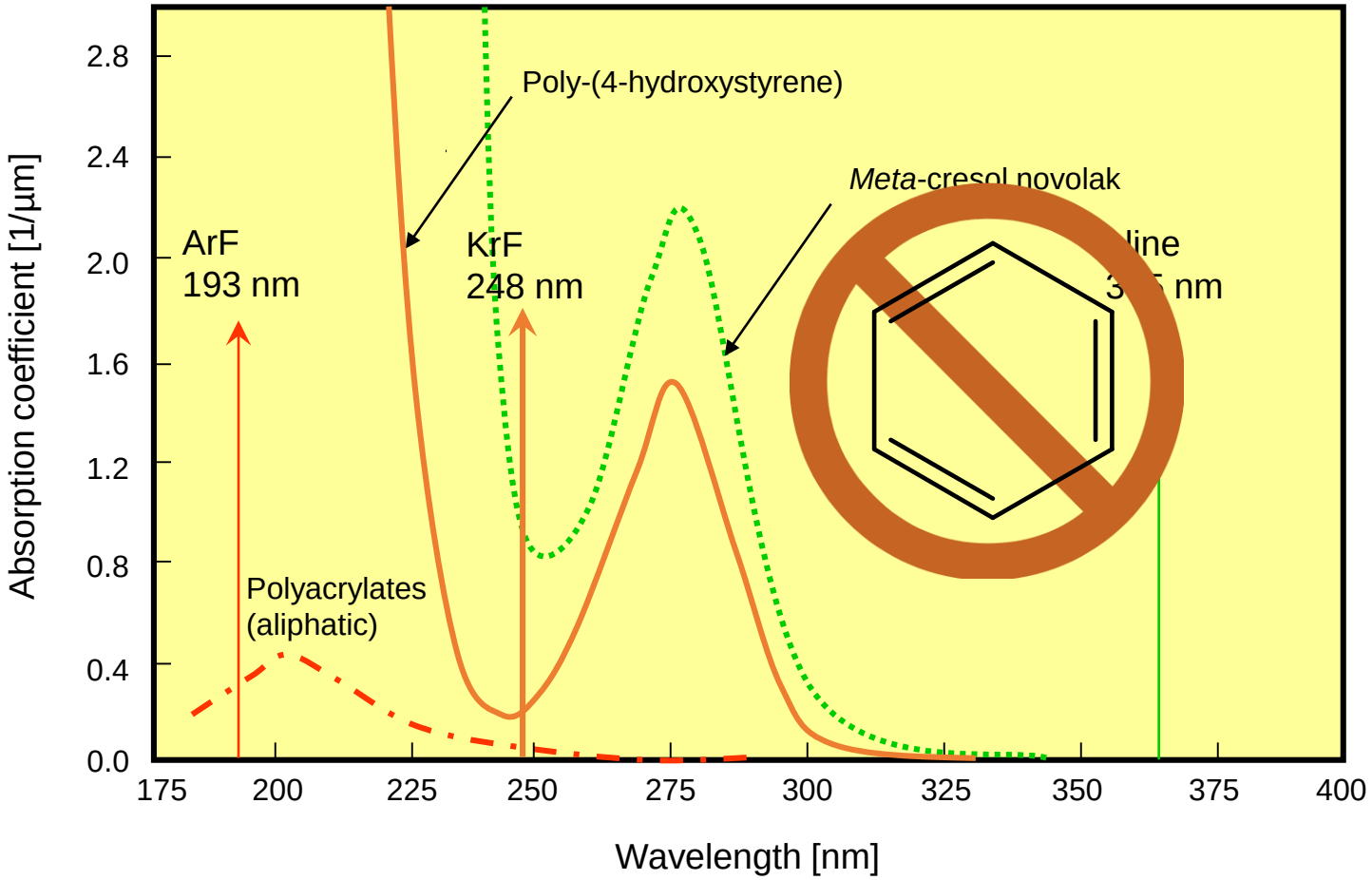
Lecture 16

Chemical Engineering for Micro/Nano Fabrication

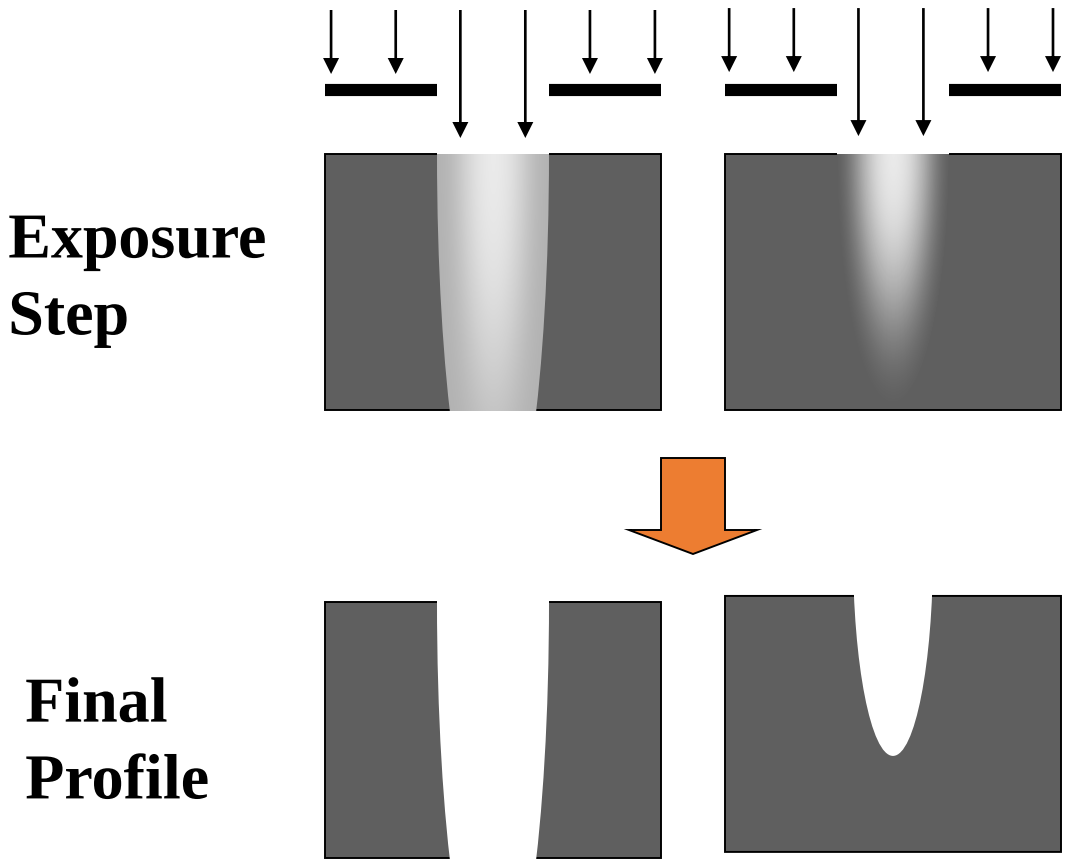
Next:
193nm Lithography

Absorption of Photoresist Polymers

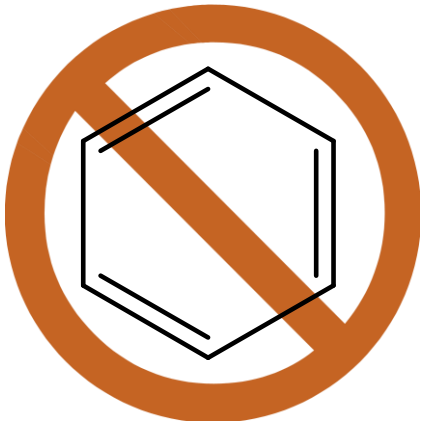


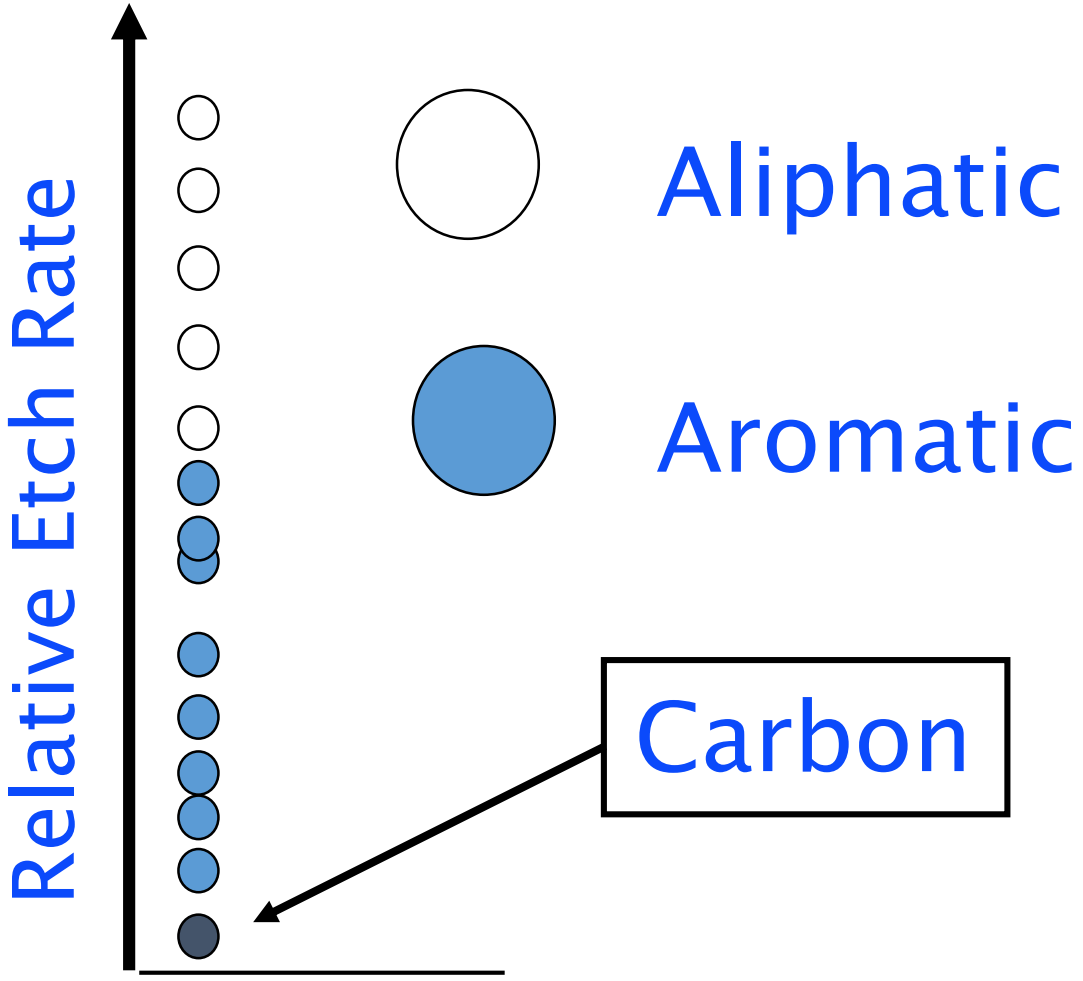
Source: R.D. Allen et al., IBM J. Res. Develop. 41 (1/2), 95-104 (1997)

Impact of Photoresist Absorbance on Developed Image Profile



Relative Etch Rate of Polymers



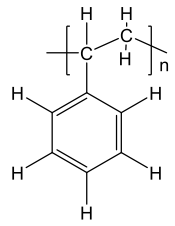


The Ohnishi Number

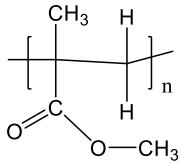
An empirical law discovered by Ohnishi states that the RIE etch rate of polymers is a linear function of the Ohnishi number O.N., i.e., the number of atoms in the polymer repeat unit, divided by the number of carbon minus the number of oxygen atoms:

