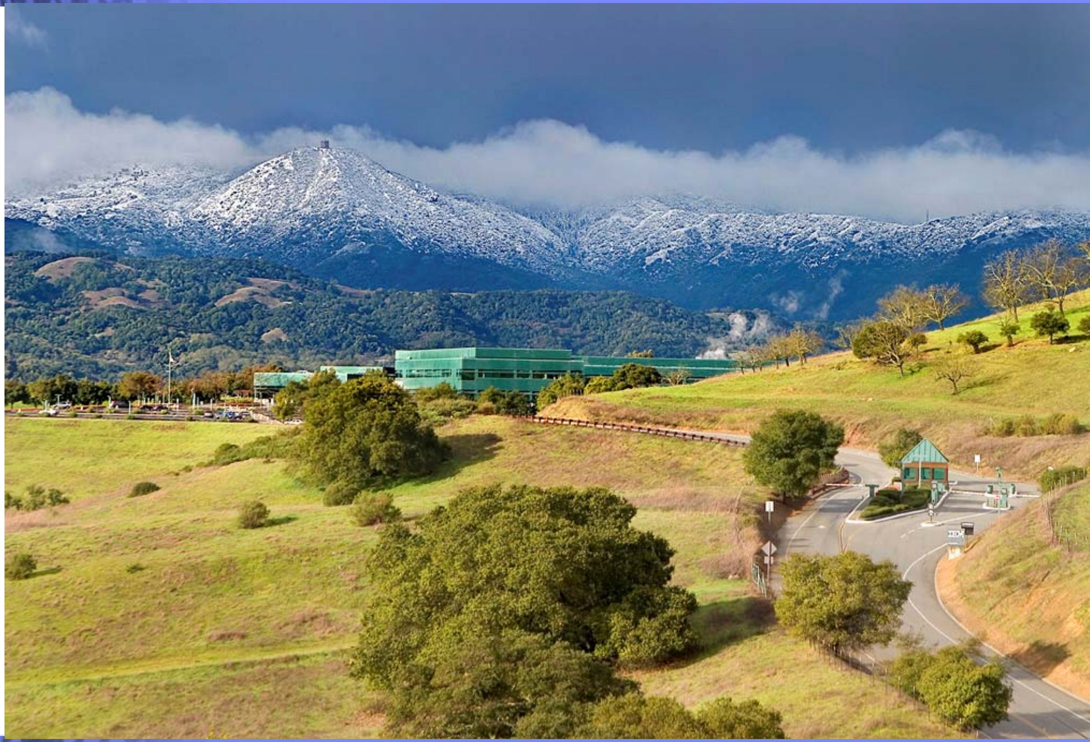
Chemistry in the design of new resists and other advanced patterning materials

Robert D. Allen
IBM Almaden Research Center

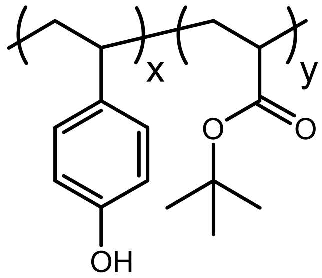


Presentation Outline: Functional photopolymers

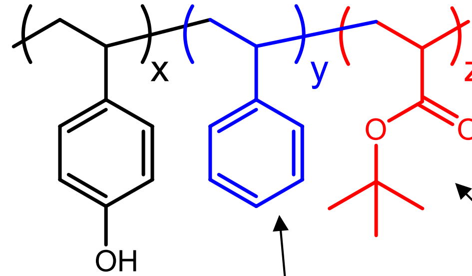
- Functional Materials for Patterning
- Extending 193nm lithography
  - FARM (Fluoro Acrylic Resist Materials) development
  - Immersion Materials: Ideal application for segregating resist design
    - Topcoats/topcoat free from FARM using segregating design
  - Extending segregating concepts to Oil-based immersion materials
- Molecular Glasses/AIR
- Another form of Chemical Amplification (Imprint)
- Progress in directed self assembly with BCPs

ESCAP—the prototype in functional materials design

Hiroshi Ito



- Dissolution control
- Adhesion
- etch resistance
- high Tg



CA switching group

Property control knob

Acrylic Ester/Phenolic Resist: A breakthrough in resist design

Materials Team on the "Austin Project"

- 1989-90
- VLPR- Fast Laser Direct Imaging resist for PC Board prototyping
- Team- Wallraff/Allen/Hinsberg/Simpson and Grant Willson

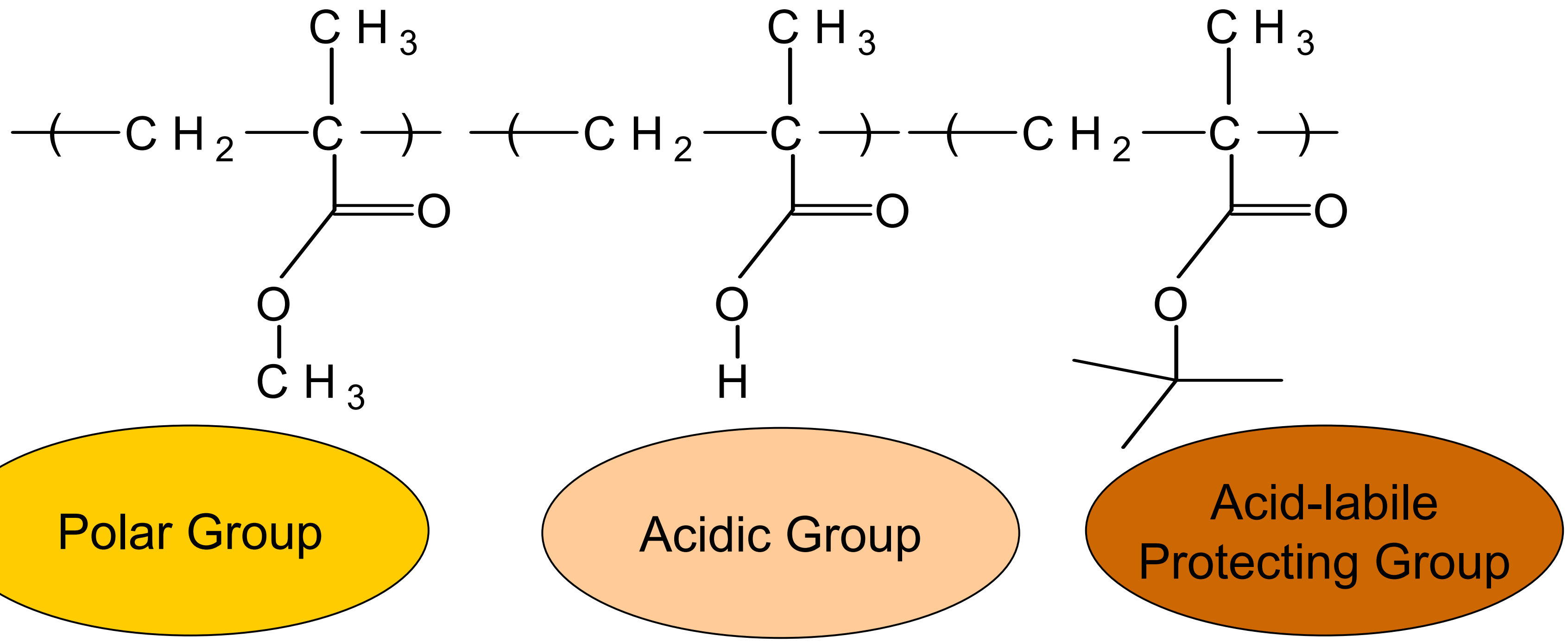
An early non-traditional exploitation of Chemical Amplification:

All-Methacrylate Resists

Allen Wallraff

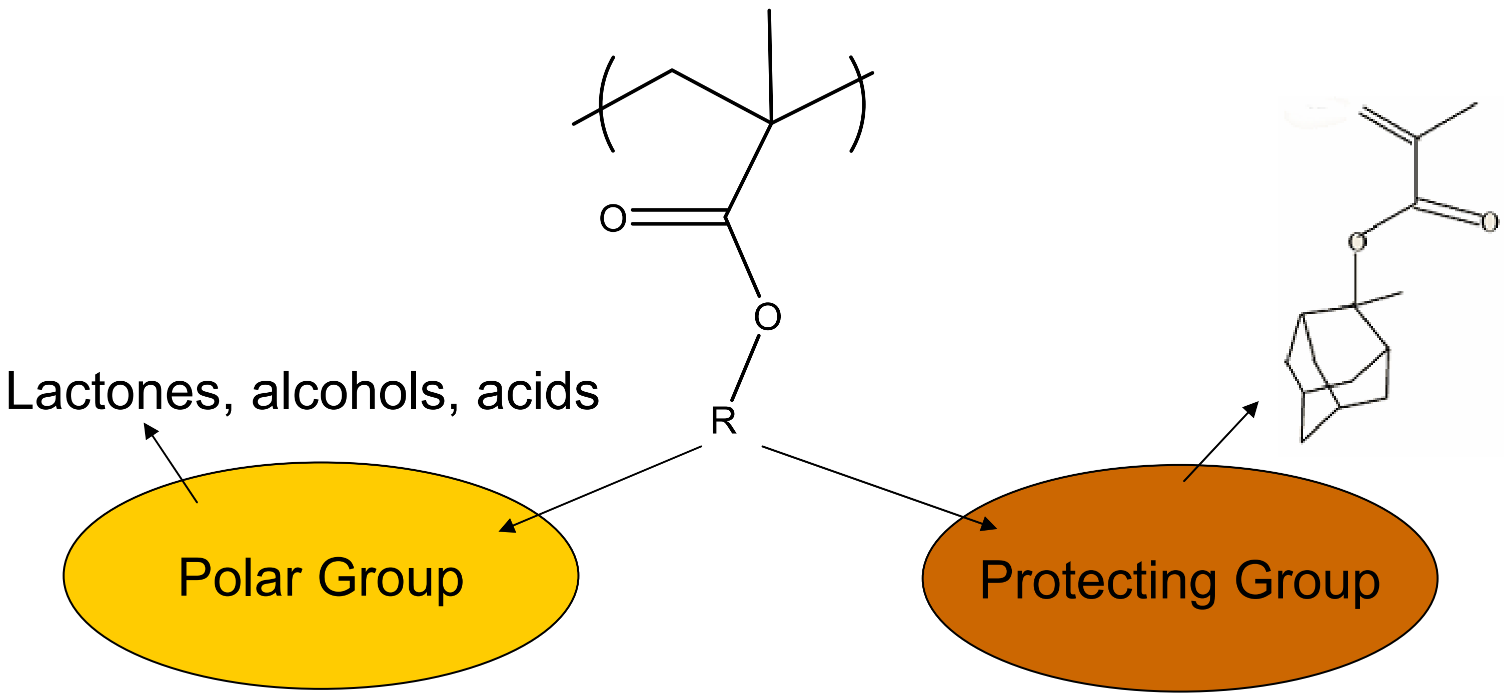
Methacrylate Resist Design-*circa* 1990 (aka IBM V1)

- Multiple Monomers-separation of function
- Minimal protecting group necessary for high contrast
- Proper balance of polarity (hydrophilicity) essential



General/Current 193nm Resist Design

- Acrylics (methacrylates) are dominant platform
- Fujitsu: alicyclic methacrylates combine transparency and etch resistance
- IBM: design of methacrylate positive resists through polar building blocks
  - Maintain modest concentration of protecting group



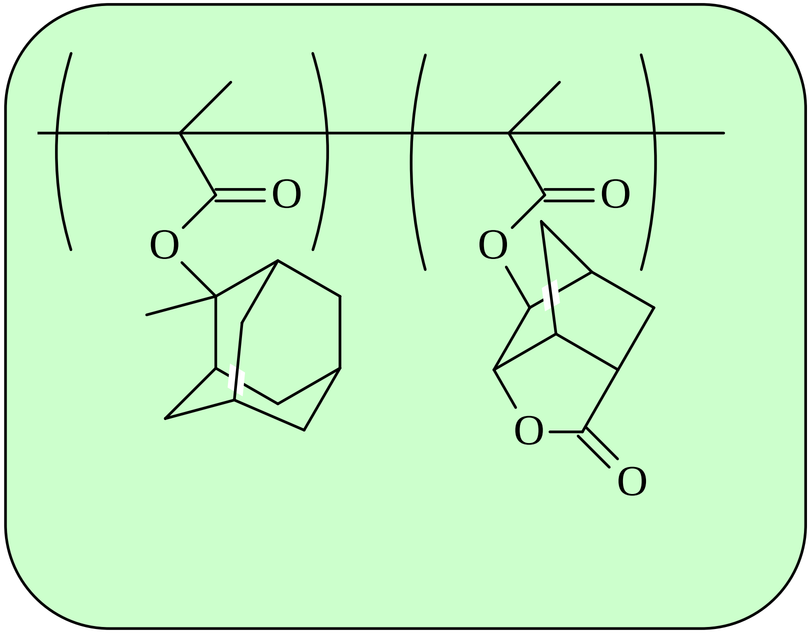
Possible Limitations: Complex and poorly controlled dissolution kinetics, complex polymers with large side groups

Strong motivation to continue 193nm materials R&D

- ArF Lithography continues to be the work horse technology for many generations
  - 90nm, 65nm, 45nm, 32nm, 22nm, ……
- Materials advances required to meet complex lithography challenges
  - Immersion lithography (high contact angle materials systems)
  - Complex double exposure schemes
  - Reflectivity demands due to hyper-NA (>1) lithography
  - Multilayer Integration Schemes
  - Fundamental CA Materials limitations: Resolution, LER and MEEF
  - Defectivity
  - High index Immersion

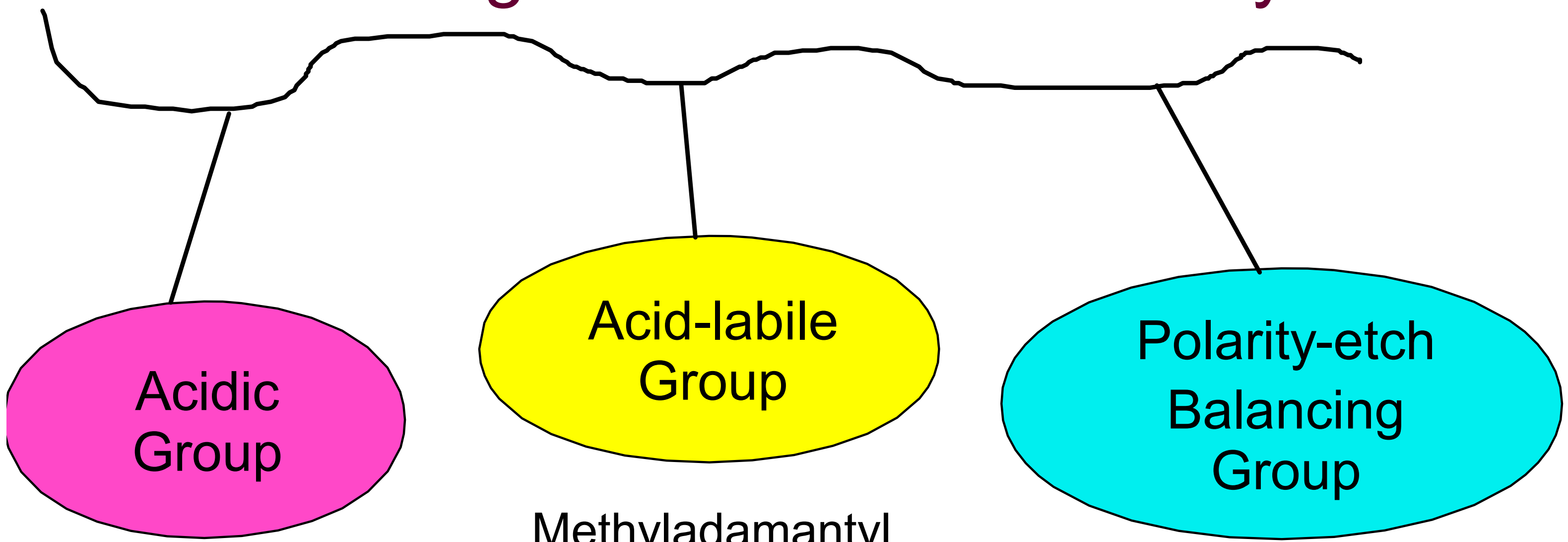
Properties of Standard 193nm Methacrylate Resist Platform:

- **Pros**
  - Well established free radical polymerization methodologies
  - Composition design flexibility
  - Etch stability through “bulky protecting groups /multicyclic polar functionalities”
- **Cons**
  - Dissolution characteristics (swelling in partially exposed area)
  - High PEB sensitivity
  - Poor Trench performance
  - Bright field- dark field compatibility
  - Defect Generation



Control of resist dissolution behavior is critical for extending lithographic performance

General IBM Design of 193nm Resist Polymers:



Methyladamantyl

Carboxylic acid (IBM) Methylcyclopentyl, etc. Lactone

⇓

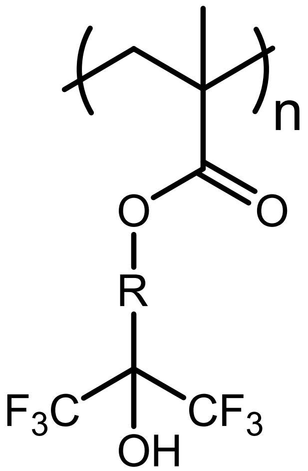
HFA/FARM (IBM)

