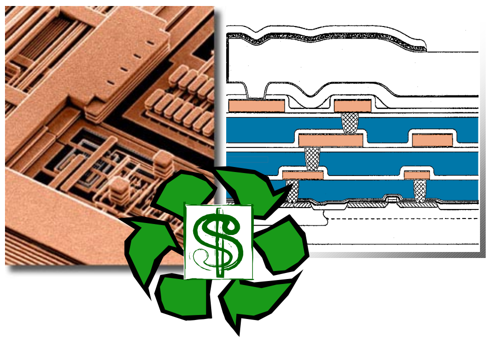
Patternable Low-κ Dielectrics Developed Using Supercritical CO_2



1999 SRC/SSA SEMATECH Excellence Award for Research in Manufacturing and Environment, Safety and Health

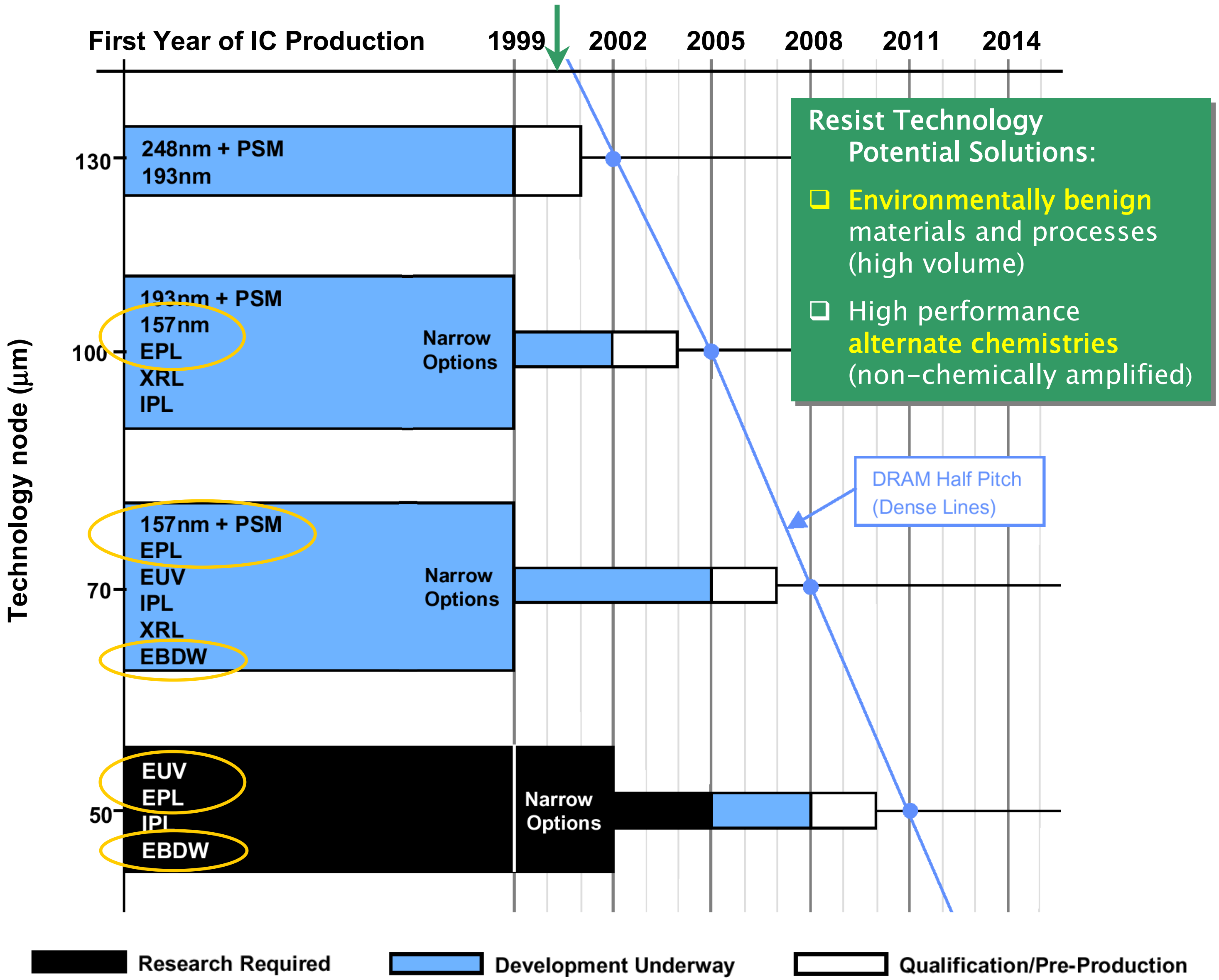
Award Presentation, 26th April 2000

by

Hilton G. Pryce Lewis
Karen K. Gleason

Gina Weibel
Christopher K. Ober

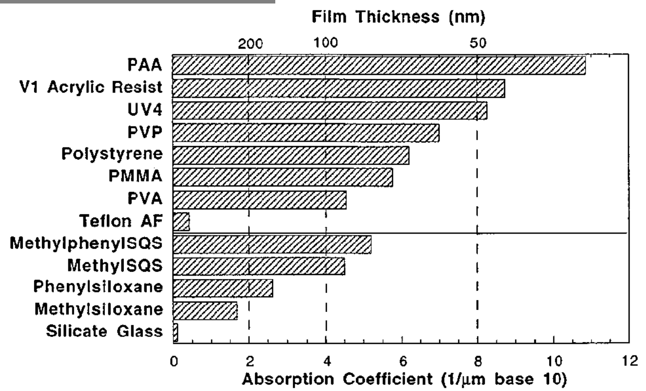
1999 Lithography Roadmap



adapted from *The National Technology Roadmap for Semiconductors, SIA, 1999*

Challenges in Resist Technology

Transparency



from Bloomstein, et al, *JVST B* 16(6),1998, pp. 3154-3157

- ❑ Existing resists inadequate at 157-nm
- ❑ "Alternative resist strategies will be based on either fluorinated polymers or organosilicon materials."