$$O.N. = \frac{N}{N_C - N_O}$$

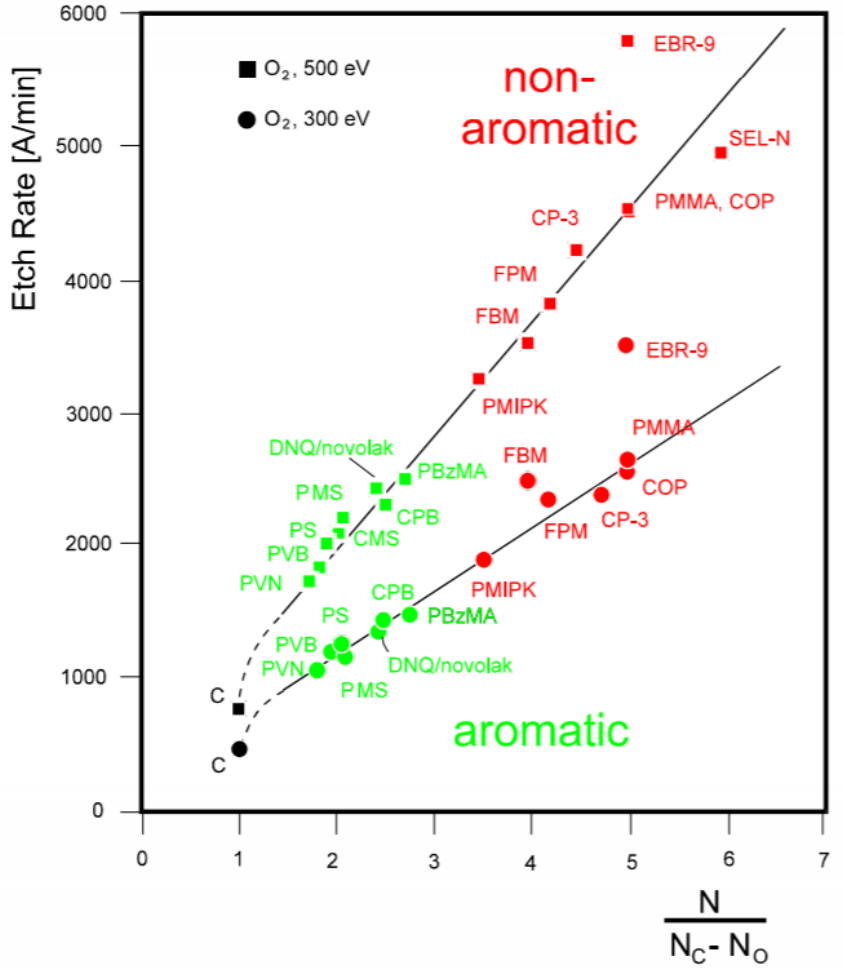
The higher percentage of carbon in aromatic structures leads to improved etch resistance, e.g.



PolyStyrene $(C_8H_8)_n$
ON = 16/8 = 2.0



PMMA $(C_5H_8O_2)_n$
ON = 15/3 = 5.0



Watanabe, F. and Ohnishi, Y., J. Vac. Soc. Technol. B,422 (1986)

193 nm Resist Materials

Challenge:

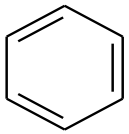
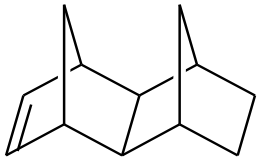
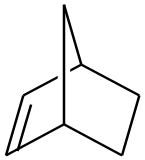
- **248 and 365 nm resists are unsuitable for 193 nm imaging because they are opaque at this wavelenth**

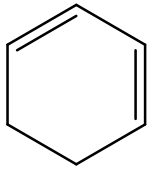
- **Etch resistance requires high carbon/hydrogen ratio but aromatics are precluded because of their absorption**

- **How do you achieve both 193nm optical transparency and etch resistance?**

High C:H Ratio of Alicyclic Hydrocarbons

The key!

Structure:				$CH_3(CH_2)_nCH_3$
Formula:	C_6H_6	$C_{12}H_{16}$	C_7H_{10}	C_nH_{2n+2}
Unsaturation Number:	**4**	**5**	**3**	**0**