⇓

New acidic group FSM (IBM)

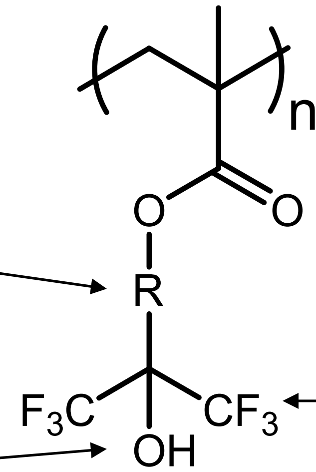
- **The industry has settled with the acid-labile and polarity-etch balancing groups**
- **The acidic group is critical to the dissolution properties of the resist polymer**

Fluorocarbinol Methacrylates



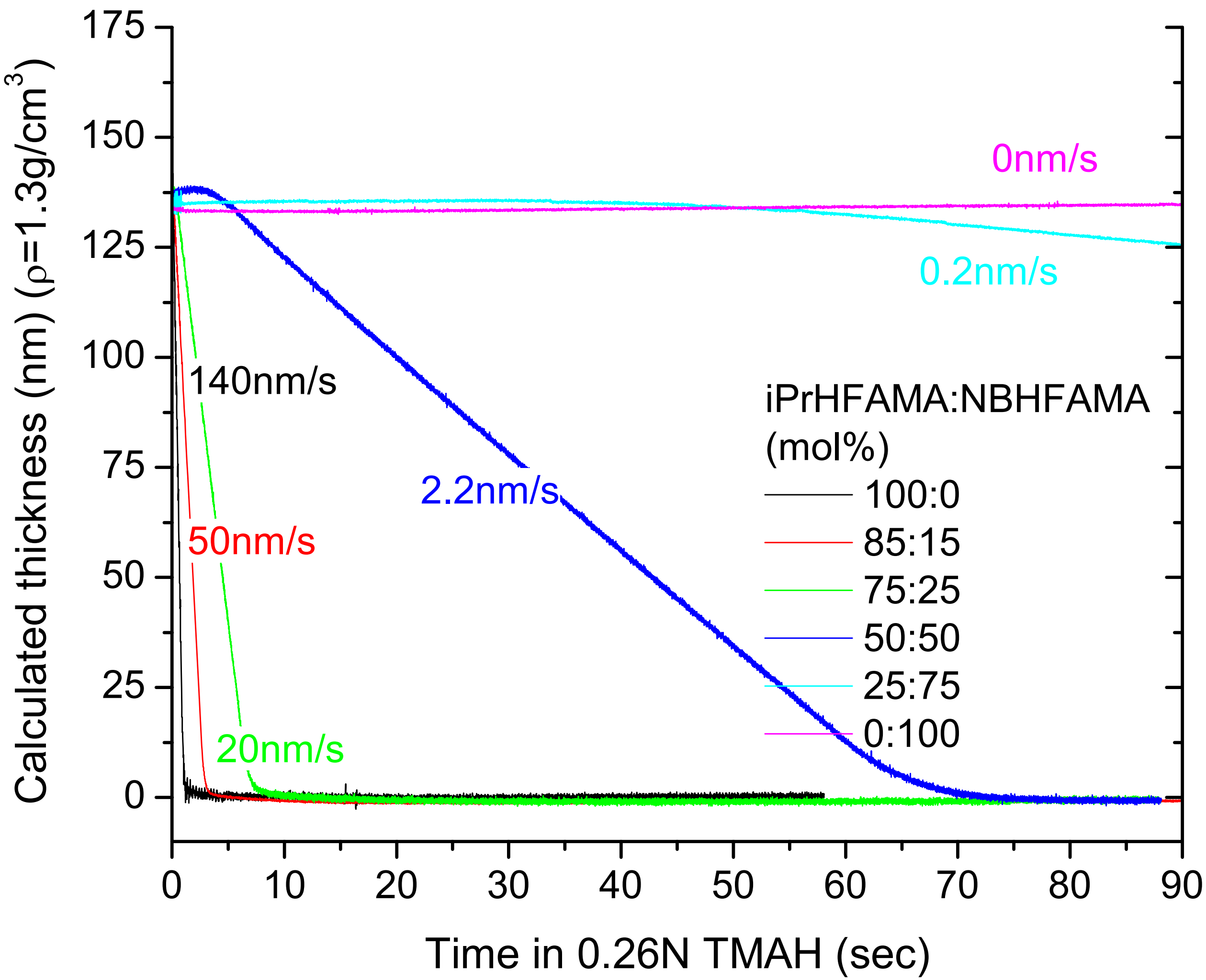
- High Optical Transparency @ 193nm
- Tunable Tg (50-150 °C)
- Linear Dissolution in 0.26 N TMAH
- Synthetic Variability
- Co-monomer Compatibility (methacrylates)
- Free Radical Polymerizable
- Polymers with unique solubility and blendability

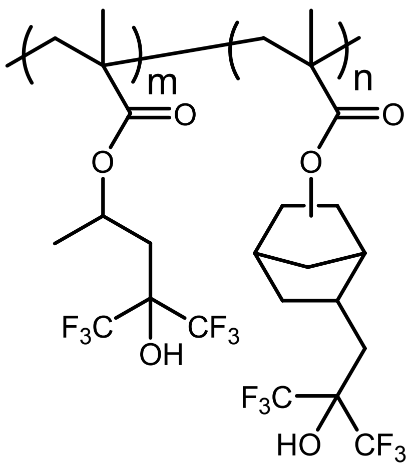
Resist and topcoat design using HFA-MA platform



- Positive resist—IBM/JSR, CPST 2005
  - Feature diminished swelling during development
- Negative resist—IBM/JSR, SPIE 2004
  - Excellent imaging
  - Processability in standard developers
- Immersion topcoats---IBM/JSR, SPIE and CPST 2005
  - Design of high performance, base-soluble topcoats
  - Importance of Tg to topcoat function
- Tunable surface properties—IBM CPST 2006

Dissolution of iPrHFAMA / NBHFAMA copolymers

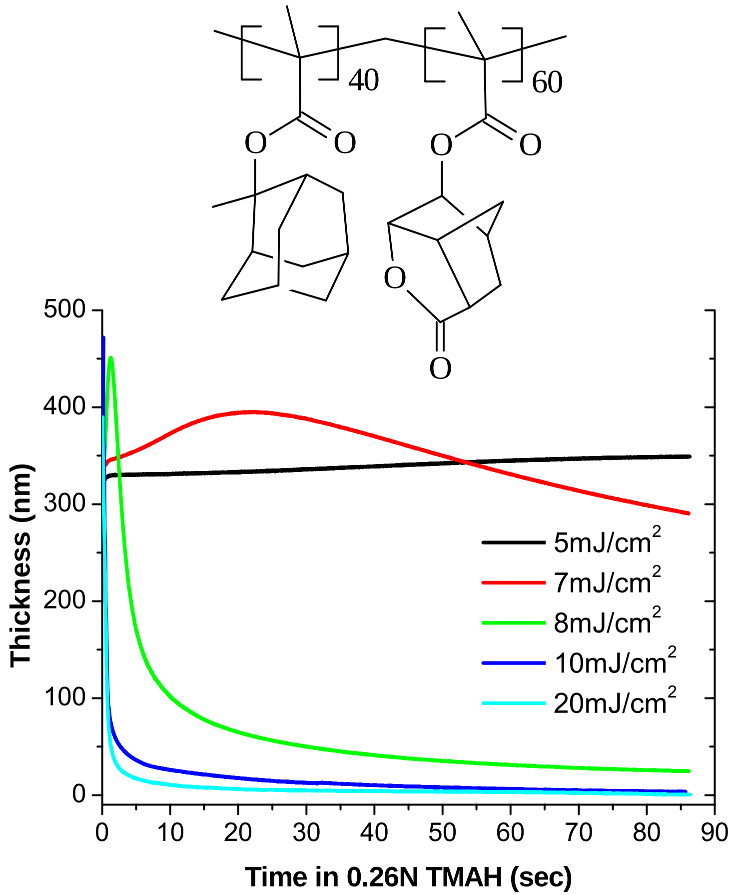




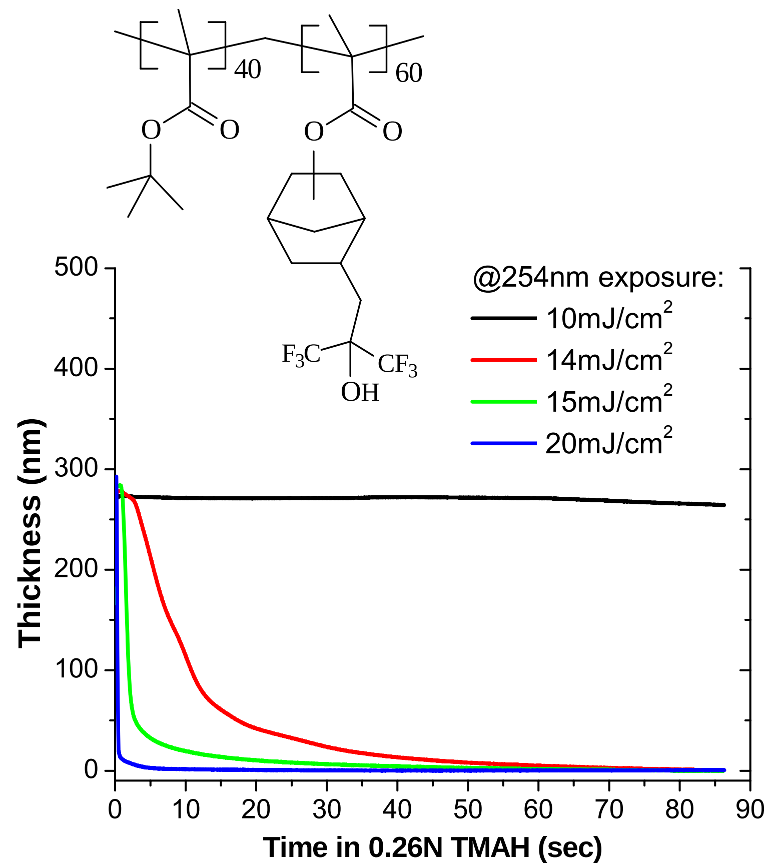
- Linear dissolution with no swelling in all cases

Fluoroalcohol Functionality Eliminates Swelling in Lightly Exposed Areas:

NB-Lactone based Methacrylate Resist

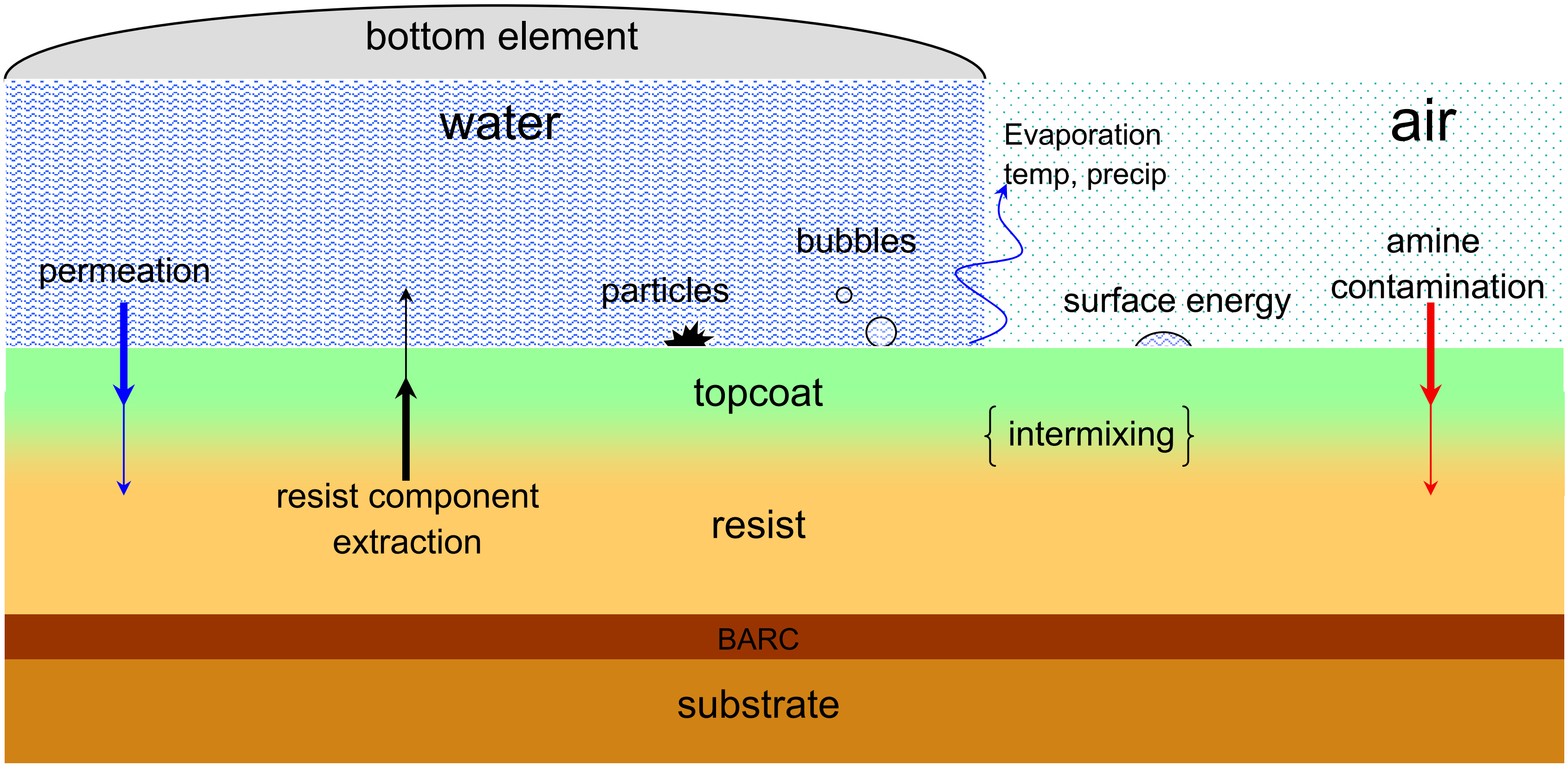


HFA based FARM Resist



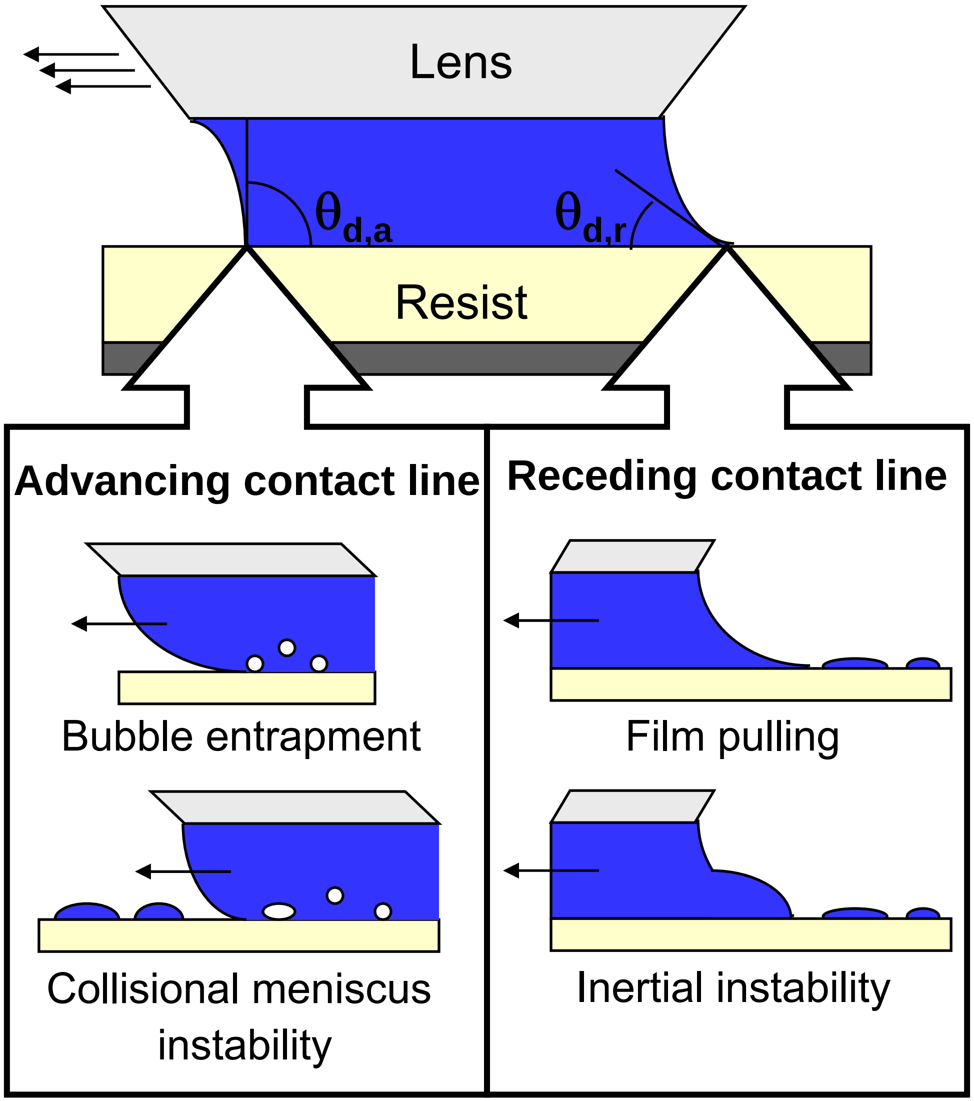
Varanasi *et al*, *Proc. SPIE*, 5753, 131 (2005)

Resist/topcoat/fluid interfaces in I-lithography



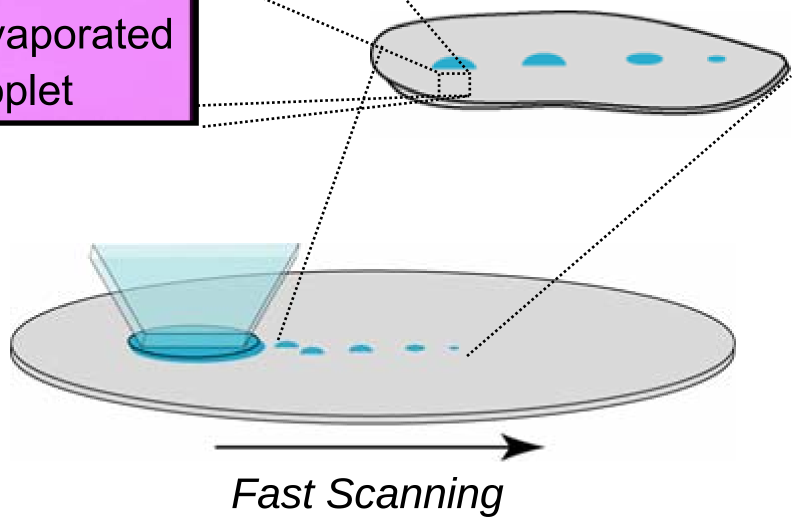
Many interfaces, all important, some more than others!