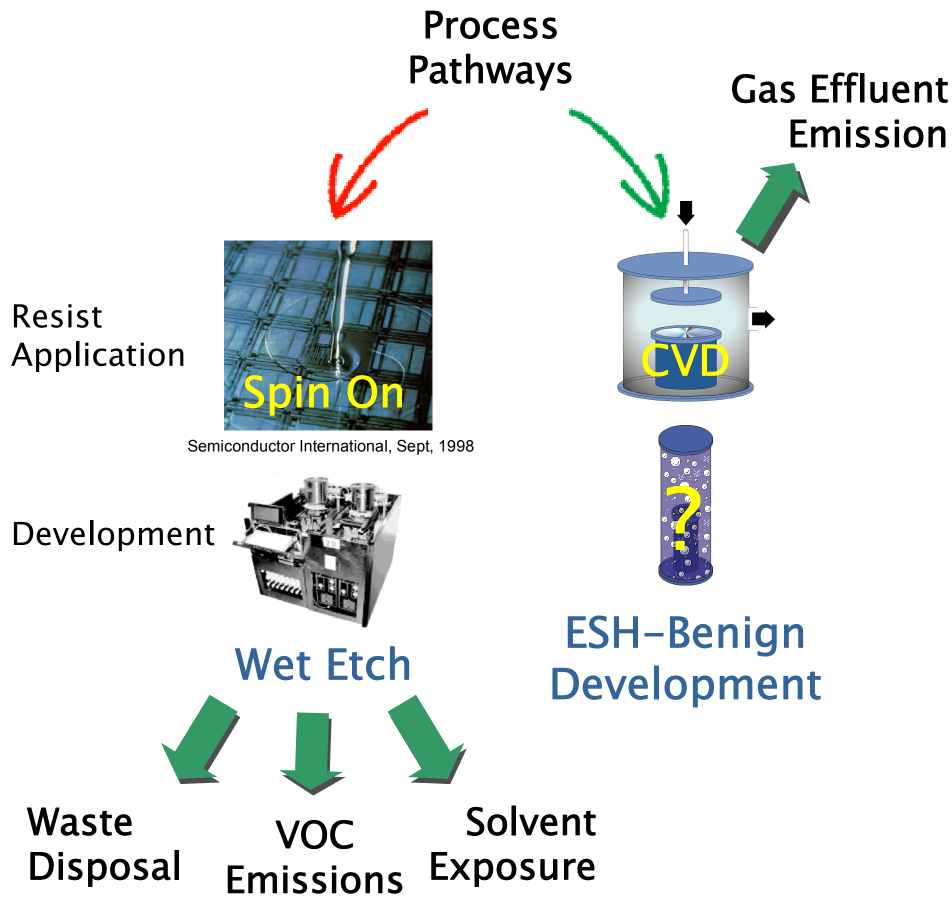
Next-Generation Lithography (NGL)

- ❑ New chemistries required

Development

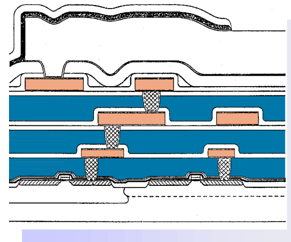
- ❑ Aqueous base compatible with new chemistries?

ESH impact of new processes



Challenges in Interconnect Technology

Reducing dielectric constant, ?



Near Term

YEAR / *TECHNOLOGY NODE*	*1999* *180 nm*	*2000*	*2001*	*2002* *130 nm*	*2003*	*2004*	*2005* *100 nm*
Interlevel metal insulator —effective dielectric constant (κ)	**3.5–4.0**	**3.5–4.0**	**2.7–3.5**	**2.7–3.5**	**2.2–2.7**	**2.2–2.7**	**1.6–2.2**

SiO_2

SiOCH, FSGs, amorphous FC & HFC…

Long Term

YEAR / *TECHNOLOGY NODE*	*2008* *70 nm*	*2011* *50 nm*	*2014* *35 nm*
Interlevel metal insulator—effective dielectric constant (κ)	**1.5**	**<1.5**	**<1.5**

porous films, air gaps…

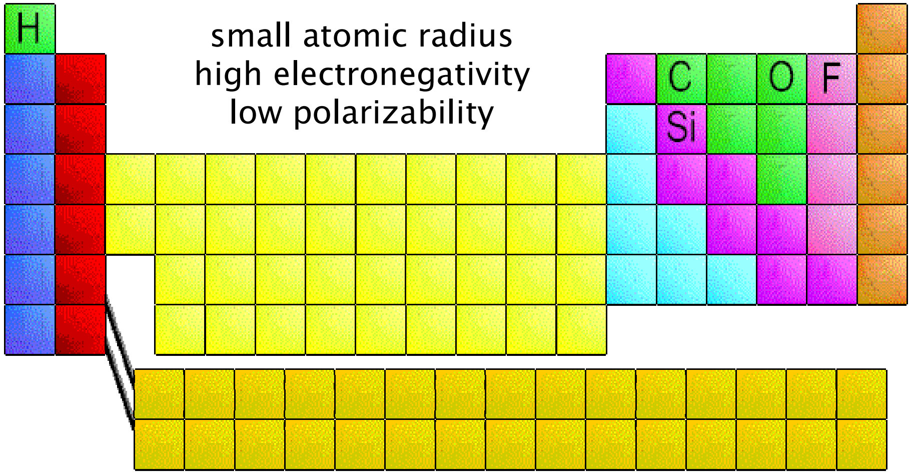
Solutions Exist

Solutions Being Pursued

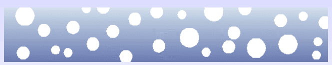
No Known Solutions

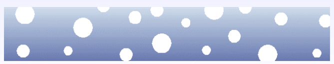
adapted from *The National Technology Roadmap for Semiconductors, SIA, 1999*

Low-? Strategy



	% porosity to reach ? ~ 2
SiO_2	55 - 65
hydrocarbon polymer	40 - 50
fluorocarbon polymer	0





FC Material	?
Bulk PTFE $(CF_2CF_2)_n$	2.1
a-C:F (Endo, NEC)	2.1-2.5
a-C:F,H (Theil, HP)	2.2-3.3
FLAC (Mountsier, Novellus)	2.0-2.5
FDLC (Grill, IBM)	2.5-2.7
CF_x (Akahori, TEL)	2.5
SPEEDFILM (Rosenmayer, Gore)	1.7-2.0

Exploiting these Issues: A New Strategy

Lithography

- 157-nm
  - transparency.
  - development.
- NGL
  - new chemistries.
  - development.