C_nH_{2n+2}

$- C_nH_X$

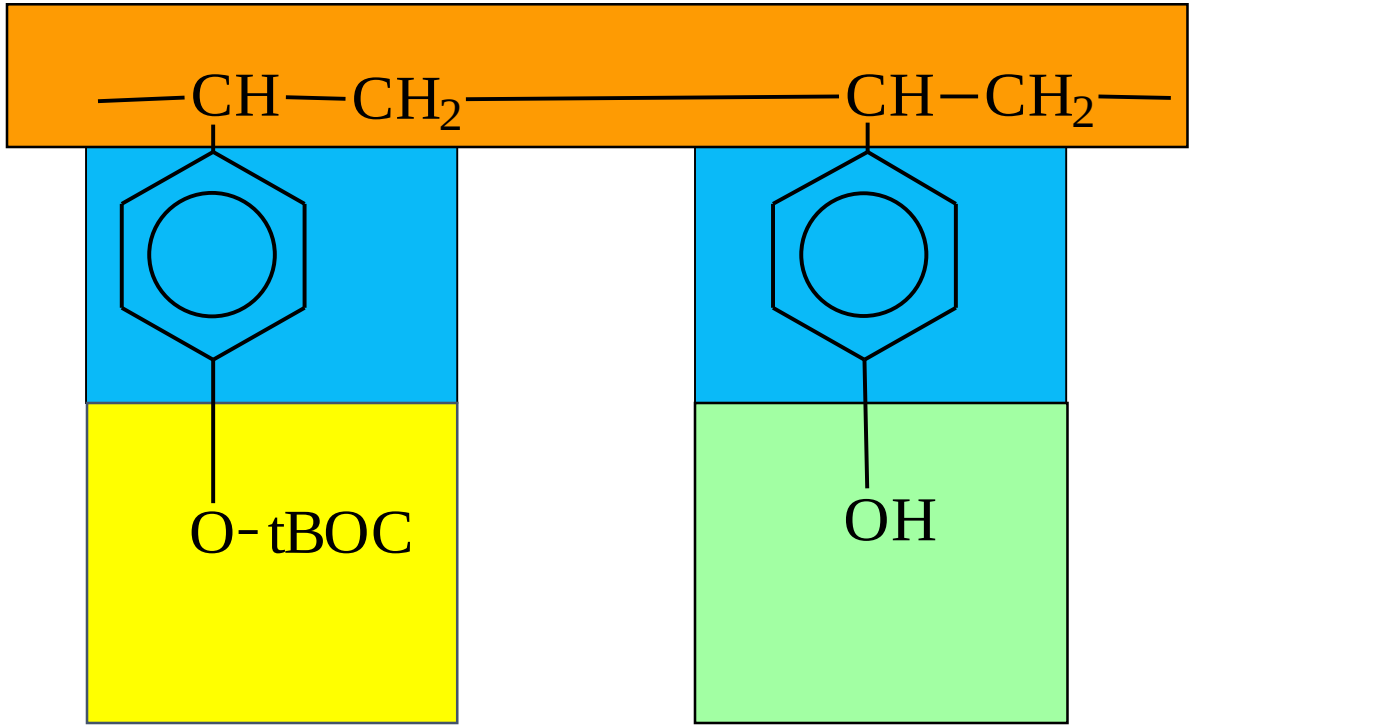
$\Delta H / 2$ = Unsaturation Number

C_6H_{14}

C_6H_8

6/2 = 3

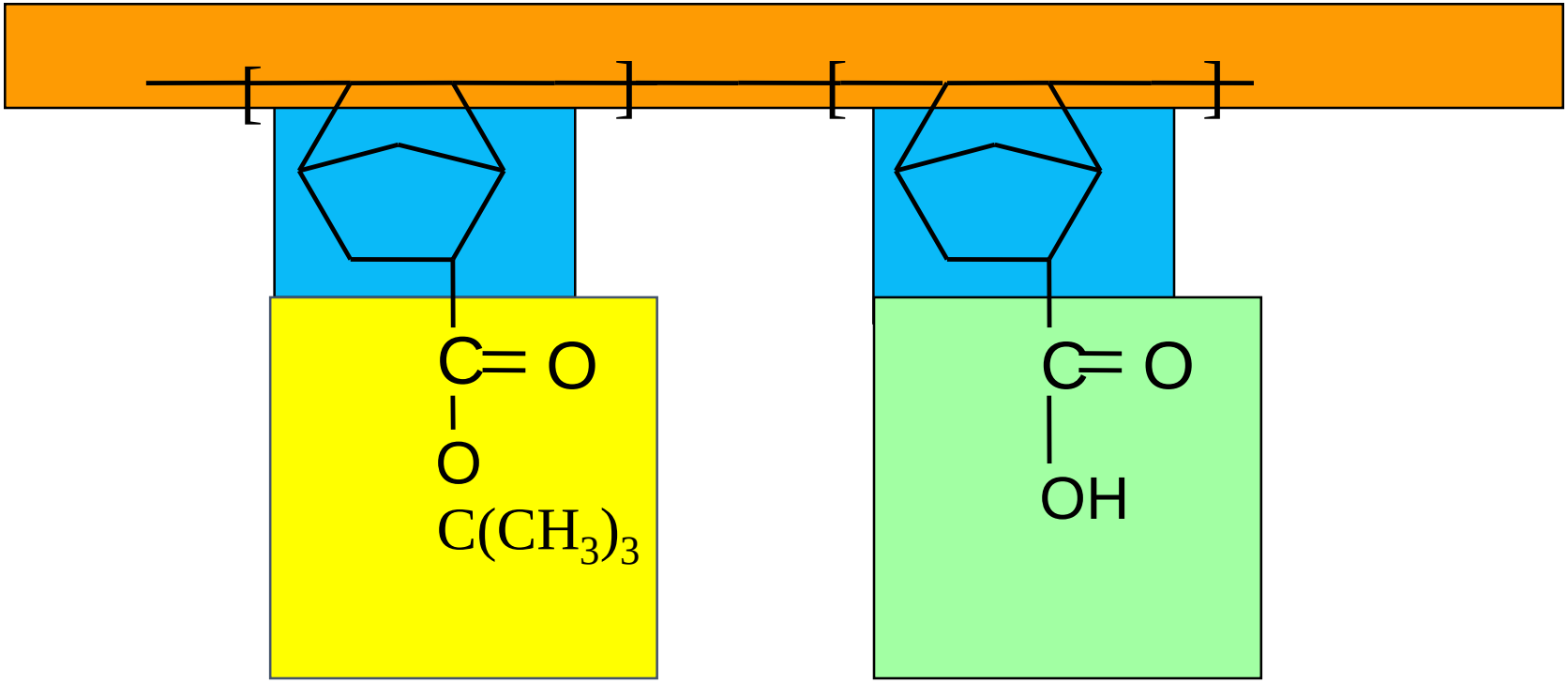
APEX 248nm Resist Design



Tethering Function Acid Lability Base Solubility

Etch Resistance

UTexas193nm Design

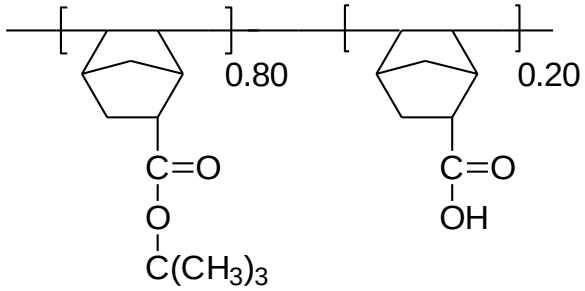