Scan rates and defectivity determined by water/polymer interface

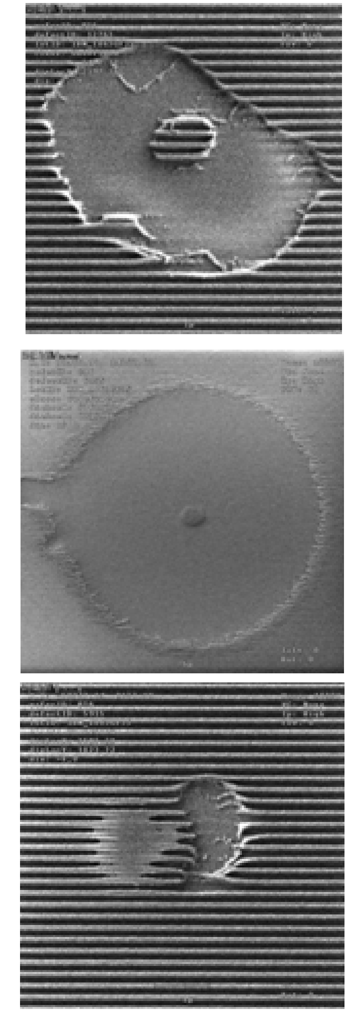


Evaporation as a defect source in immersion

193 nm Resist – No topcoat



Examples of defects

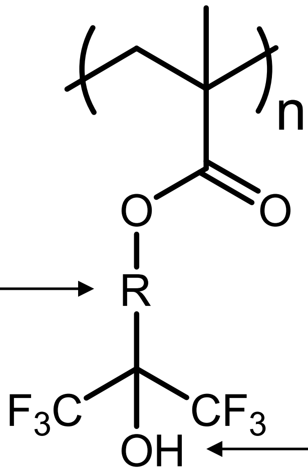


G. Wallraff *et al. Proc. SPIE*, **2006**, *6153,* 61531M.

C. Grant Willson 2006 Best Paper Award

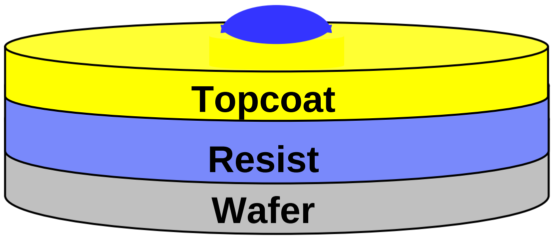
Fluoroalcohol methacrylates for 193 nm imaging materials

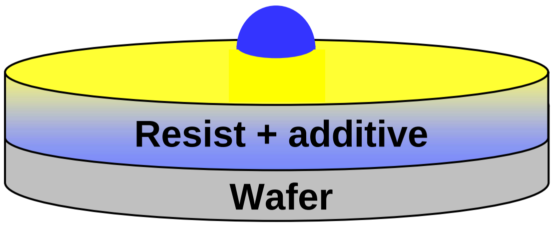
Property control knob



Acidic group for dissolution

How can we tailor these materials for better immersion surfaces?



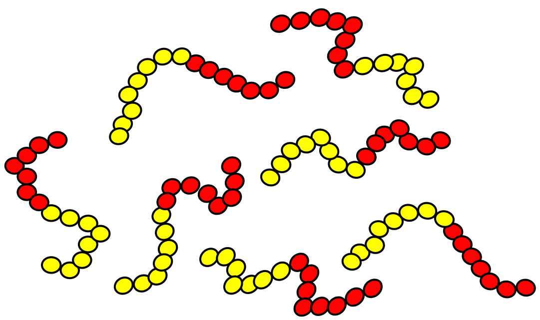


Dan Sanders et al., Proc SPIE

C. Grant Willson 2007 Best Paper Award

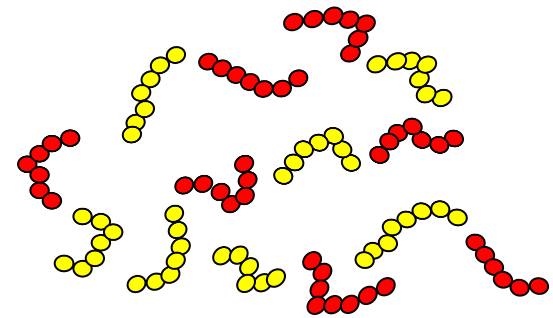
Methods to create structured films

Self-assembly

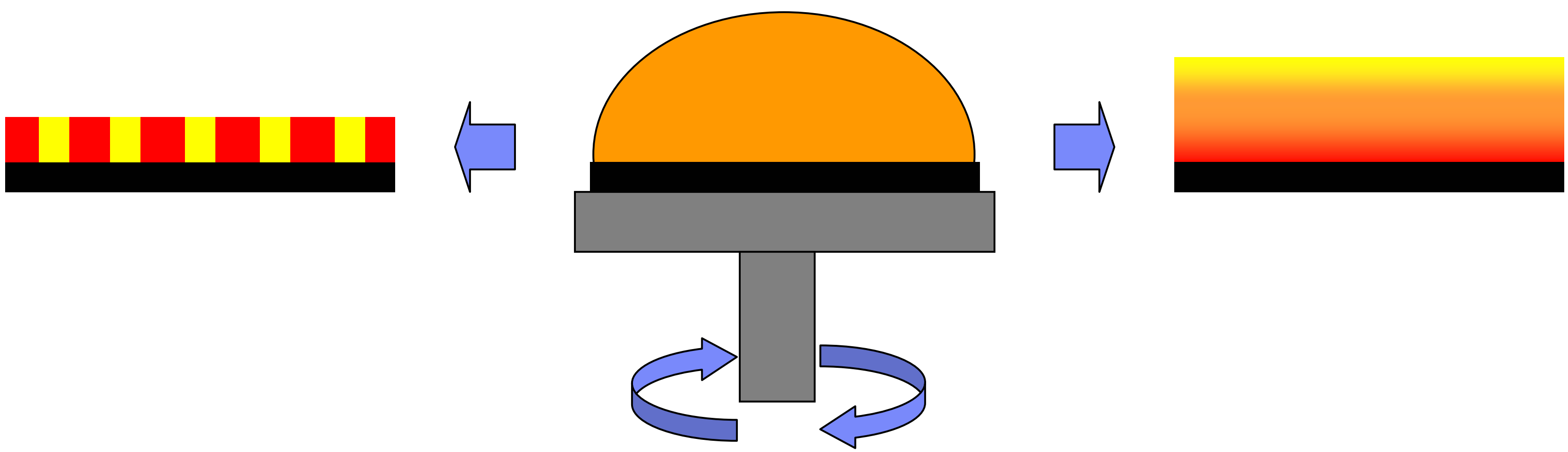


Block copolymer

Self-segregation



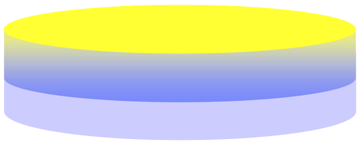
Polymer blend



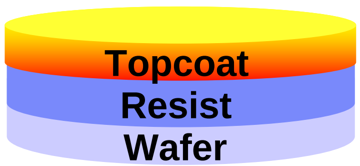
How can self-segregating blends impact immersion lithography?

- Topcoat-free resists for water immersion

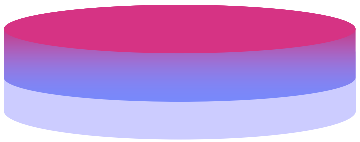
(2007 SPIE & 4th Int. Symposium on Immersion Lithography)



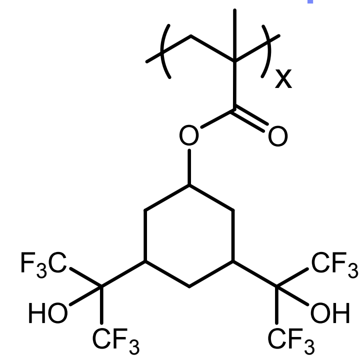
- Graded topcoat materials



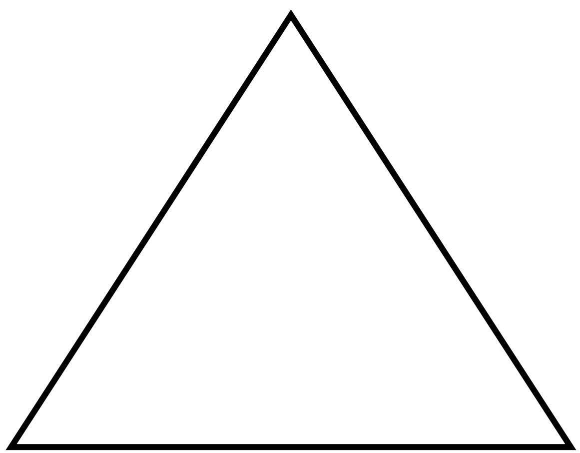
- Topcoat-free resists for high index immersion

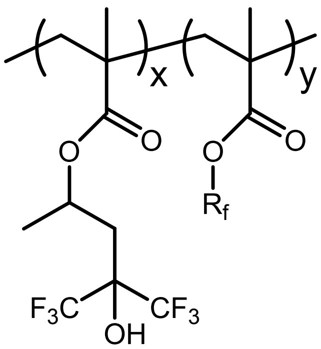


Property trade-offs limit topcoat performance

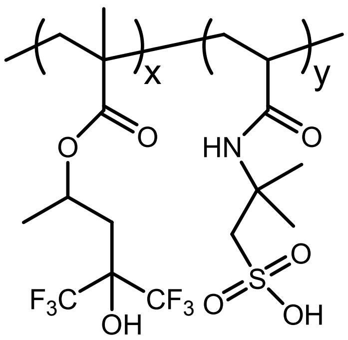


Allen *et al. Photopolymer*, **2005**.





Sundberg *et al. Proc. SPIE*, **2007**.

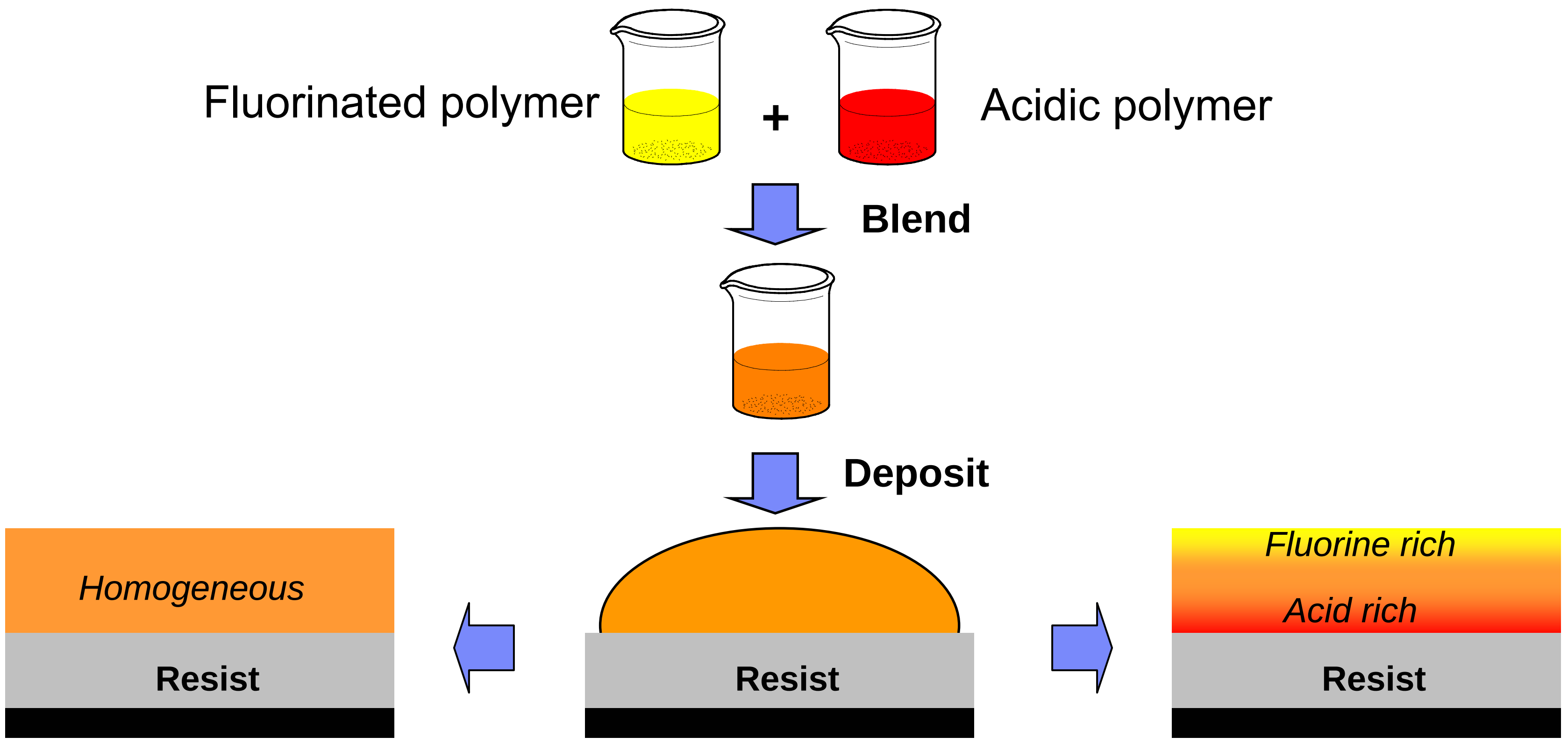


Khojasteh *et al. Proc. SPIE*, **2007**.

Tradeoffs create barrier to progress

How do we improve performance and retain practicality?