Interconnect

- Low-? candidates
  - doped oxides.
  - fluorinated glasses.
  - porous films.
  - air gaps.
- Must be compatible with Damascene.

* fluorocarbon & organosilicon materials.

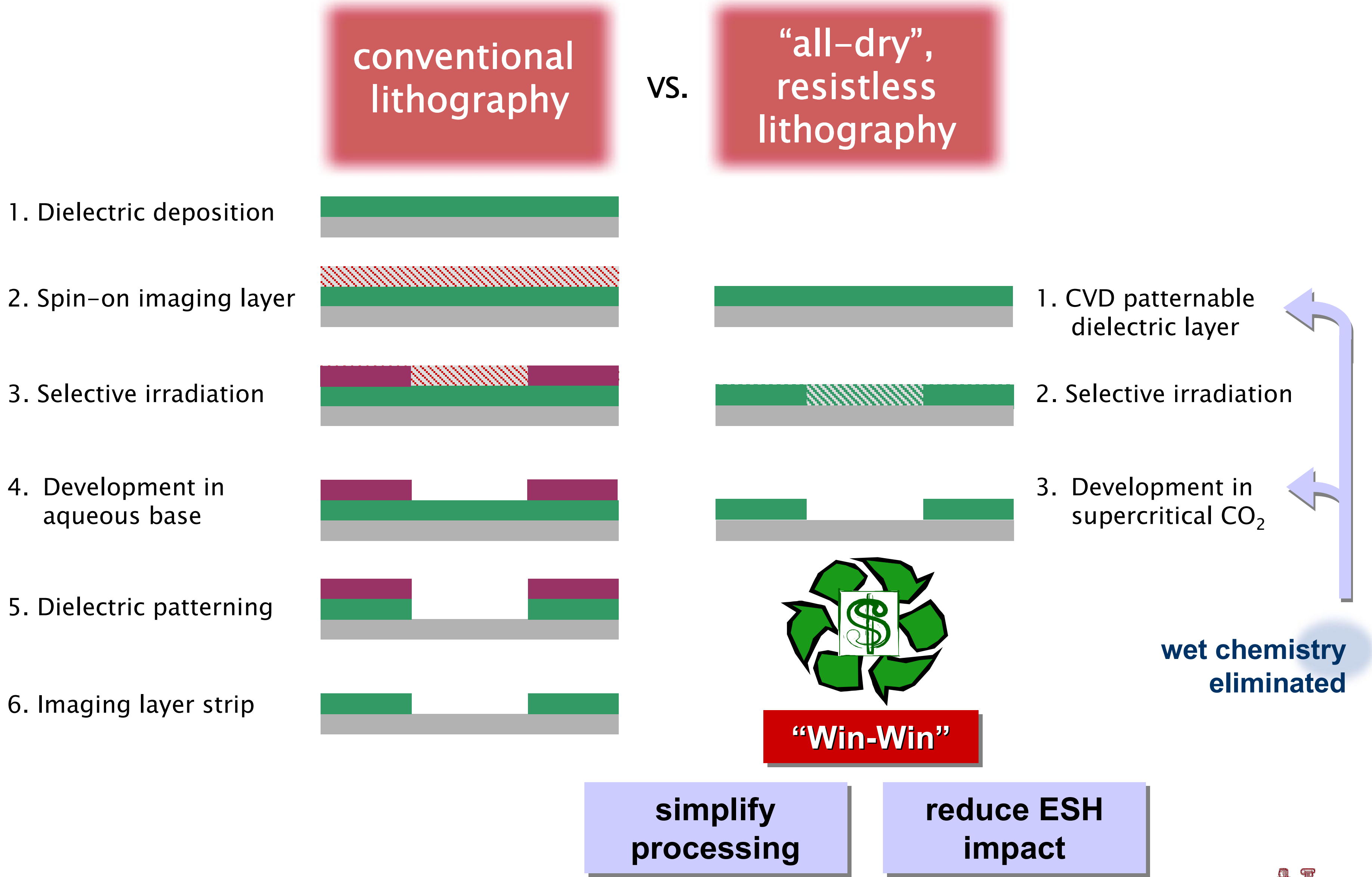
* CVD processing.

* ESH impact of new processes.

Directly Patternable Low-κ Dielectric

Developed using…?

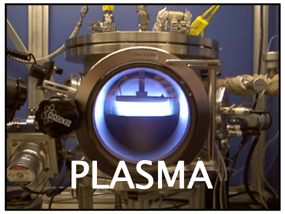
Goal: Simplified Lithographic Processing



How Do We Choose Candidate Materials?

