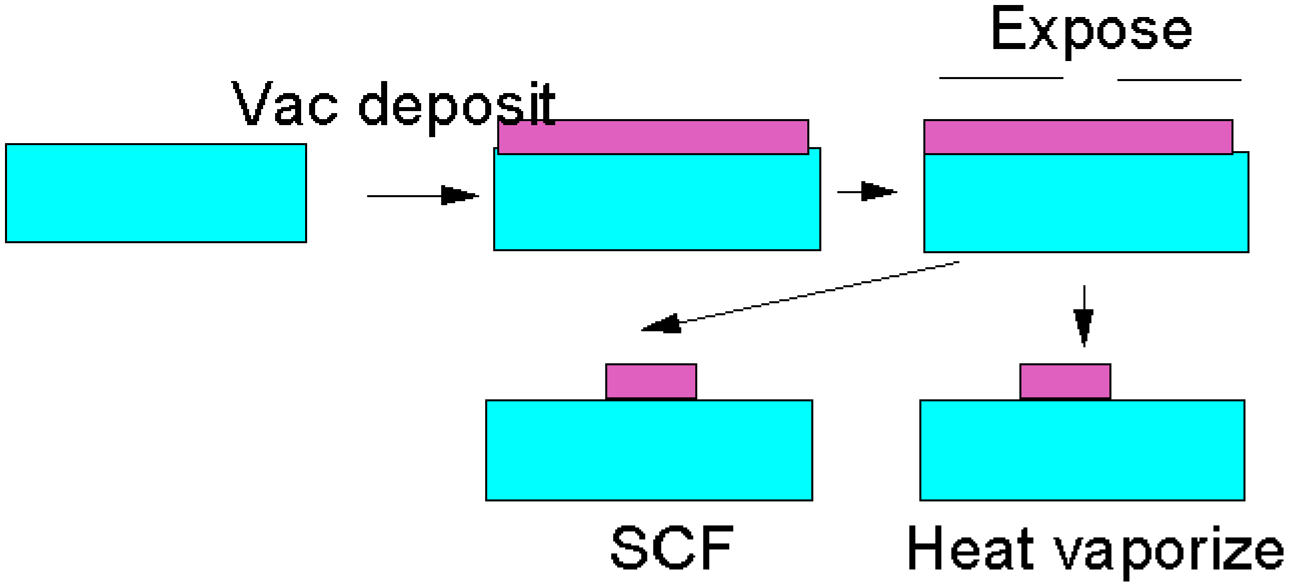
Millions gal

lbs/liters gas

# Example- Dry Lithography



Cycloalkylvinylsiloxane monomer



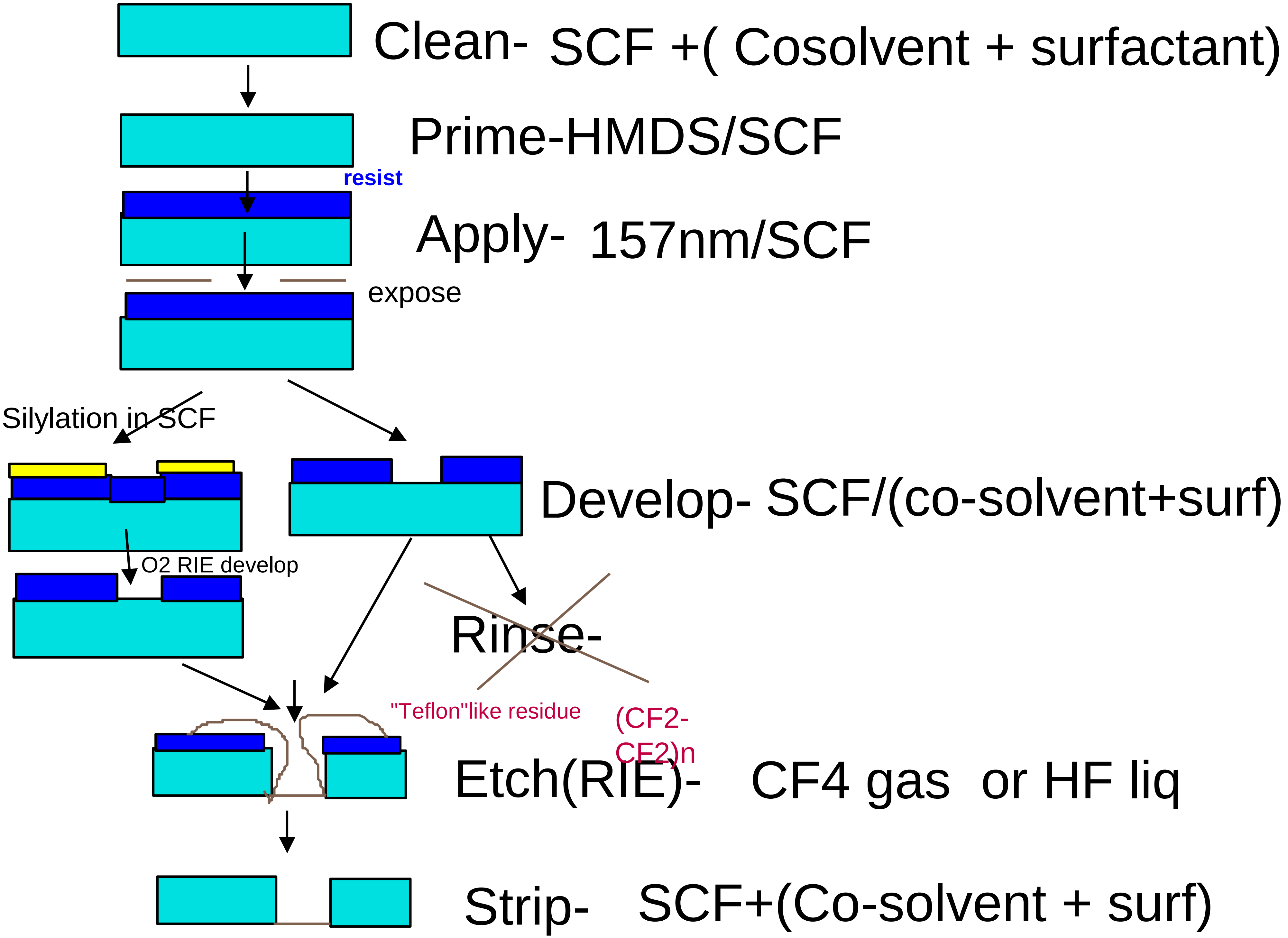
Vac deposit

Expose

SCF

Heat vaporize

# SUMMARY of SCF FLUID LITHOGRAPHY



Clean- SCF +( Cosolvent + surfactant)

Prime-HMDS/SCF

Apply- 157nm/SCF

Develop- SCF/(co-solvent+surf)

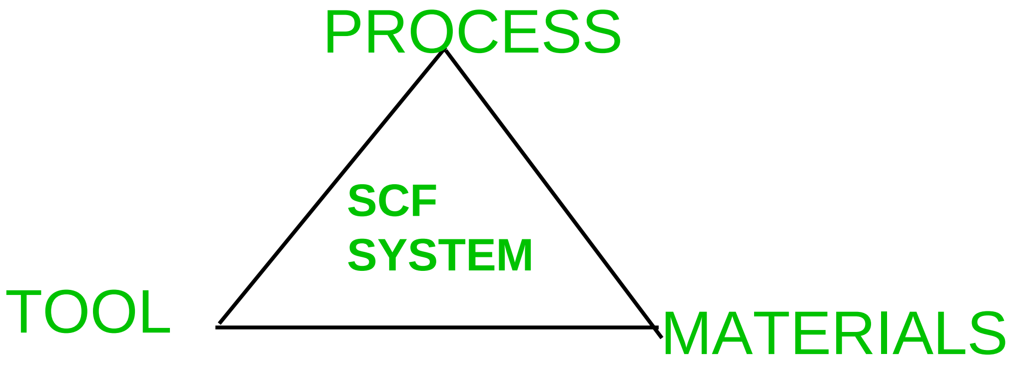
~~Rinse-~~

Etch(RIE)- CF4 gas or HF liq

Strip- SCF+(Co-solvent + surf)

# SUMMARY of SCF applied to Semiconductor Lithography

- Can it replace/displace water based process
- Can it replace/reduce organic solvents
- Can it fit into  into existing process
- Initial Feasibilty in cleaning and drying
- New Applications
- Future Integrate



PROCESS

**SCF SYSTEM**

TOOL

MATERIALS

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