Graded topcoats via polymer blending

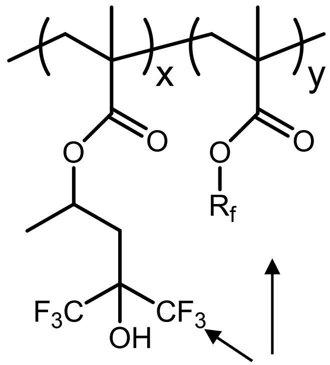


- Average properties
- Modest improvement

- Breaking trade-offs
- Superior performance

Blending typical topcoat polymers gives only average properties

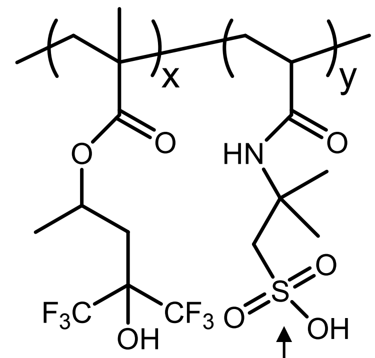
Fluorinated copolymer
surface energy control



RCA = **67.6°**

+

Sulfonic acid copolymer
profile control



RCA = **55.4°**

Surface activity
High contact angles

Acidic group for dissolution

Profile control

Homogeneous

RCA = 61.3°
Δ = -0.2°

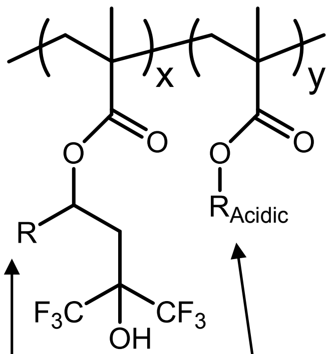
Resist

Δ is the difference between observed RCA and average RCA of components

Materials design produces graded topcoats

Fluorinated copolymer

surface energy control

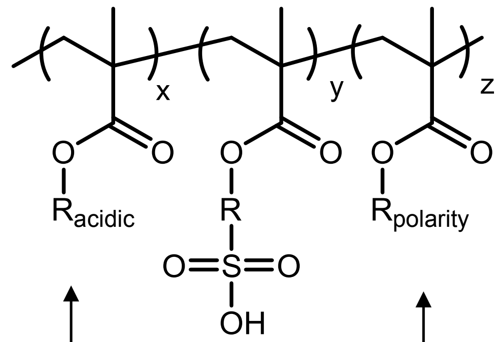


RCA = **72.9°**

+

Sulfonic acid terpolymer

profile control



RCA = **42.1°**

Surface activity

High contact angles

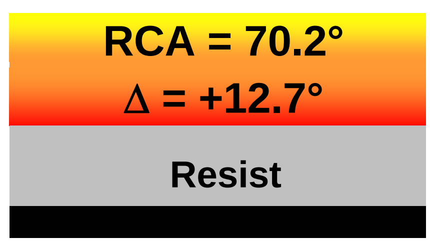
Acidic group to boost dissolution

Dissolution

Profile control

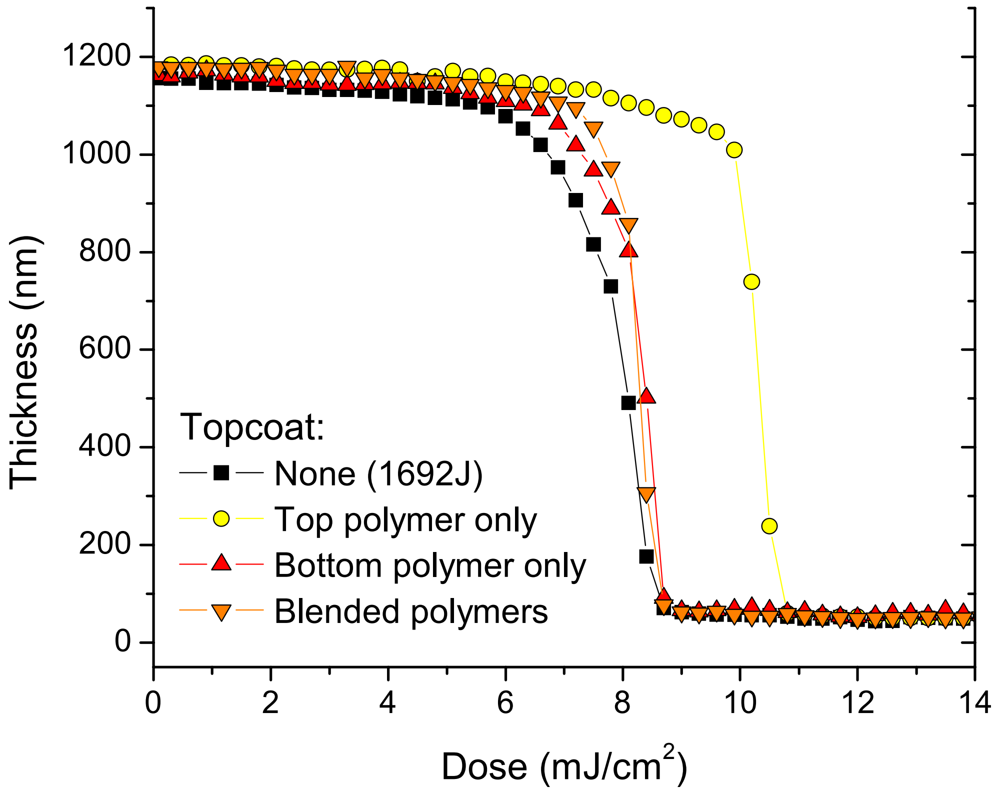
T_g/polarity

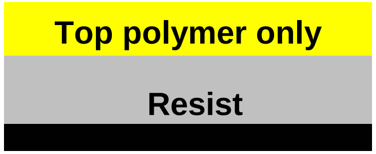
Segregation to both interfaces

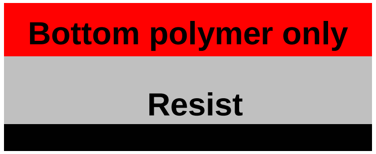


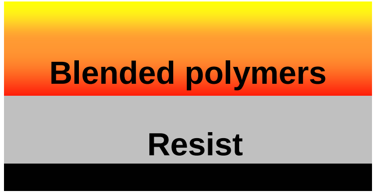
Film distribution: SIMS, XPS, ellipsometry, QCM, contact angles, contrast curves

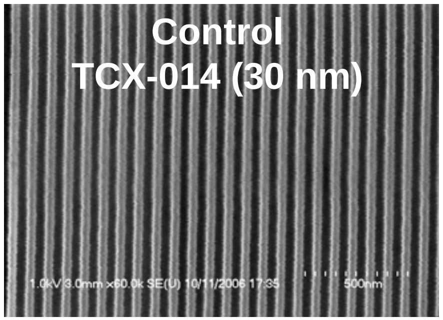
Contrast curves suggest segregated film structure

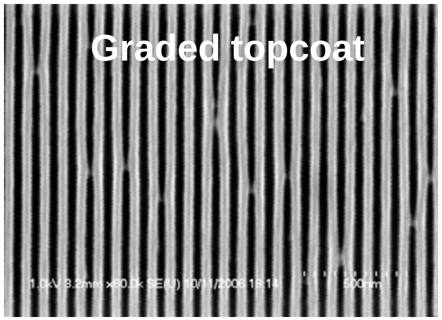


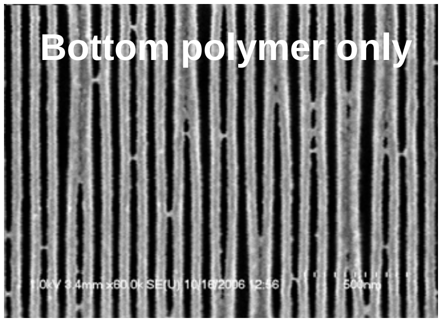






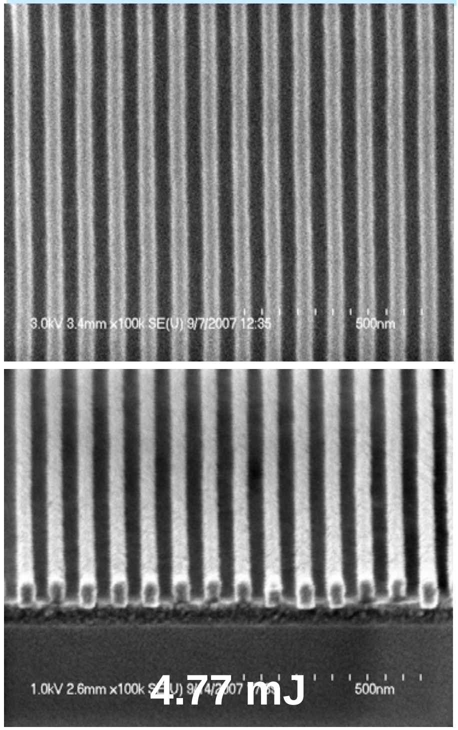






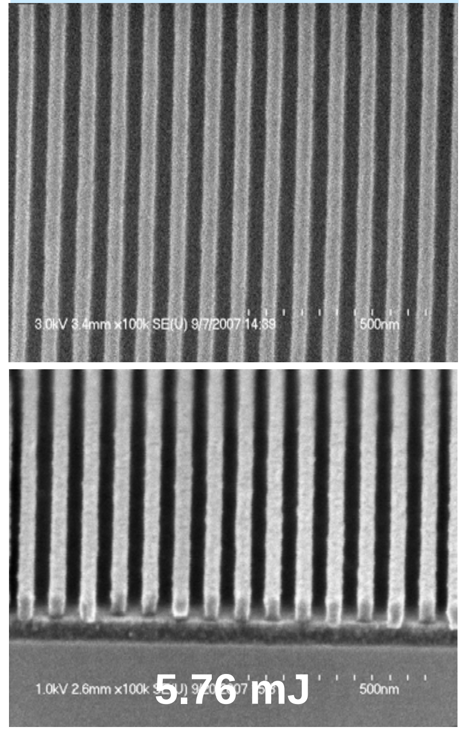
Re-engineering of component polymers resolves issues

Reference TCX-014 (30 nm)



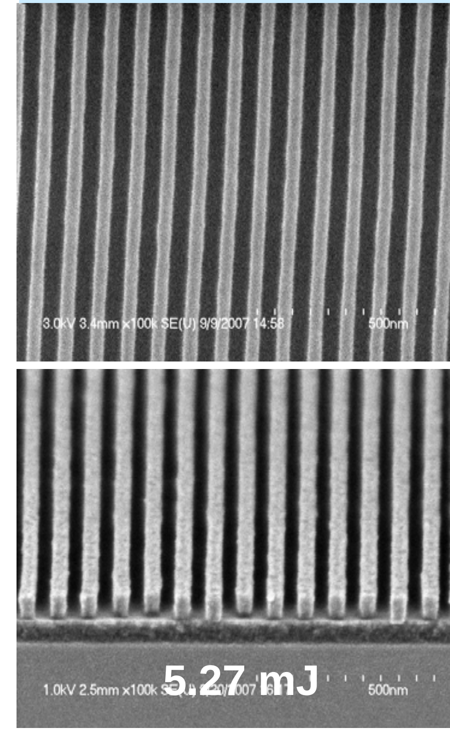
RCA: 55.6°

Fluorine-free bottom material



RCA: 59.2°

Alternative sulfonic acid group



RCA: 61.4°

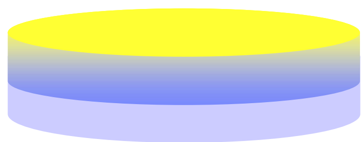
Commercial topcoat
Resist

Graded topcoat
Resist

Resist: JSR AR1682J, 45 nm hp, 193 nm water immersion interference lithography

Approach more effective in topcoat-free resists

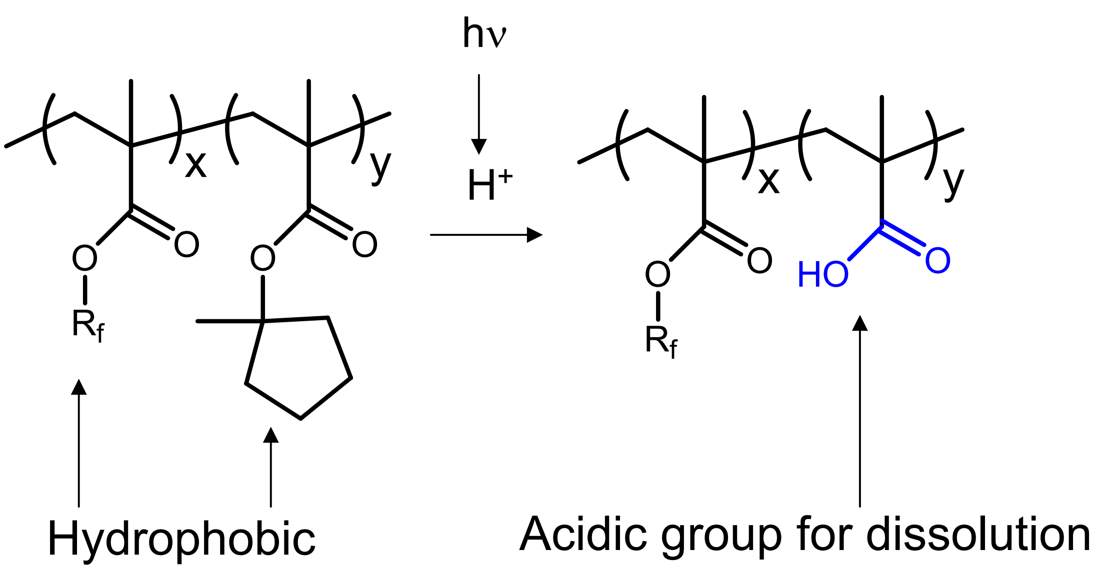
Topcoat-free resist

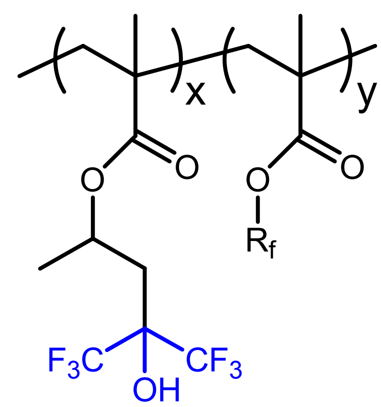


- Must dissolve ~2 nm
- Can rely on nearby photoacid to
  - Generate acidic groups where needed
  - After PEB!

Graded topcoat

- Must dissolve 100+ nm
- Need acidic groups for dissolution
  - Higher hysteresis
  - Lower receding contact angle





45nm hp immersion interference lithography (IBM NEMO)

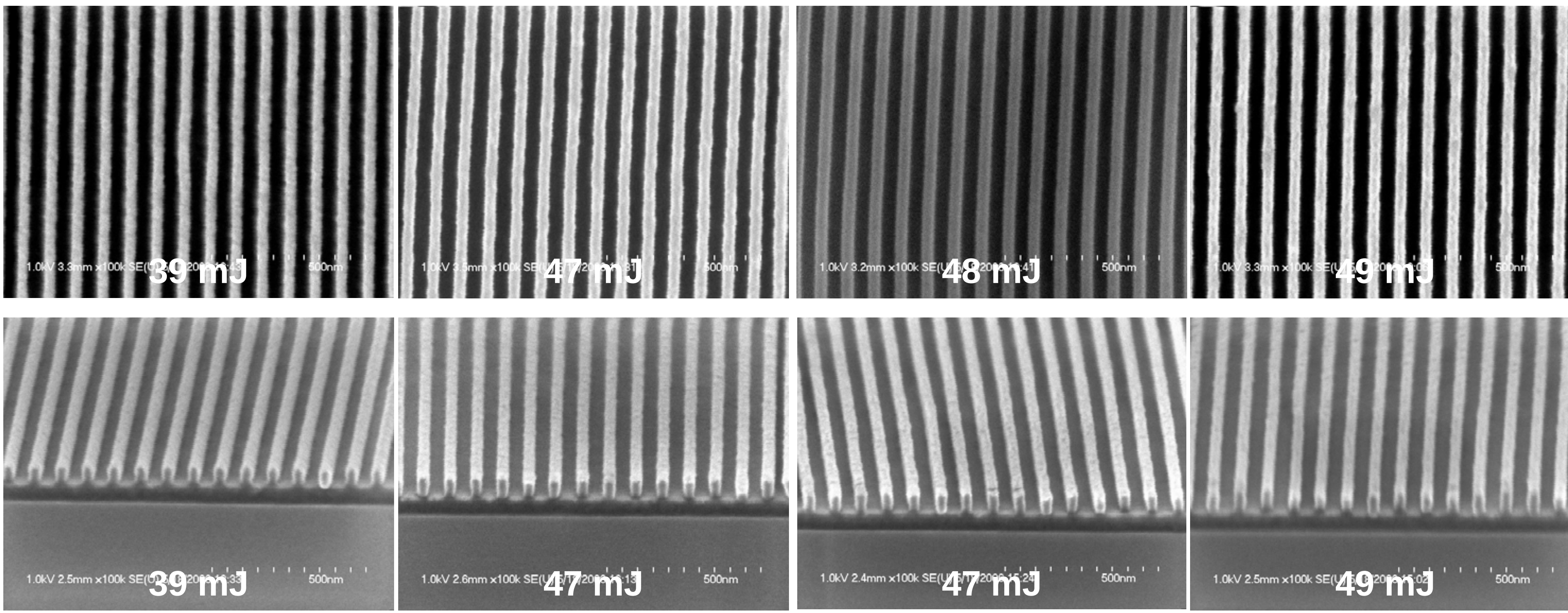
***In-situ topcoat*: AR1682J**

Control:
AR1682J + TCX-014

+ 5% Additive 3A

+ 5% Additive 3B

+ 5% Additive 3D

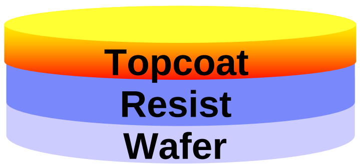


Topcoat-free resists for high index immersion

Base-soluble topcoats

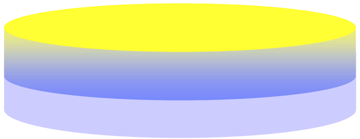
Graded topcoat materials

- Fluorine-free bottom polymers may allow cost reduction
- Further optimization can yield 5-10° increase in RCA
- Unprotected acidic groups for base solubility limit CA

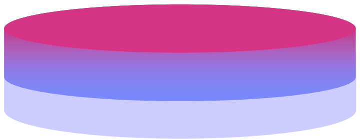


Topcoat-free resists for water immersion

- Superior contact angles due to protecting groups
- Reduced process complexity and cost