CVD technology

type of film



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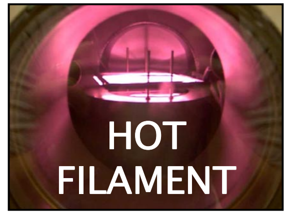


Organosilicon
$-SiMe_2-O-SiMe_2-$

and

Fluorocarbon
$-CF_2-CF_2-$

Criterion	Value
low dielectric constant, κ	❑ lower RC delay ❑ less cross-talk noise
transparent at 157-nm	❑ shorter λ for lithography
sensitive to e-beam exposure	❑ next-generation lithography
soluble in supercritical CO_2	❑ higher resolution ❑ ESH-benign development

+ESH responsibility

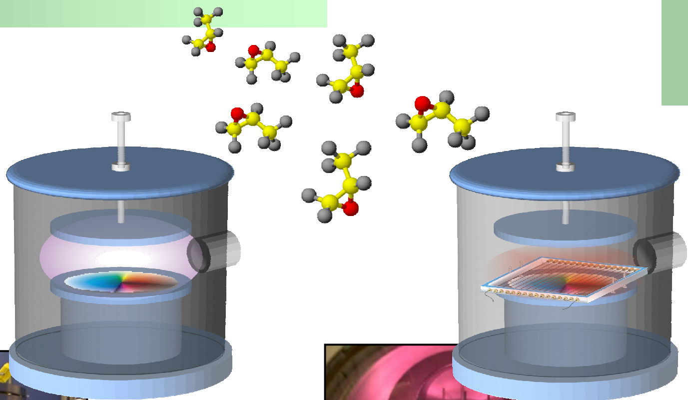
ESH Responsibility in Design of CVD Process

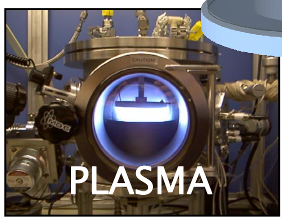
1

Select CVD process:
- plasma CVD
- hot-filament CVD.

2

Select precursors with:
- low global warming potential
- low ozone depleting potential
- low safety and health hazard.





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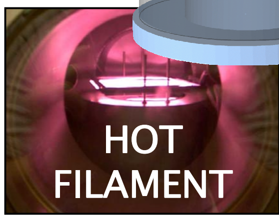
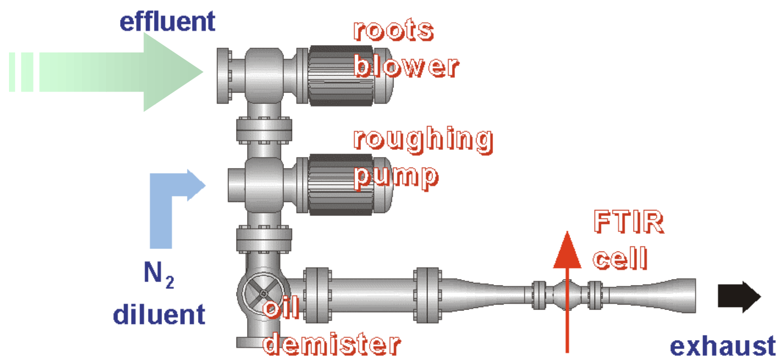




3

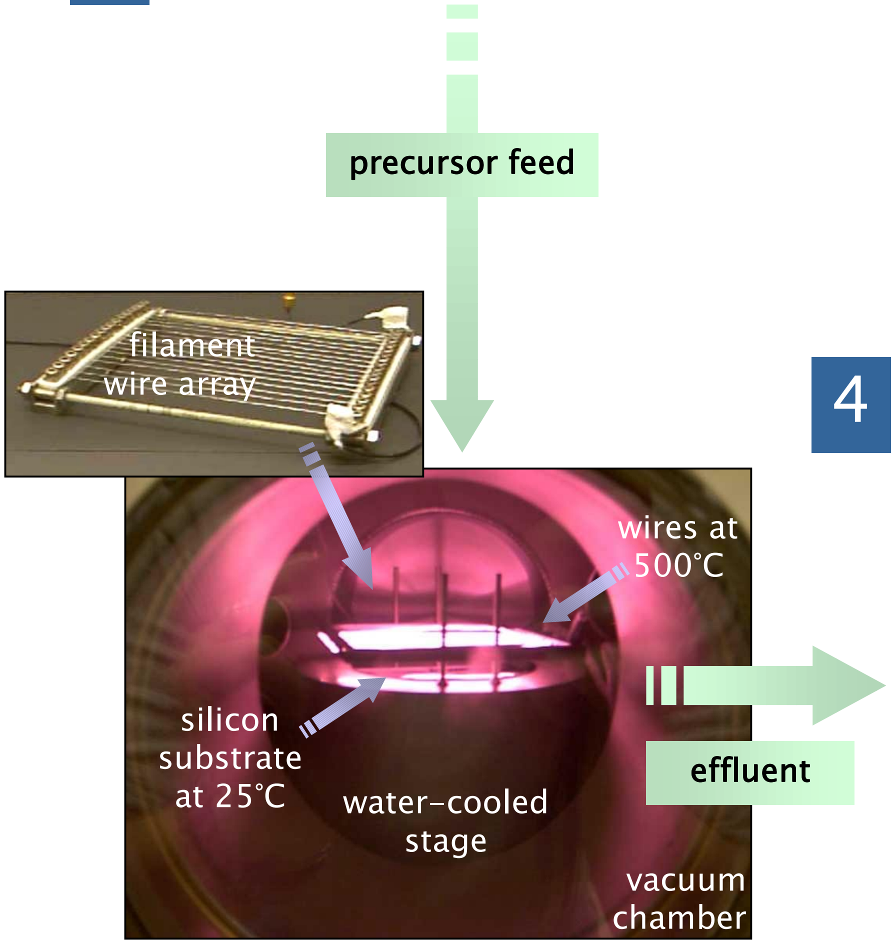
Reduce extent of unwanted precursor fragmentation which may lead to undesirable byproducts.

Analyze composition of reactor effluent using gas phase FTIR.