Tethering Function Acid Lability Base Solubility

Etch Resistance

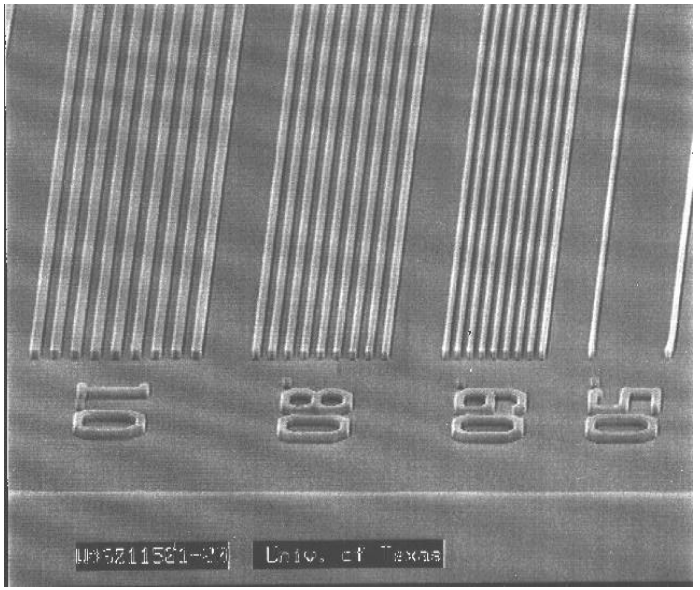
Early Lithography

Resist



+ $Ø_3SSbF_6$

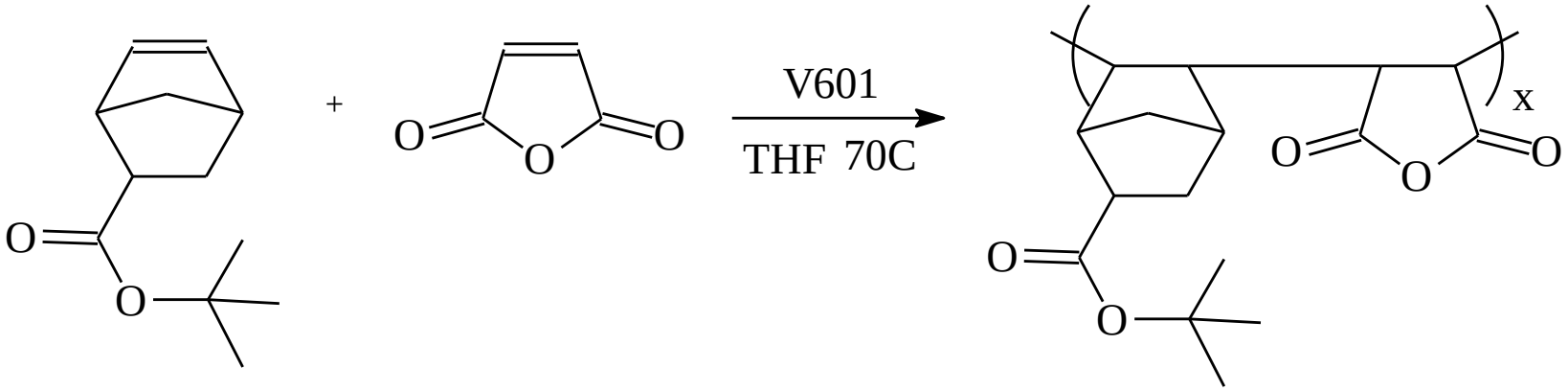
poly(NBCA-*co*-CBN)



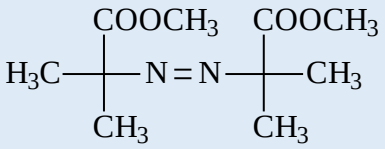
- Synthesis requires metal catalyst!