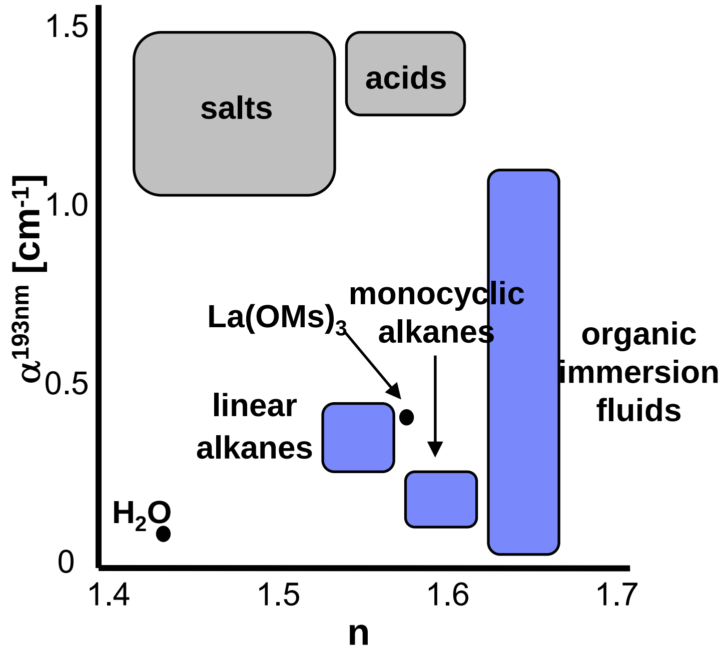


Topcoat-free resists for high index immersion

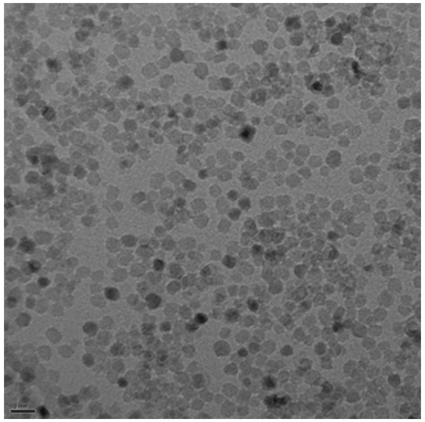


High index immersion progress

2nd generation fluid screening

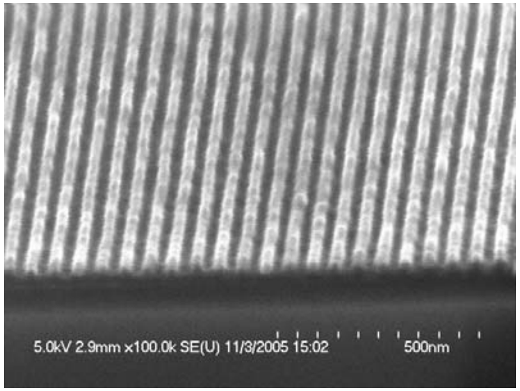


3rd generation fluids



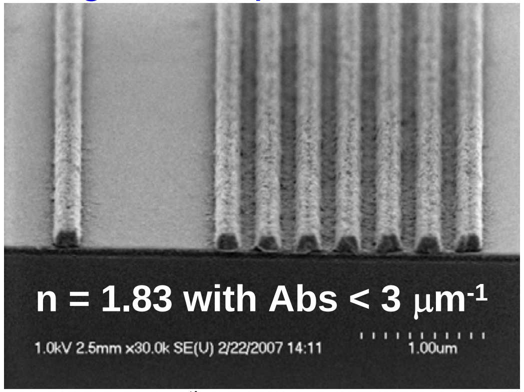
Hoffnagle, 4th Int. Symp. Immersion Litho.

30 nm imaging



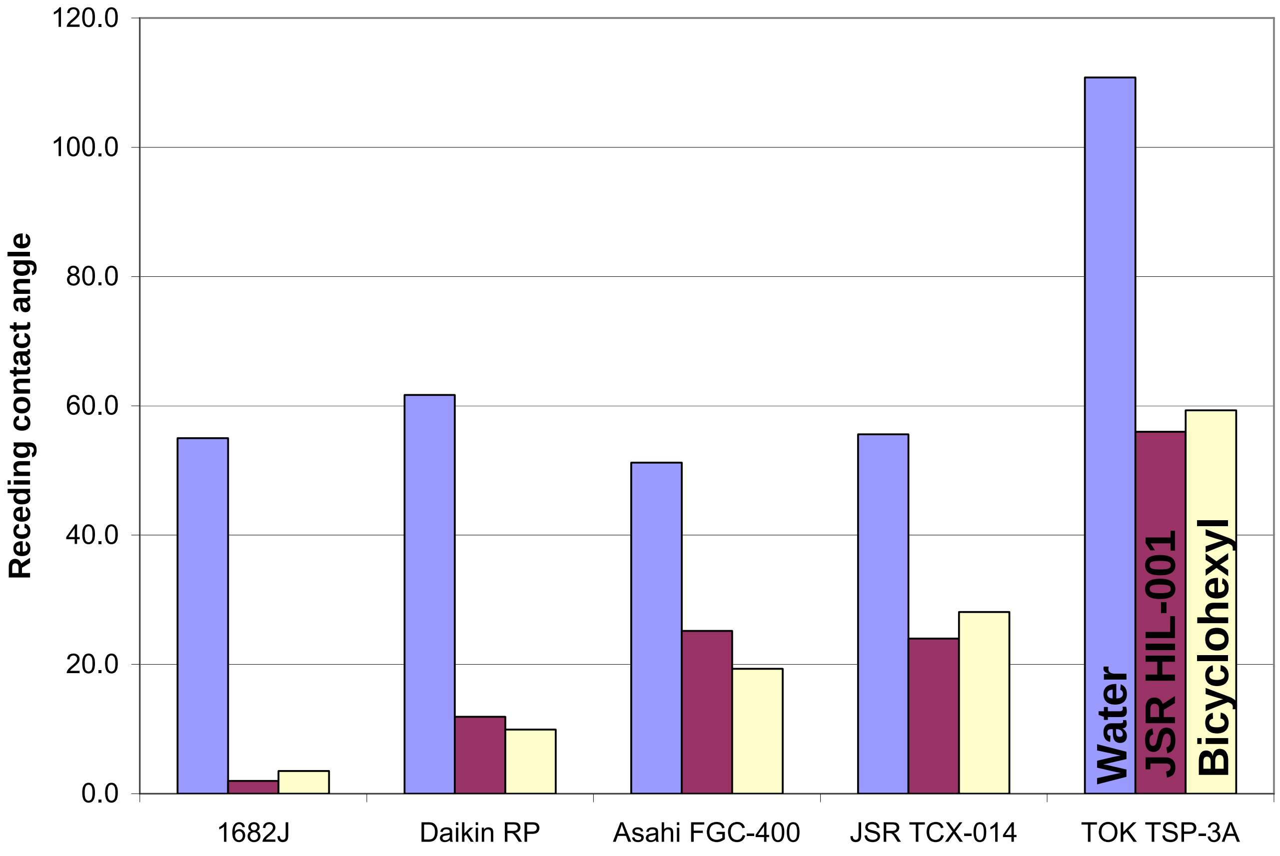
Wang (JSR), 2006 SPIE

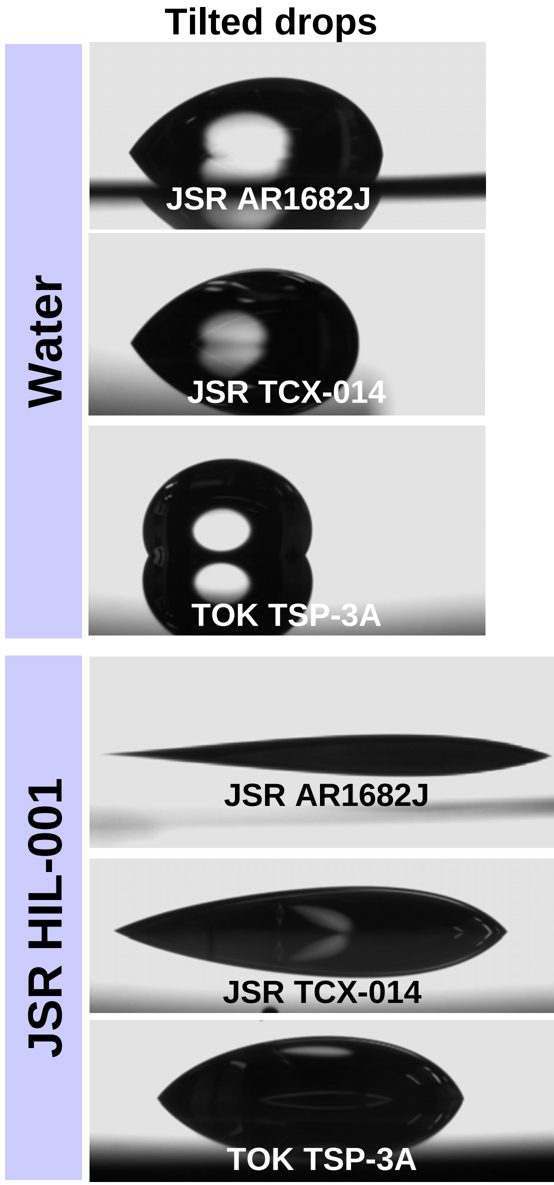
High index photoresists



Sooriyakumaran, 4th Int. Symp. Immersion Litho.

Lower contact angles of high index fluids

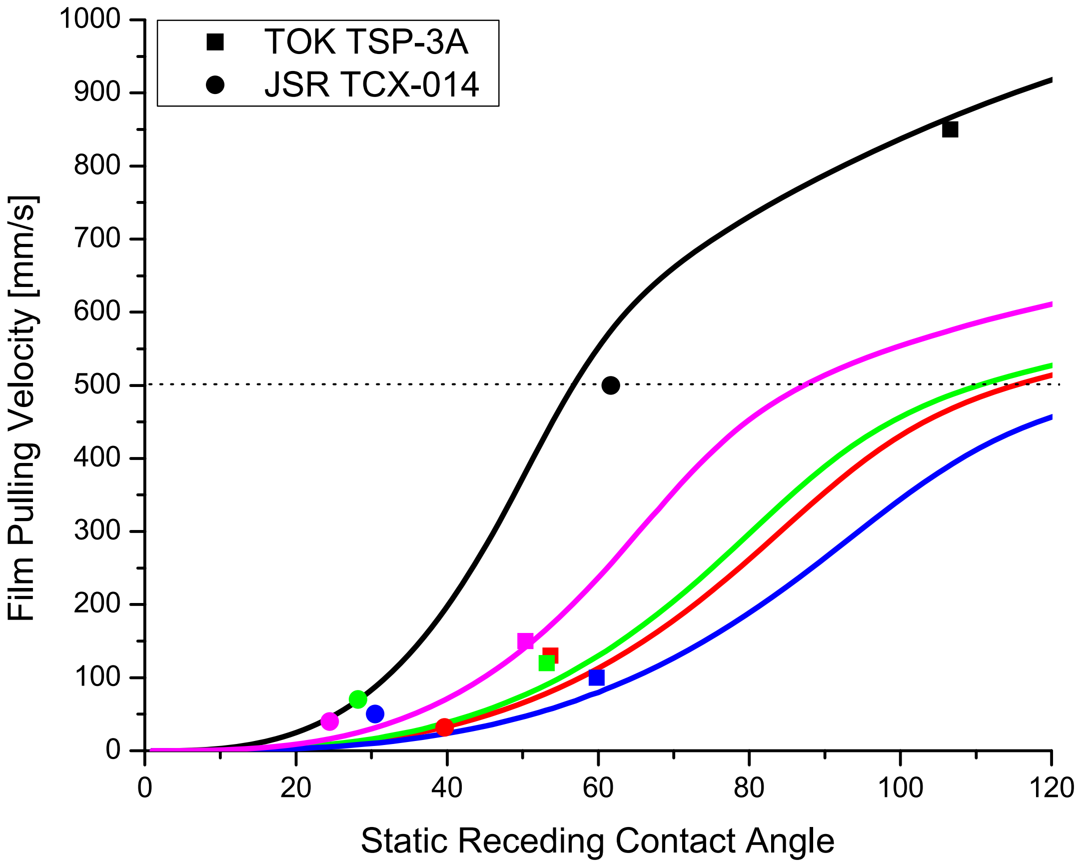




Even highly fluorinated, solvent developable topcoats only get us half-way to the required contact angles!

Organic immersion fluids film pull at low velocities

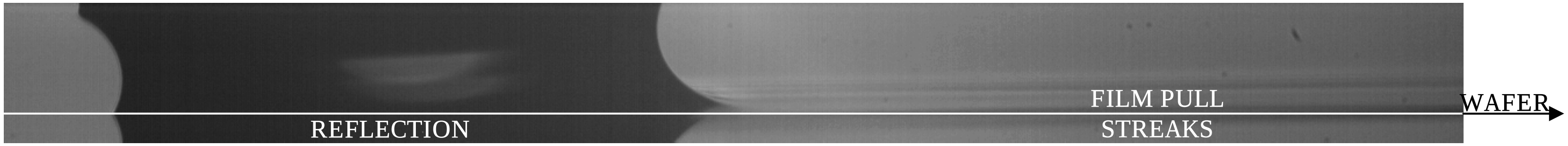
Collaboration with: P. Harder, S. Schuetter, T. Shedd (*University of Wisconsin*)



$$\upsilon_{crit} = \left(\upsilon_{fp}^{-m} + \upsilon_{in}^{-m}\right)^{-1/m}$$

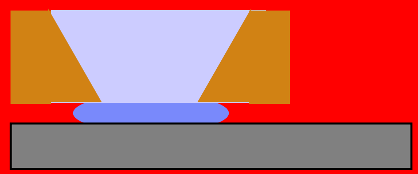
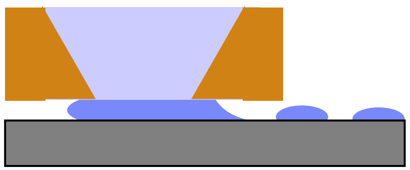
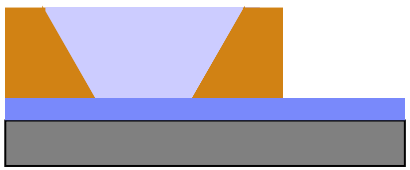
$$\upsilon_{fp} \propto \frac{\gamma}{\mu}\theta_{s,r}^{3}$$

	Film pulling velocity (on TSP-3A)
Water	850 mm/s
Decane	150 mm/s
trans-Decalin	120 mm/s
Cyclooctane	130 mm/s
Bicyclohexyl	100 mm/s



Sanders *et al. 3rd Int. Symp. Immersion Lithography (2006).*

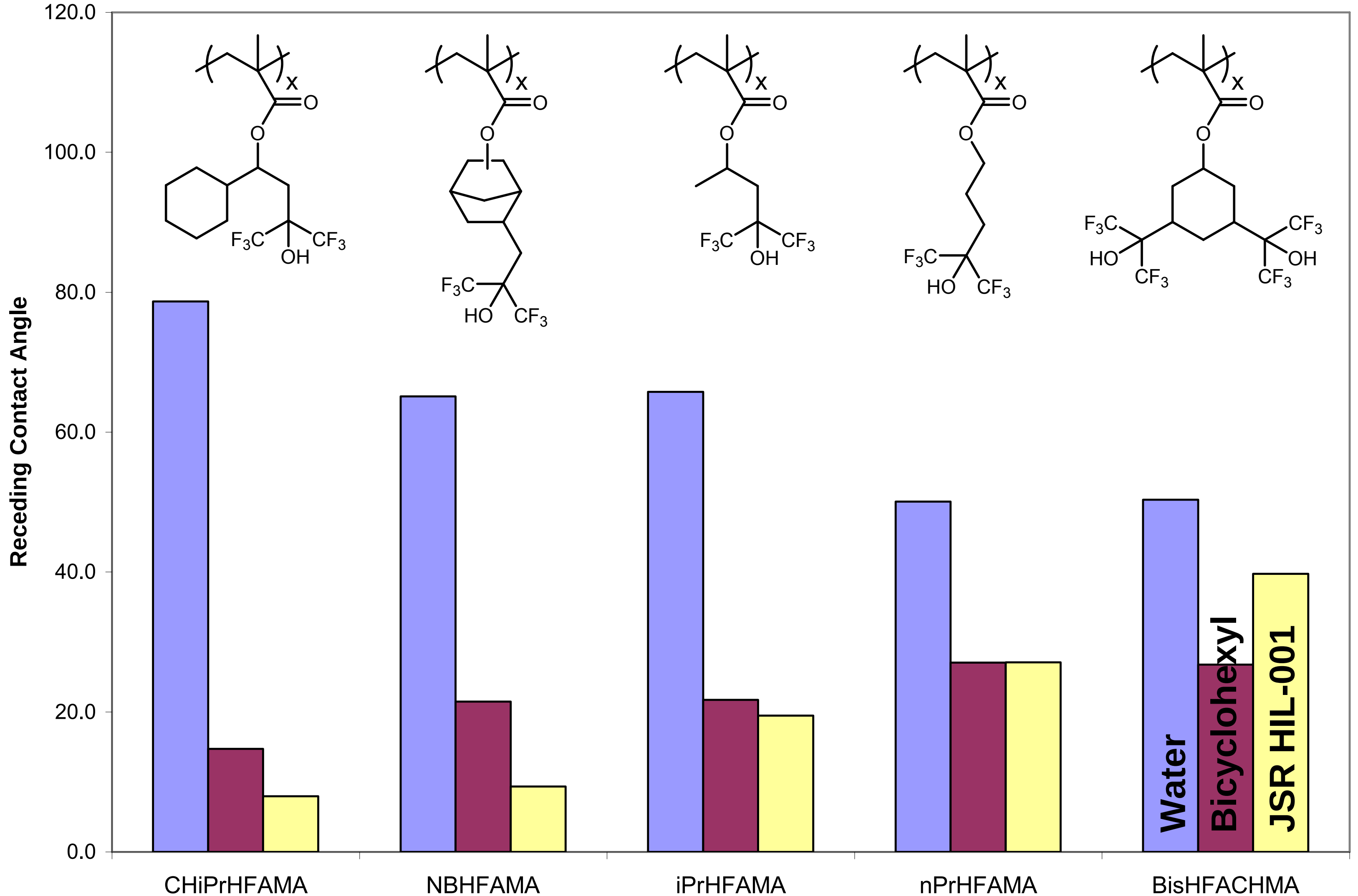
Need resist materials which are tolerant to high index fluids