4

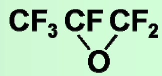
Hot-Filament CVD of Fluorocarbons (FC)

1 Choice of Process



2 Choice of Precursor

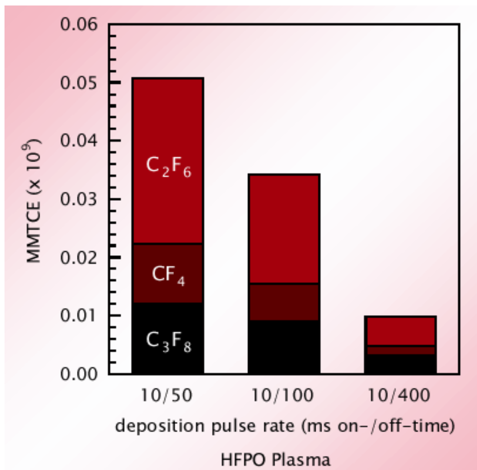
HFPO
(hexafluropropylene oxide)



- short atmospheric lifetime (cf. CF_4 ~50,000 yrs.)
- low GWP

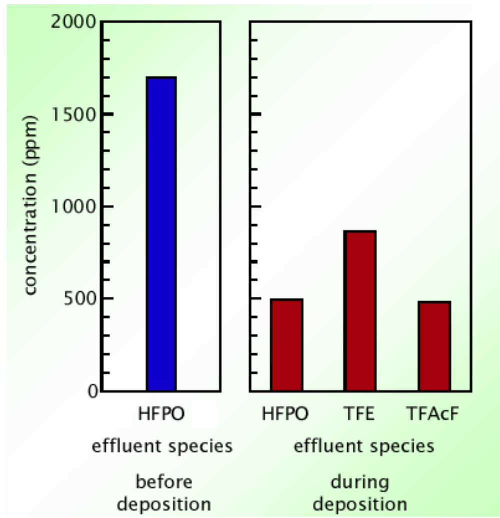
4 Effluent analysis

Pulsed-Plasma



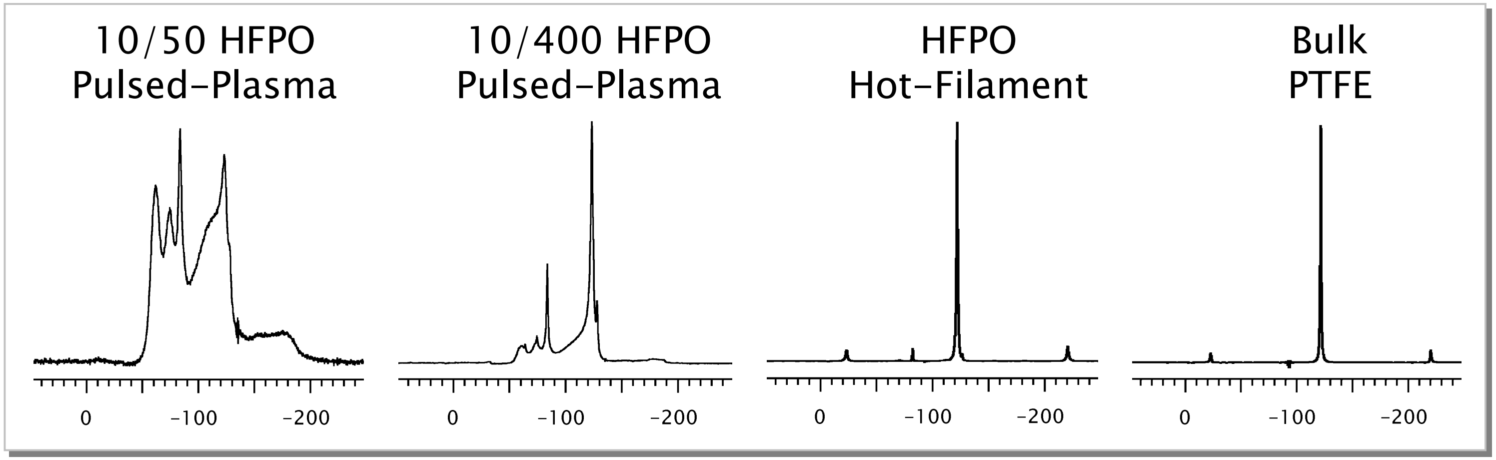
(Labelle et al, *JVST A*, 17(6), pp. 3419-3428, 1999)

Hot-Filament



Molecular Tailoring of Film Structure

3 Minimize unwanted reactive species

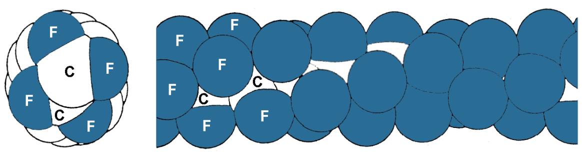


^{19}F NMR

Reduce precursor fragmentation and breakdown

Higher CF_2 concentration and more CF_2 polymerization

More PTFE-like composition and structure



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NSF/SRC ERC for Environmentally Benign Semiconductor Manufacturing

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ESH Benefits of Supercritical CO_2

Traditional: Spin-coating Resist → **Innovative: CVD Resist**

- Excessive polymer & solvent use
- Exposure to solvents/ vapors

- Little effluent
- Controllable disposal

Traditional: Aqueous Development → **Innovative: CO_2 Development**

- Solvent and water consumption/ waste
- Exposure to solvents/ vapors

- Reduced waste
- Increased safety

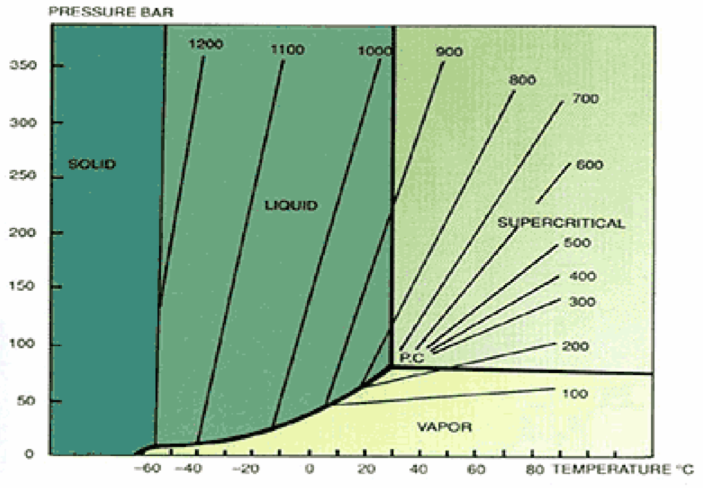
Reduced Waste

- Recyclable effluent
- No aqueous waste
- No organic solvents
- CO_2 extracted from waste stream or from atmospheric sources