- Excellent image quality
- Adhesion failure

Trading Etch Resistance for Adhesion: Alternating Systems: COMA



V601

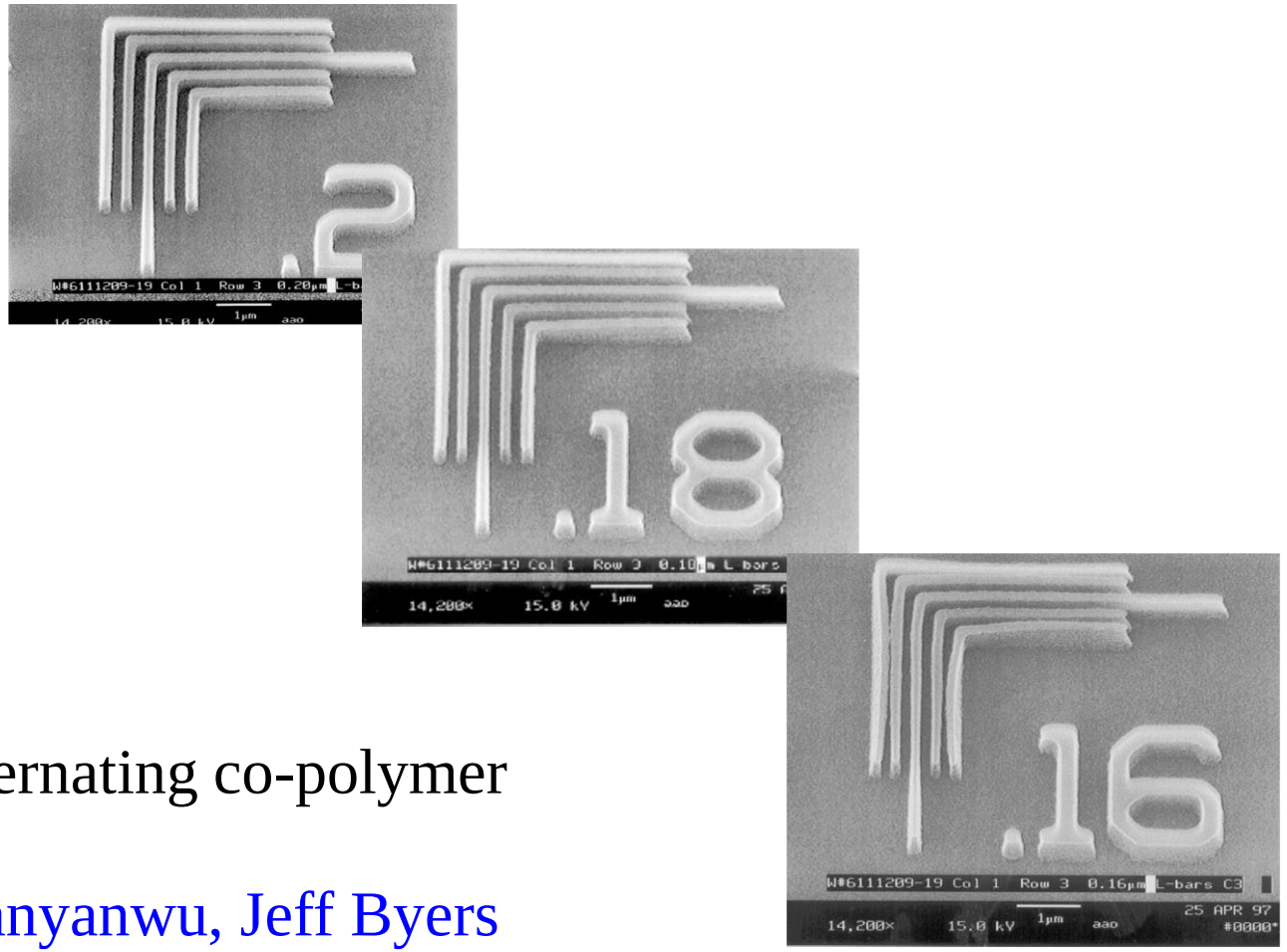


Waco Chemical
No Metal!

Yield :	60%
M_n :	4,660