	Local delivery “wafer dry”	**Allowed film pulling “partially wet”**	**Submersed/Pool “wafer wet”**
			
Process	Conventional	New fluid removal process	New fluid removal process
Materials	Topcoats w/ RCAs > 120°	Inert resist or topcoat	Inert resist or topcoat

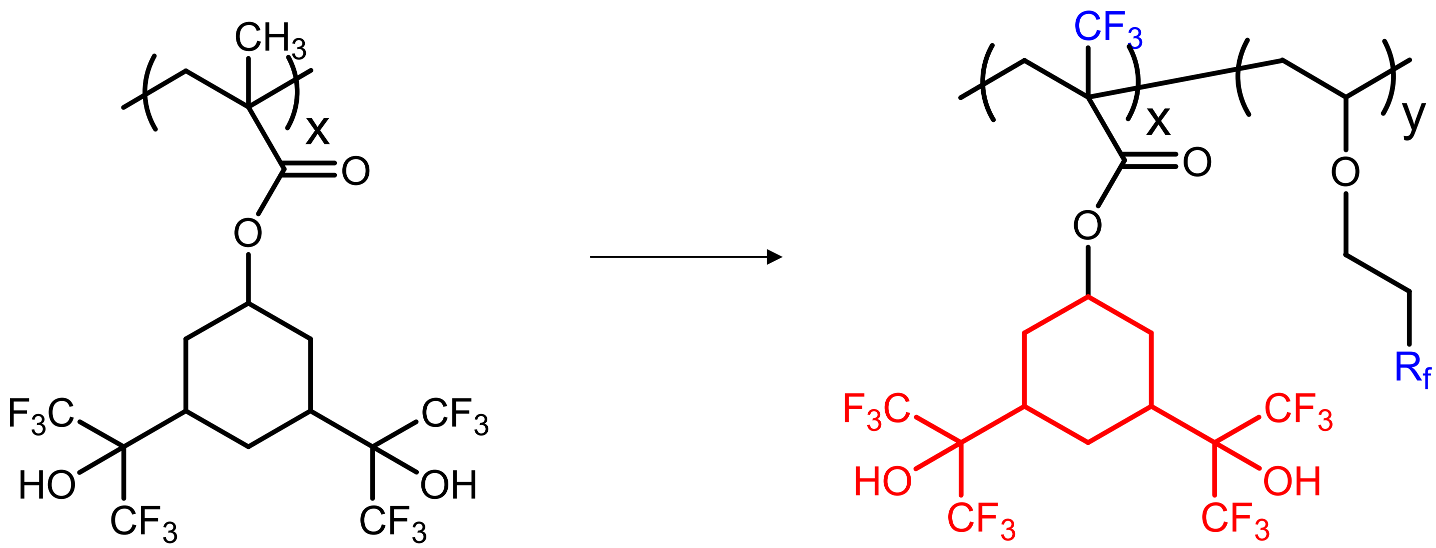
Contact angle targets unknown
Higher is presumed better

A topcoat-free resist approach is ideal for this application

Designing additives for high index immersion



Molecular design features of an example additive



Eliminate exposed hydrocarbon structures

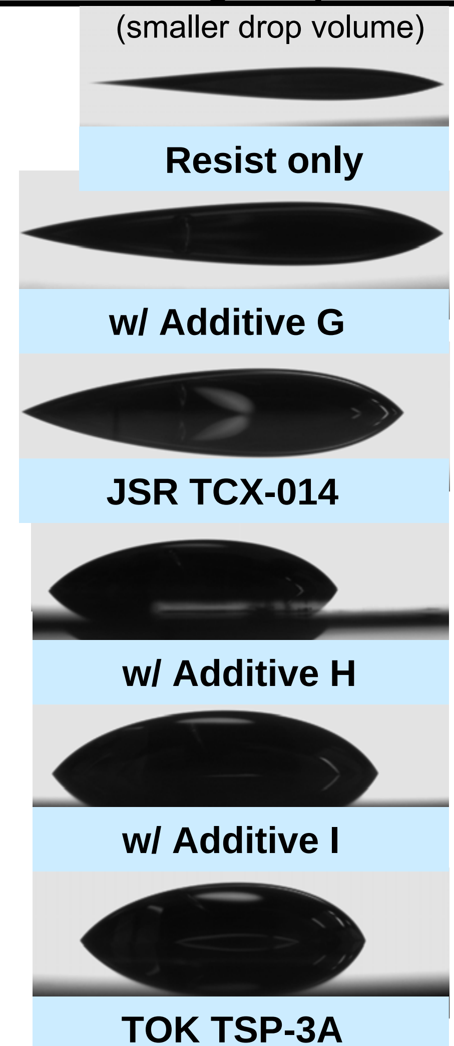
Fluoroalkyl groups lower surface energy and facilitate surface segregation

Bis(hexafluoroisopropanol)cyclohexyl groups boost TMAH dissolution rate

Improved additives for high index immersion

		Receding contact angle (HIL-001)	
Application	Additive	Additive-only	Resist w/additive
	None	-	< 2°
Water	Additive G	8.0°	14.2
Water	JSR TCX-014	-	24.0
High index	Additive H	48.7°	42.1
High index	Additive I	49.0°	48.3
	TOK TSP-3A	-	56.0

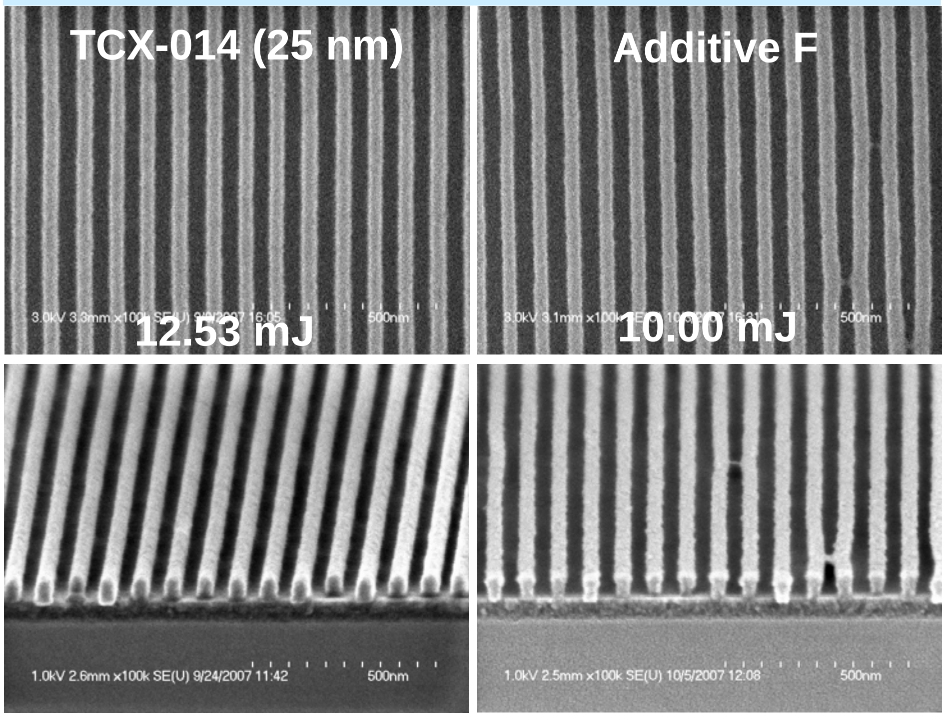
Tilting drop

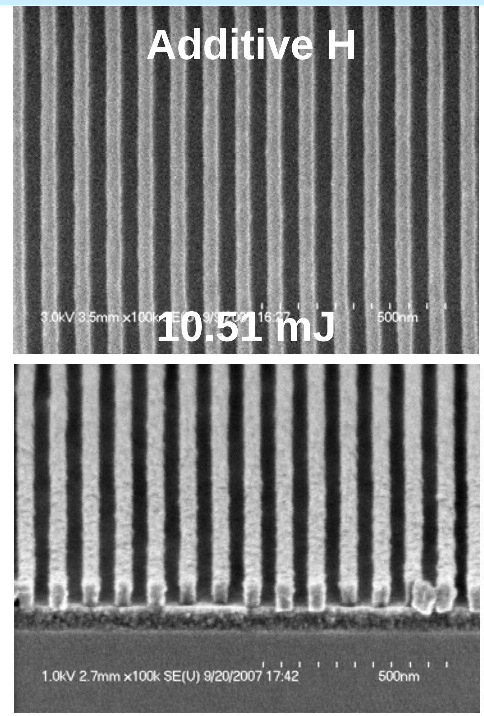


Additives compatible with high index immersion achieved

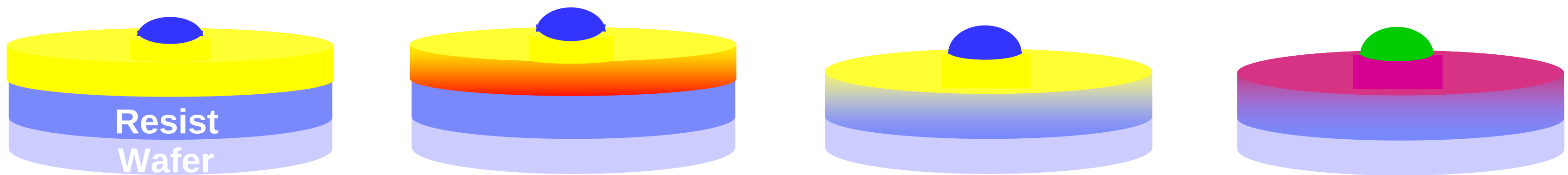
193 nm interference immersion lithography (45 nm hp)
Resist: Resist (80 nm) on ARC29a (780 Å)
Immersion Fluid: JSR HIL-001

Materials designed for water	Material designed for high index





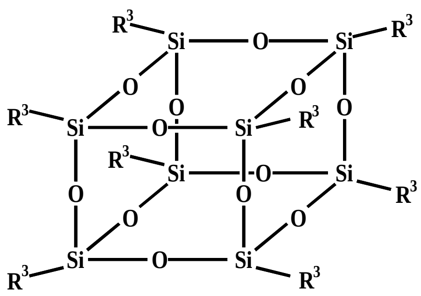
Summary: Self-segregating materials offer the opportunity to reduce process complexity and increase performance



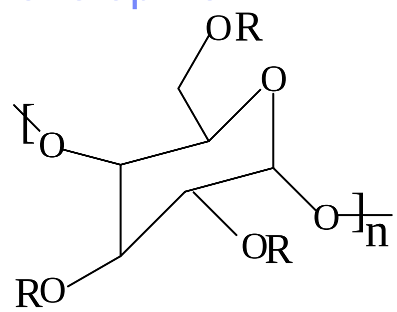
	Conventional Topcoats	*Graded Topcoat*	*Topcoat-free Resist (water)*	*Topcoat-free Resist (high index)*
RCA (water)	TCX-014: 55.6° TCX-041: 61.9°	59° - 72°	65.0°- 80+°	42+° (HIL-001)

- Graded topcoats show potential for improved performance/reduced cost
- Additive-based topcoat-free resists are superior way to break trade-offs
  - Can use acid-labile protecting groups
  - Simpler and more cost-effective
- Designed additives specifically for high index immersion
  - Moderate RCAs with high index fluids
  - Tailor additives differently than for water-based immersion

AIR
(Architecturally Interesting Resists)
Non-Polymeric Macromolecules
Two Platforms for Molecular Resist Development



POSS

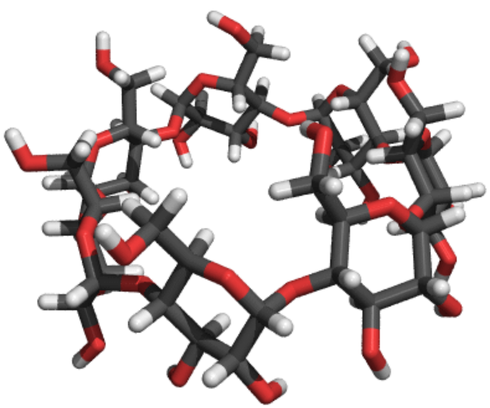


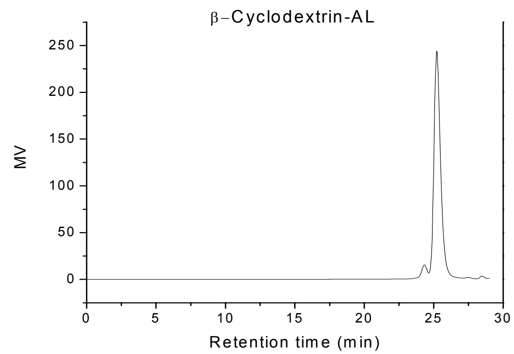
Oligosaccharides linear and cyclic

- Commercially available starting materials
- Easy to functionalize
- Defined Molecular Weight (single compound)
- Suitable for 193-nm resist design
- Do these architectures vary from polymeric resists in Diffusional Characteristics and Development?

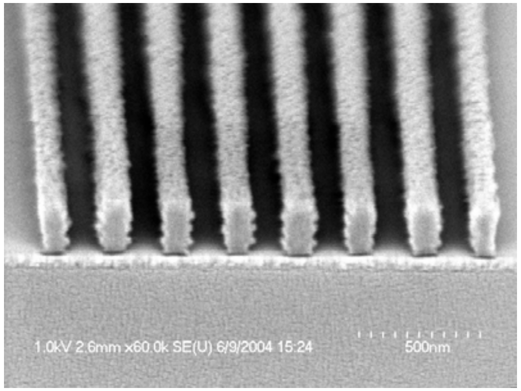
Sooriyakumaran, CPST (2005), '*Positive Resists Based on Non-Polymeric Macromolecules*' (aka Molecular Resists)

Cyclodextrin Molecular Glass Resist

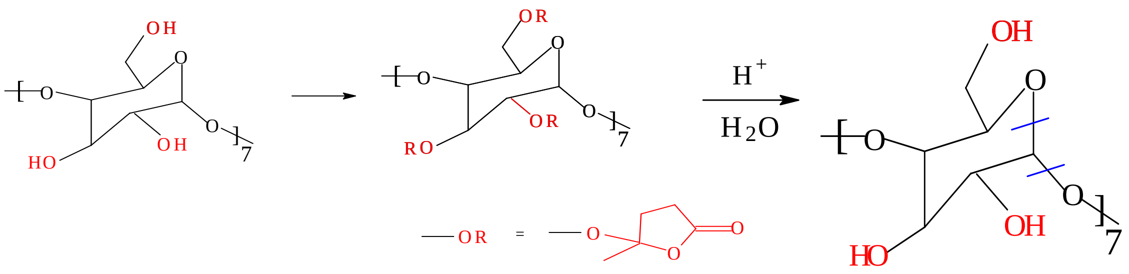




120nm l/s



PAB = 100C
PEB = 70C

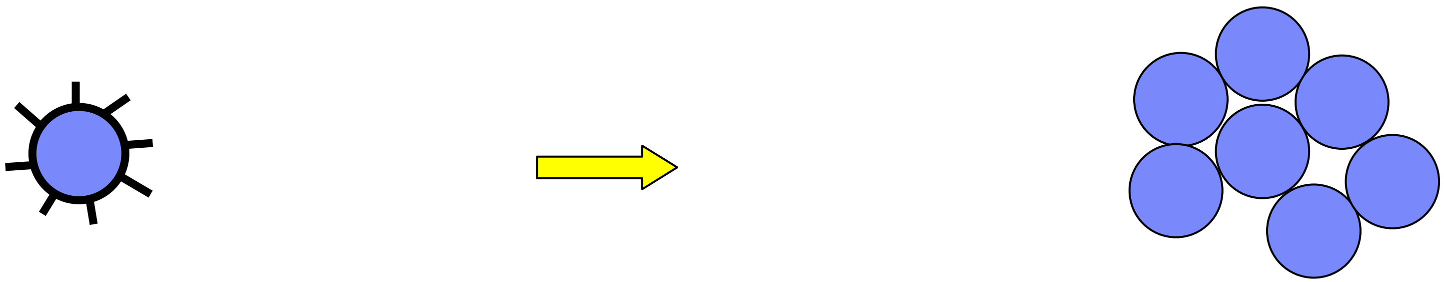


MW reduction!