Increased Safety

- No solvent exposure
- Non-flammable
- Non-toxic

Supercritical CO_2 as a Developer



Phase diagram of CO_2. Constant density lines (g/l)

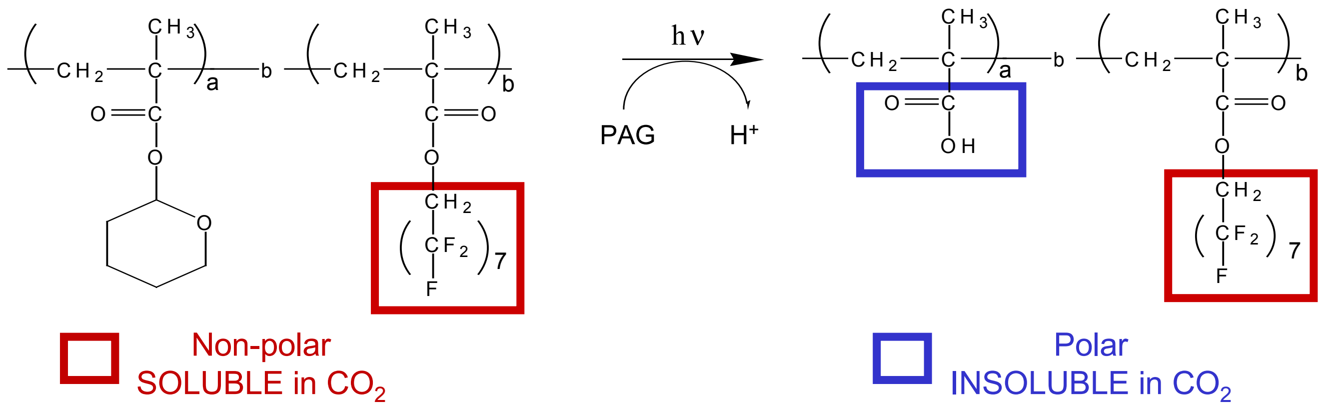
	Vapor	Supercritical Fluid		Liquid
	P = 0.1 MPa T= 15 °C	P_c T_c	$4P_c$ T_c	P = 0.1 MPa T= 15°C
Density (g/cm^2)	0.0006 – 0.002	0.2 – 0.5	0.4 – 0.9	0.6 – 1.6
Viscosity (μPa·s)	10 – 30	10 – 30	30 – 90	200 – 3000
Diffusivity (cm^2/s)	0.1 – 0.4	$0.7 \cdot 10^{-3}$	$0.2 \cdot 10^{-3}$	$0.2 \cdot 10^{-5} – 2.0 \cdot 10^{-5}$

- High and variable density
  - Dissolution selectivity can be manipulated
- Digital control of temperature and pressure
  - Tunable solvating power

- Low viscosity: comparable to gas
  - No surface tension
  - Pattern collapse of features avoidable
- Higher diffusion coefficient than liquid
  - Accurate and rapid development

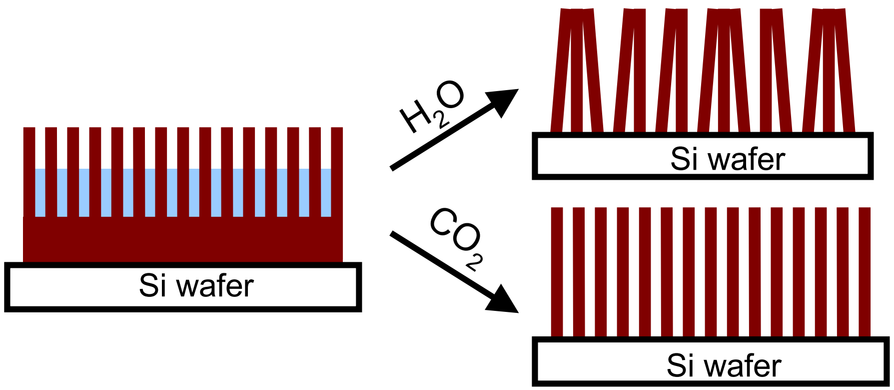
Supercritical CO_2 as a Developer: Pattern Limits

- Low Viscosity of SCF CO_2 allows for drying features **without pattern collapse**
- Studies underway to examine limits to SCF CO_2 as developer. E-beam at Cornell; Negative tone processing of THPMA-F7MA