Soori

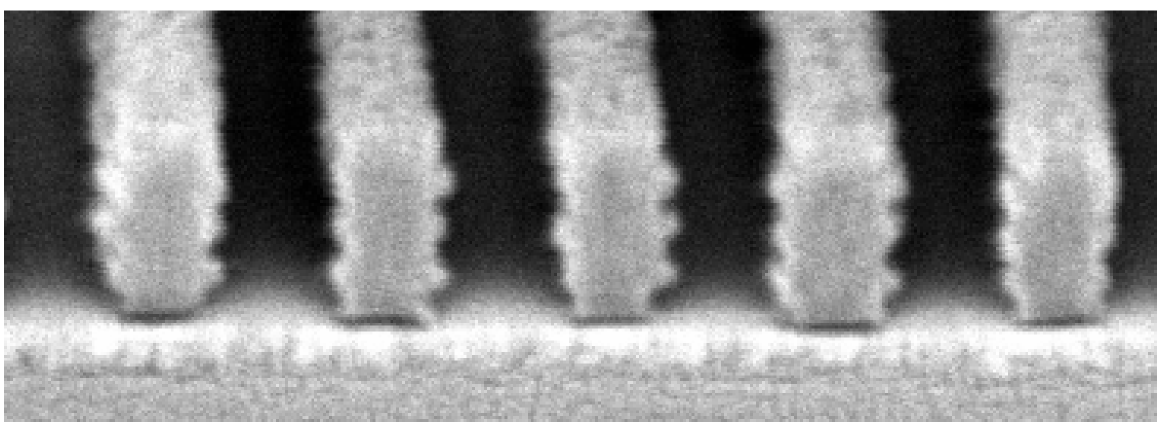
Sooriyakumaran, CPST (2005), '*Positive Resists Based on Non-Polymeric Macromolecules'*
(aka Molecular Resists)

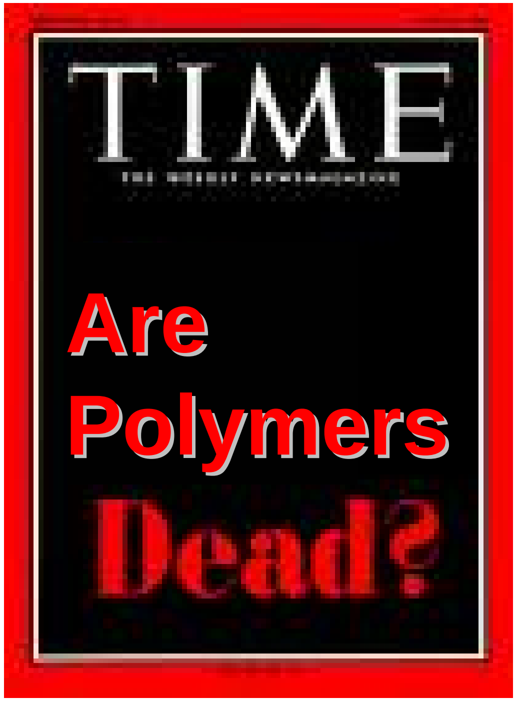
A new stone wall model for the 21st century?



Molecular glass resist

- Low density packing
- No entanglements
- No Gel
- Can acid ‘hop’ across gap?
- Is this intrinsically Low Blur?





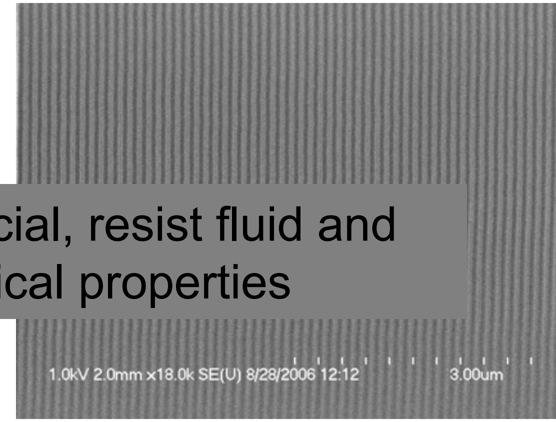
SRC student Anuja DeSilva from Chris Ober's group is currently at Almaden to answer this question!

What about Imprint Lithography?

- High fidelity patterning at reasonable cost
- Template focus required now
- Our initial focus is on Storage Class Memory application using MNAB device*
- Broader application further down semiconductor roadmap?
- Materials Challenges abound, for templates, interfaces, resists
- Defectivity, Overlay Tolerance, Throughput?

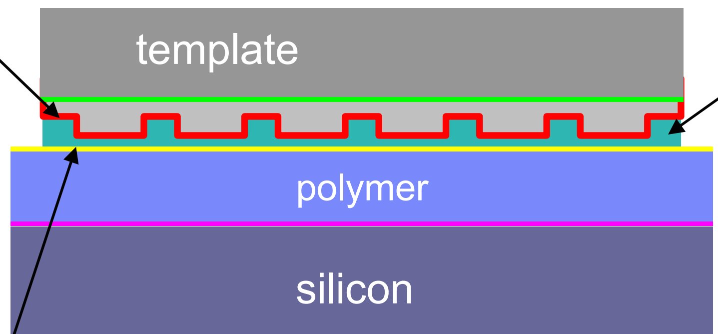
* Mark W. Hart, EIPBN, Denver (2007)

UV curable resists and interfaces as a system



Simultaneous optimization of interfacial, resist fluid and cured resist chemical and physical properties

Weak resist-template interface

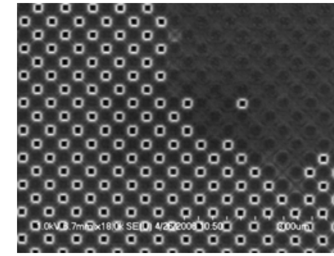


Strong resist-substrate interface

Photocurable resist

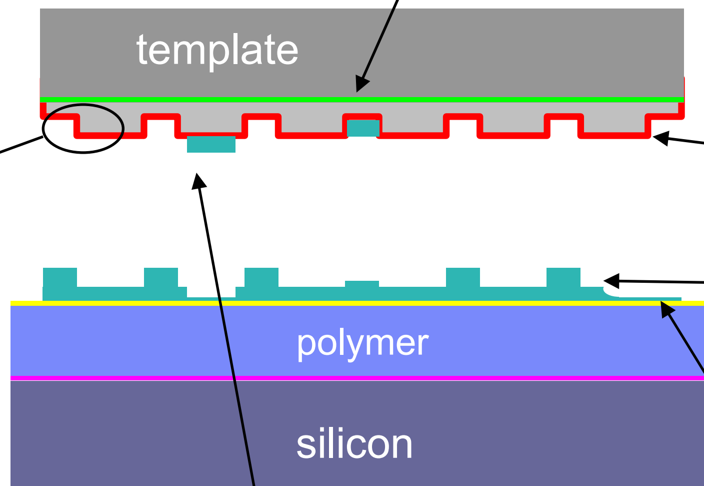
- Monomer viscosity
- Polymerization rate and degree of crosslinking
- Modulus vs extent of cure
- Stress
- Shrinkage
- Elasticity

Interfaces in nanoimprint lithography: sources of defectivity



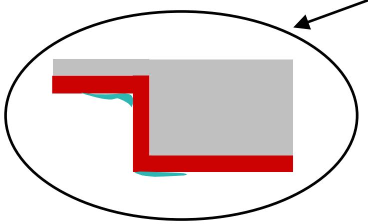
Cohesive failure of cured polymer

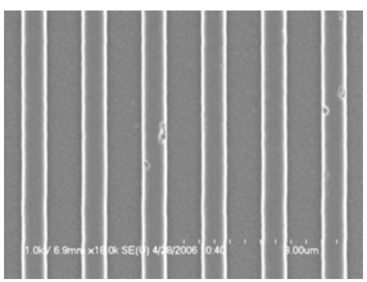
Polymer adhesion to template despite release layer



Release layer

Cured/embossed resist

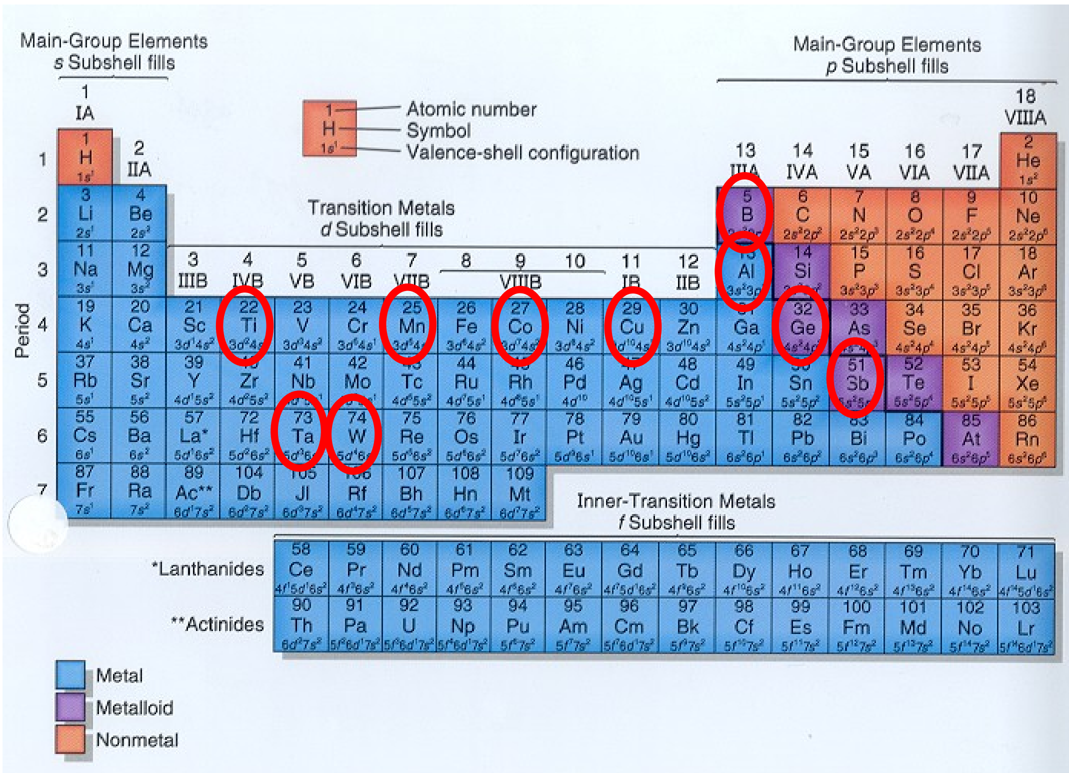




Failure of UV-curable liquid to wet surfaces

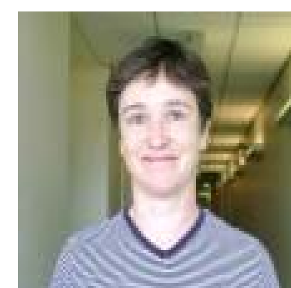
Adhesion failure at bottom interface

Interfacial chemistry control using metal oxides and nitrides as release coatings



- Optically thin
- Physically thin
- Conformal
- Amorphous
- Chemically stable

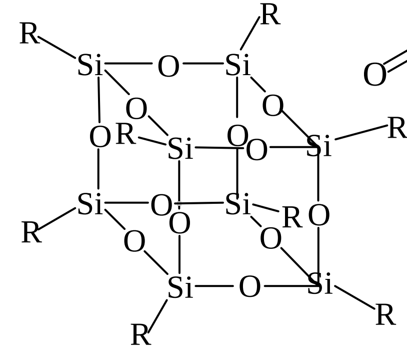
http://library.tedankara.k12.tr/chemistry/

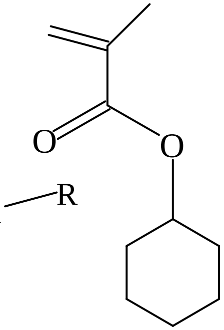


Frances Houle
SPIE 2008

Adhesion energies mPSS-CHMA 1:2

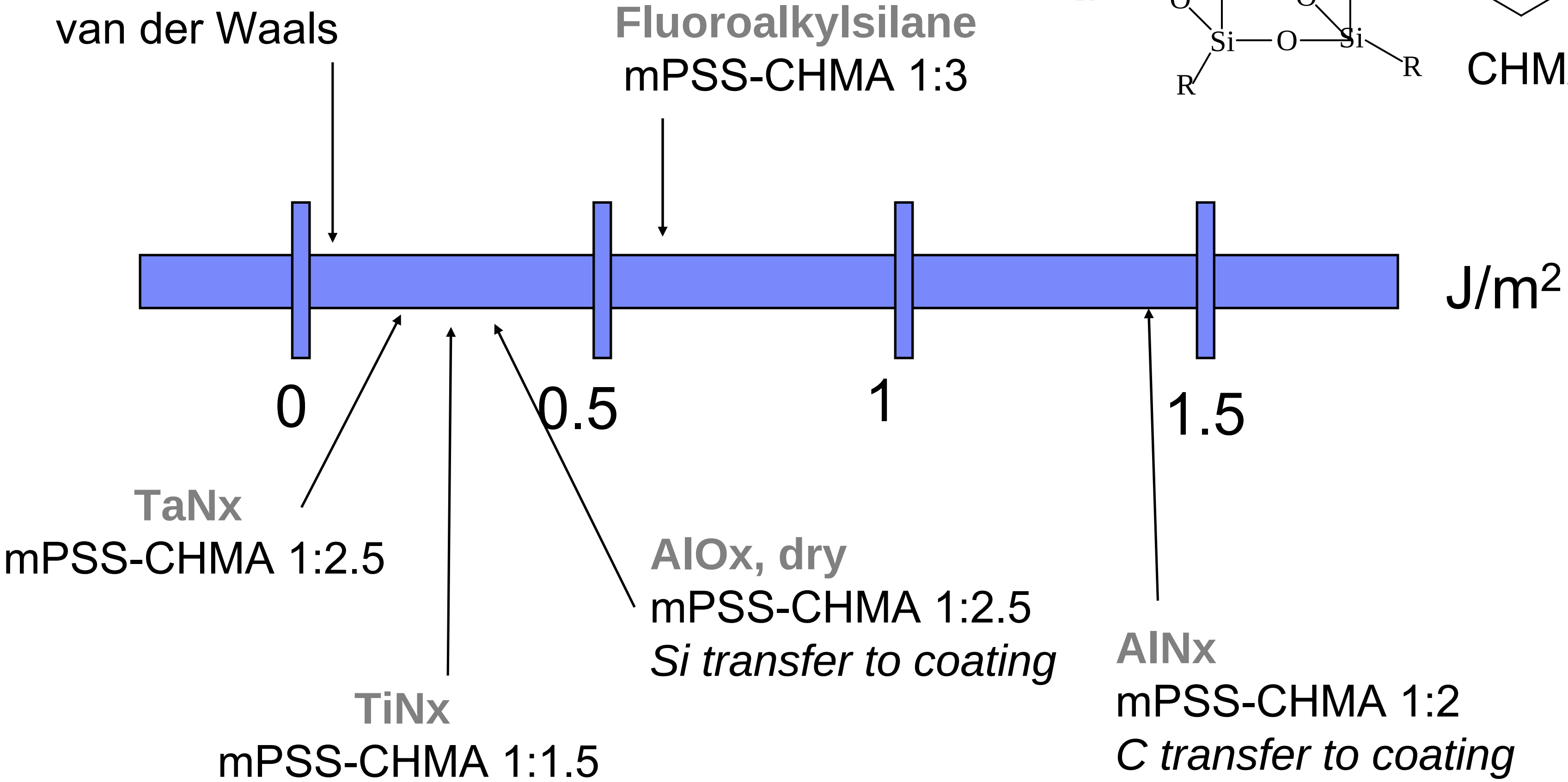
mPSS





CHMA

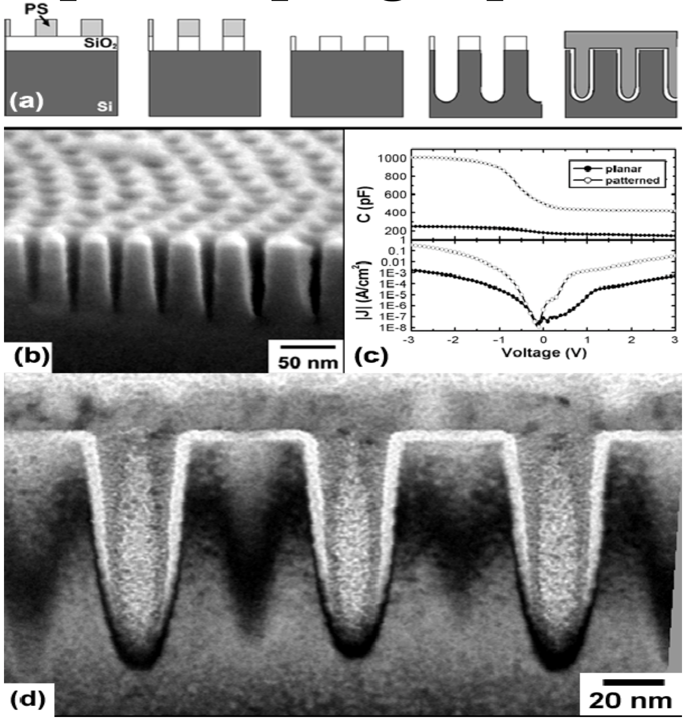
Release coating influences resist structure