•High aspect ratio (>5) lines and spaces

•Aqueous developer surface tension creates lateral forces



•Forces during drying cause breaking of features: Pattern Collapse

•SCF CO_2 has no surface tension

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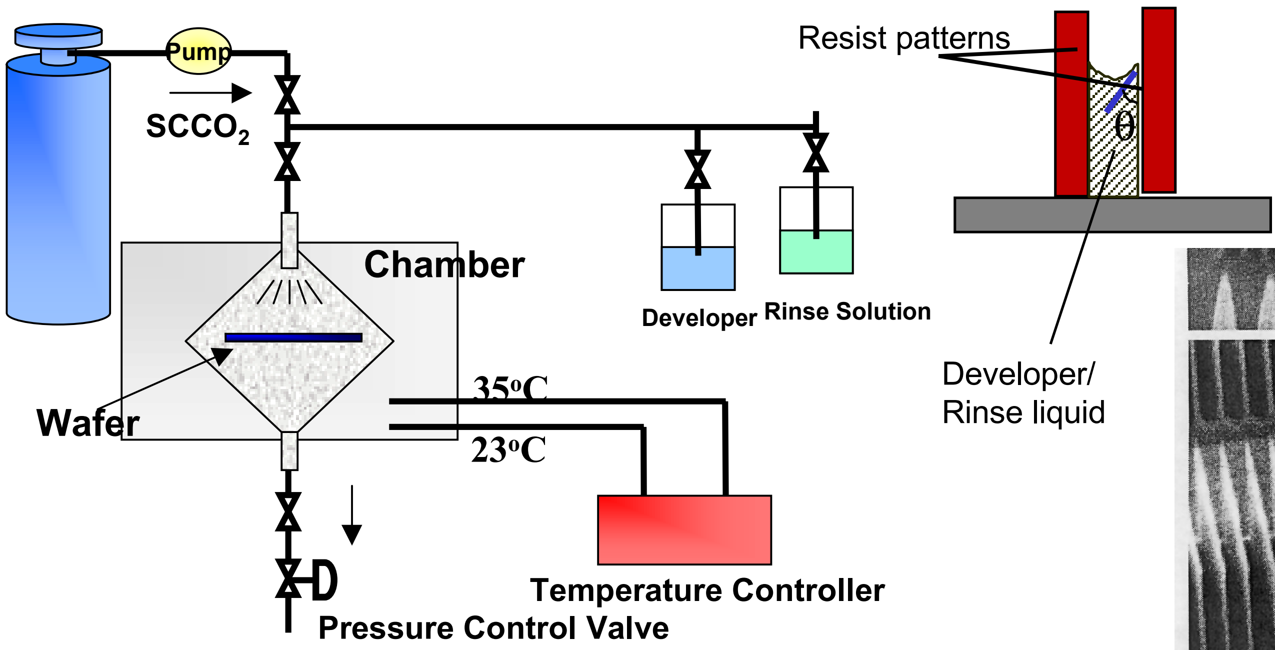
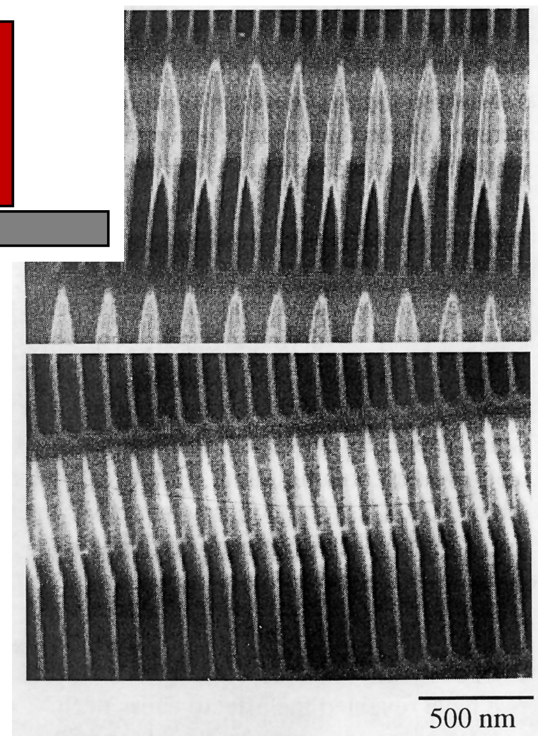
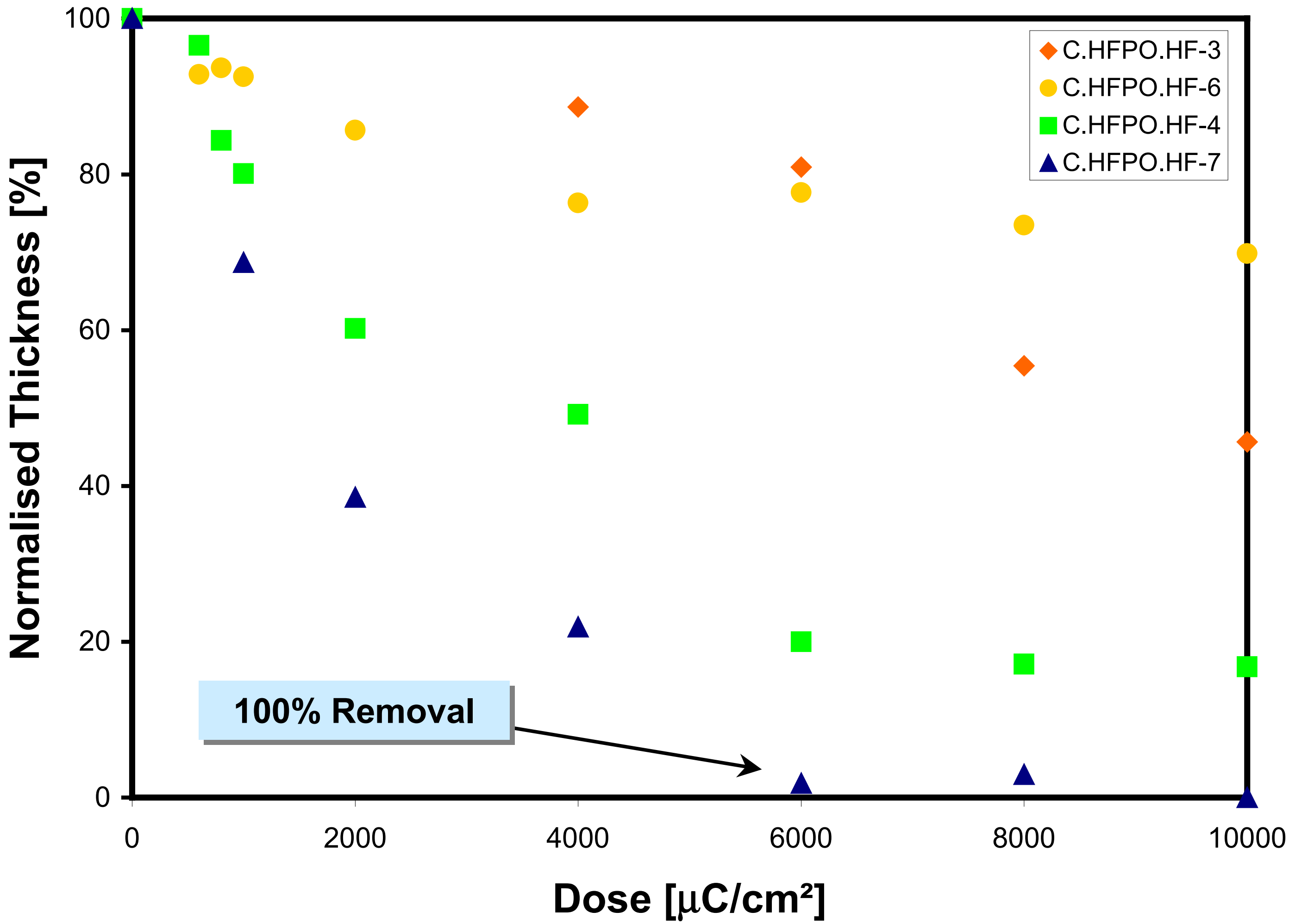
NTT Process – Avoiding Pattern Collapse

- Use CO_2 to replace water or polar solvents
- Reduce/ eliminate capillary forces that lead to pattern collapse
- Combinations of N_2 and CO_2 used in successful processing
- Remarkably fine features possible





E-Beam Patterning & Development of FC Films I



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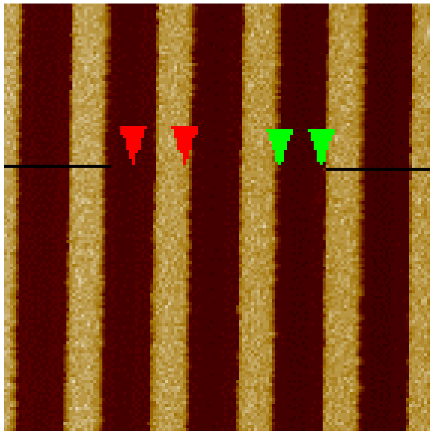
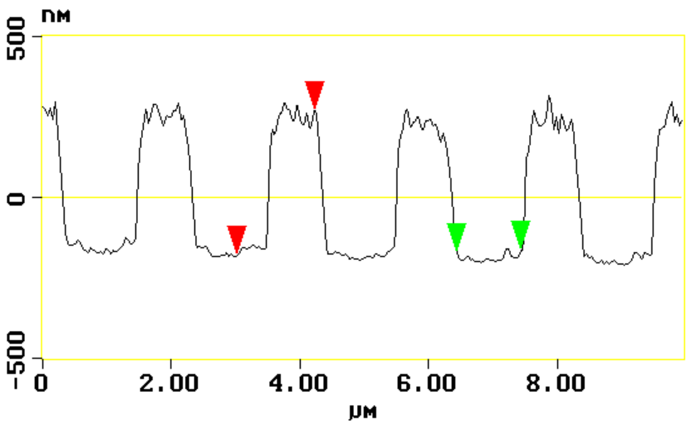
E-Beam Patterning & Development of FC Films II

Atomic Force Micrographs

Sample 8 post-development, 6000 μC

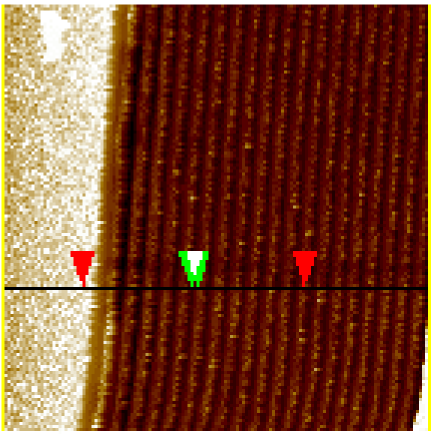


1.0 μ Lines/ spaces

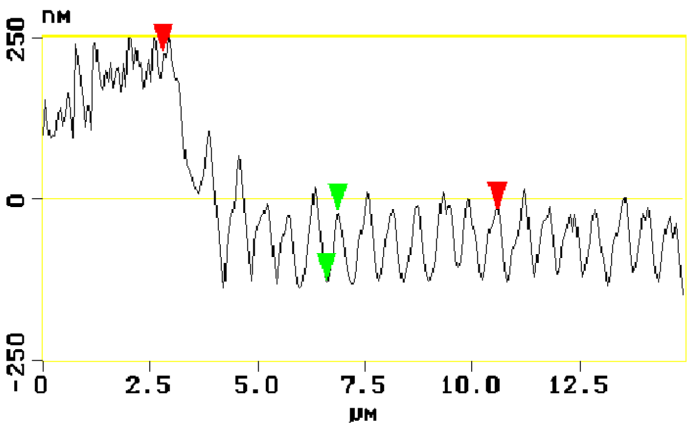


Cross section

- High selectivity (450 nm)
- Complete development
- 1 μm lines
- Positive-tone developing



0.25 μ Lines/ spaces



Cross section

- Possible charging of film
- 0.25 μm lines
- AFM tip profile interference
- Positive-tone developing

Summary

- Demonstrated patternable hot-filament CVD fluorocarbon films.
  - Film composition can be tailored.
  - E-beam used to effect solubility change.
- Successfully developed CVD polymer with supercritical CO_2.
  - Density/solvating power of CO_2 can be controlled.
  - Promise of ESH benefits for semiconductor processing.

Future Work

- Determine detailed mechanism(s) of irradiation chemistry.
- Improve sensitivity and resolution in patterning.
  - Incorporate irradiation-sensitive moieties.
  - Demonstrate patterning using 157-nm photolithography.
- Optimize supercritical CO_2 development.
  - Investigate dissolution mechanisms in supercritical CO_2.
  - Establish resolution limits of CO_2 development.

Acknowledgements

- NSF/SRC ERC for Environmentally Benign Semiconductor Manufacturing

- Cornell Nanofabrication Facility (CNF)
- MIT Lincoln Labs
- MIT MRSEC Facilities
- Semiconductor Research Corporation (SRC)
- Department of Education (D. of Ed.)

- Gleason Research Group
- Ober Research Group