Patterning Using Block Copolymers

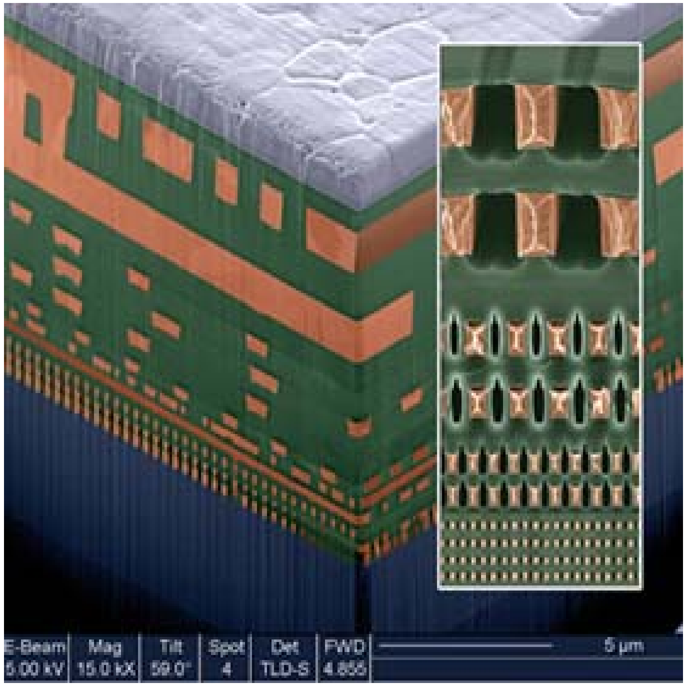
Type 1: Uniformity, order and registration not critical

On-chip decoupling capacitors



Facilitate space-saving on the wafer by increasing surface area

Air Gaps



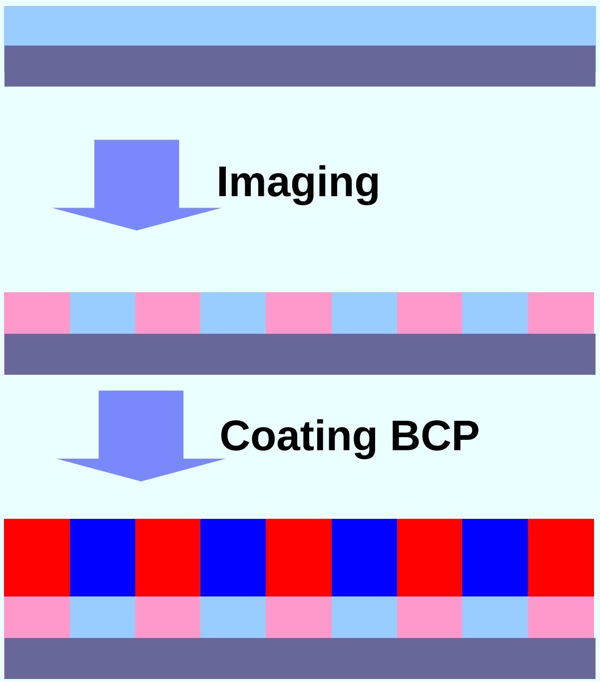
Reduce dielectric constant for fast and low power computing

C. T. Black, K. W. Guarini et al. *Appl. Phys. Lett.* **79**, 409 (2001).
IBM Announcement 05-03-2007, http://www-03.ibm.com/press/us/en/presskit/21463.wss

Directed Polymer Self-assembly
on Chemical Patterns

Dense Chemical Patterns

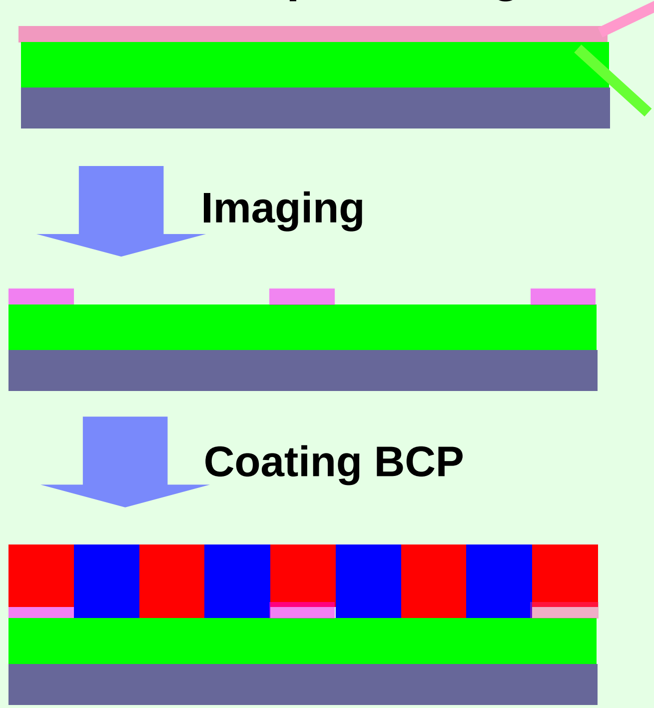
1:1 patterning
Nealey/ U. Wisconsin



Improve CD control
No resolution or throughput gain

Sparse Chemical Patterns

2:1 patterning

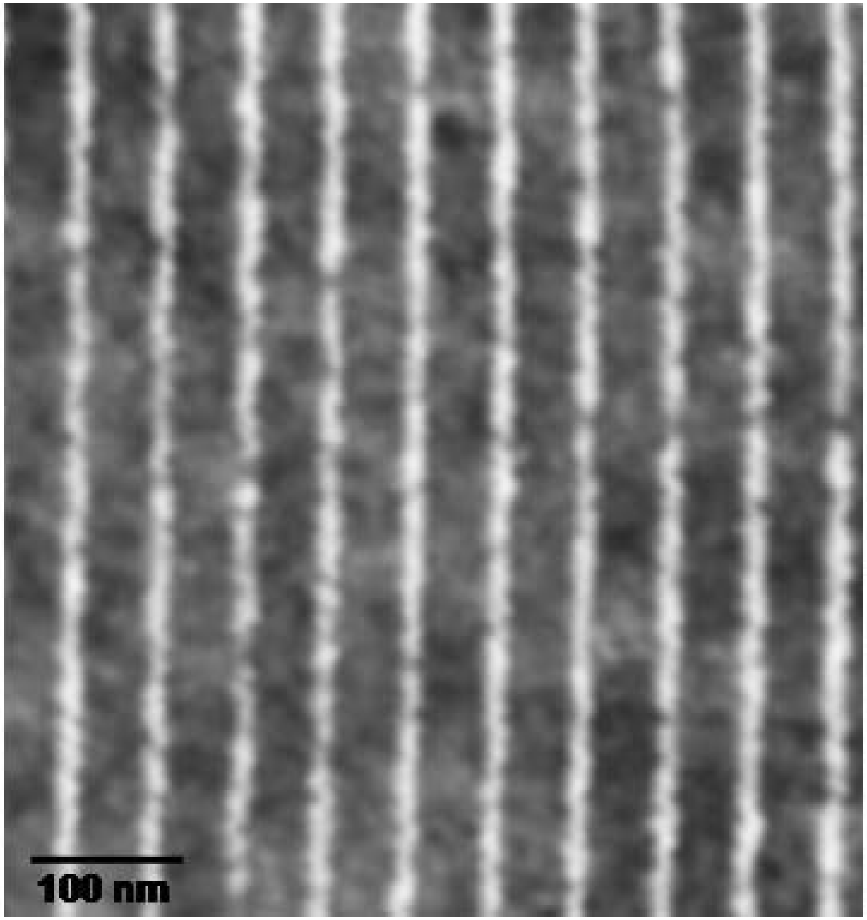


Improve CD control
Resolution enhancement

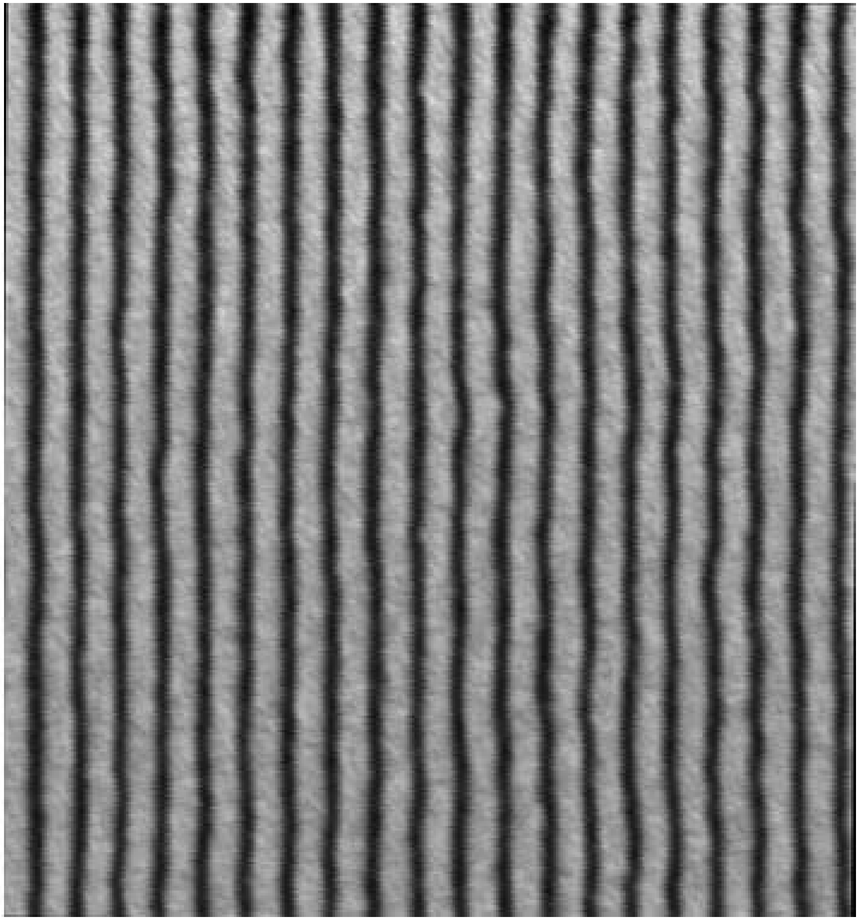
Joy Cheng
SPIE 2008

Resolution Enhancement
assisted by polymer self-assembly (SA)

Resist Lines (P = 57.5 nm)

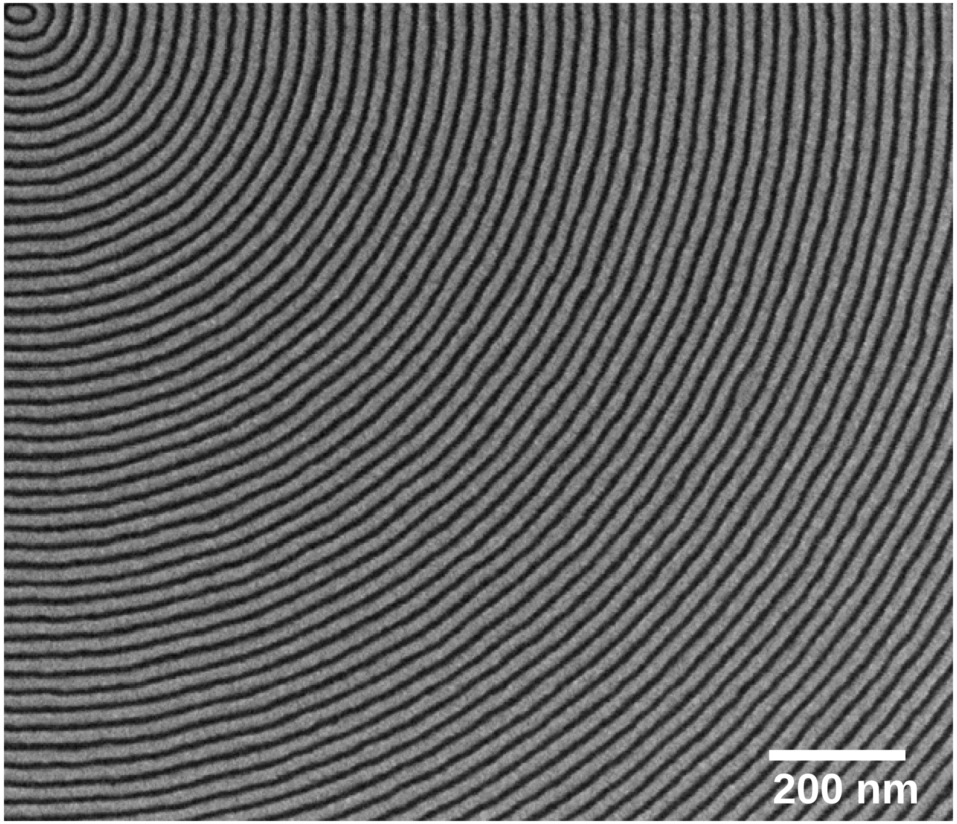


SA Lines (P = 28.8 nm)

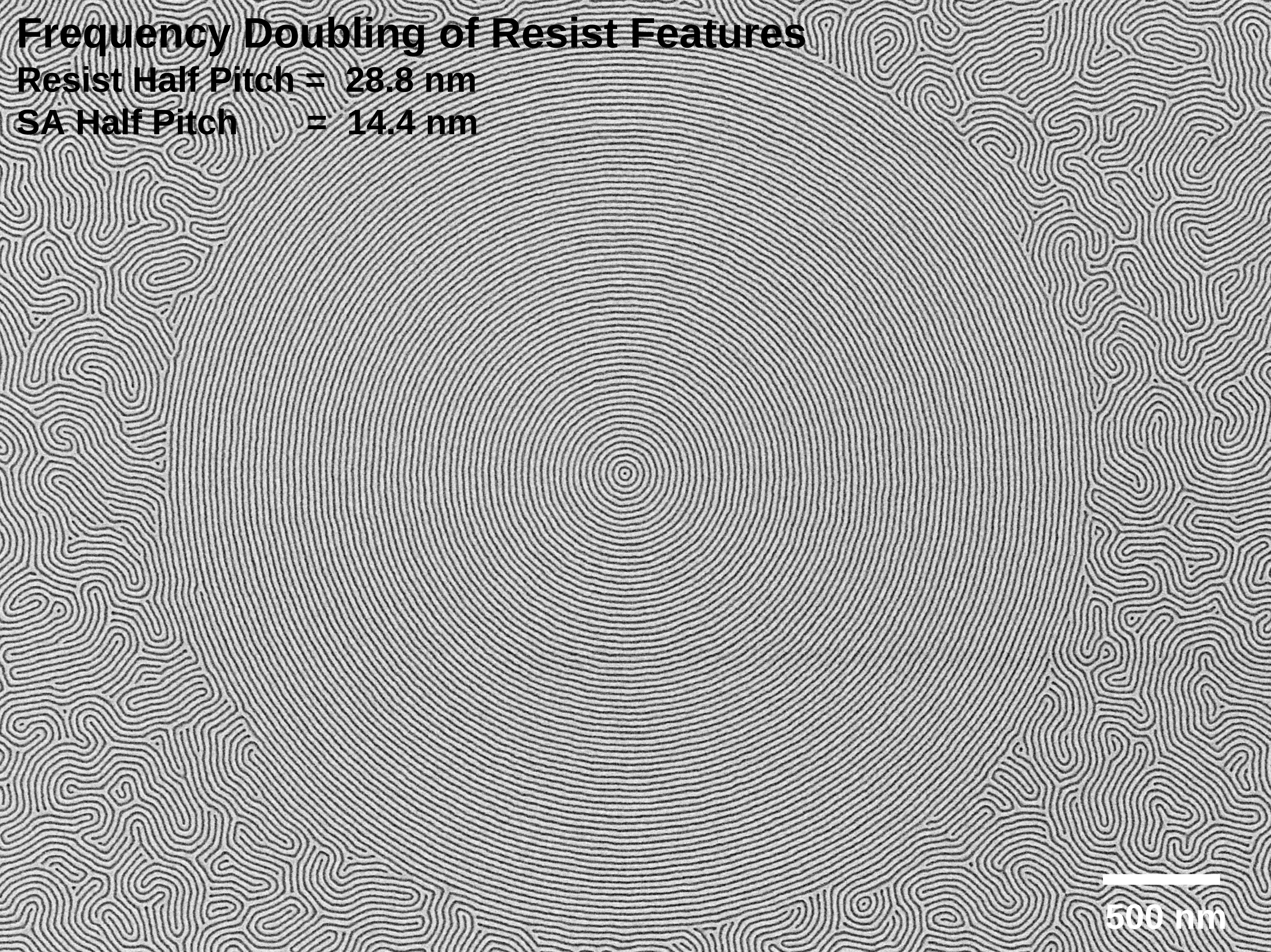


Frequency Doubling
of curved line-space patterns

Resist lines (P = 57.5 nm) **SA lines (P = 28.8 nm)**



This indicates the feasibility of generating arbitrary periodic patterns with higher spatial frequency based on directed self-assembly on resist patterns.


Frequency Doubling of Resist Features
Resist Half Pitch = 28.8 nm
SA Half Pitch = 14.4 nm
500 nm

Acknowledgments

- Almaden Lithography Group
- Dan Sanders, Frances Houle, Soori and Joy Cheng
- IBM Lithography Community in Yorktown, East Fishkill and Albany
- Chris Ober

Current Projects

- Extending 193nm lithography
- EUV Materials
- E-beam resists
- Nanoimprint Materials
- Directed Self Assembly materials and processes
- Patterning with DNA tiles
- Nanomembranes for future water purification/desalination

We are hiring!

(resist and synthetic chemists, materials scientists, engineers)

Contact me rdallen@almaden.ibm.com