M_w :	6,860
Pd :	1.472

Shelf Life issues?

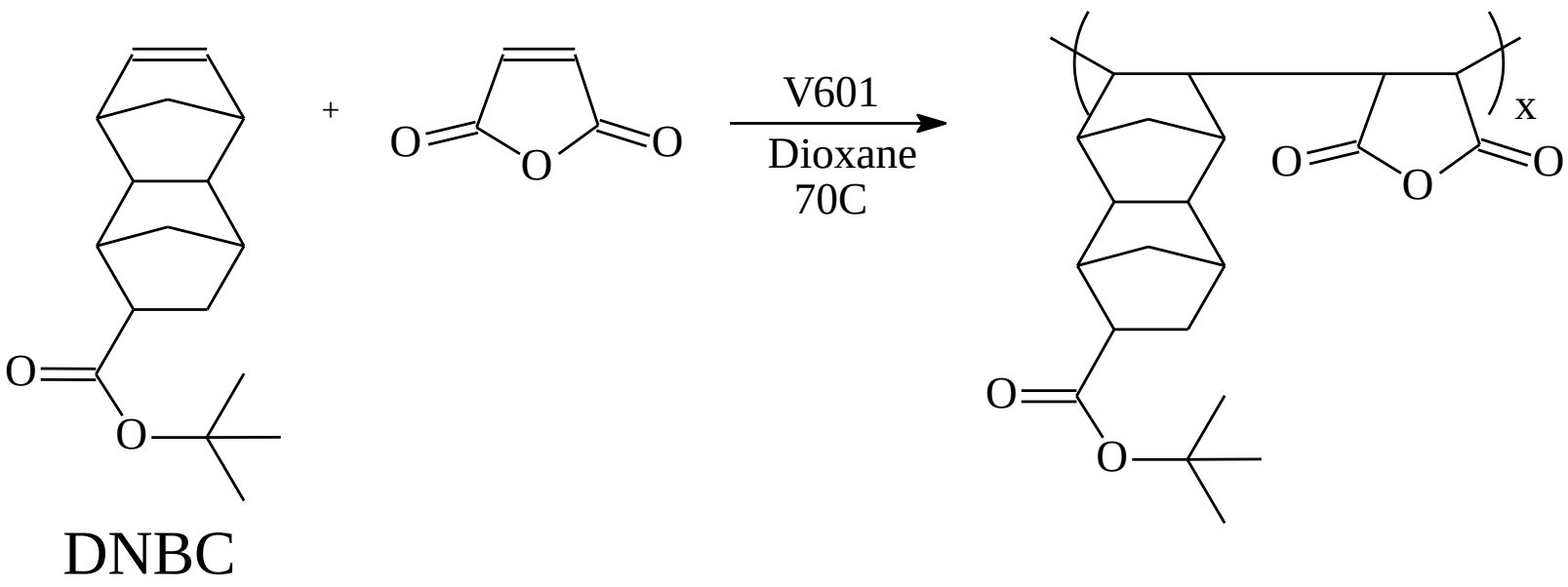
Images in UT 193nm COMA Resist



Alternating co-polymer

Uzo Okoroanyanwu, Jeff Byers

Improving Etch Resistance



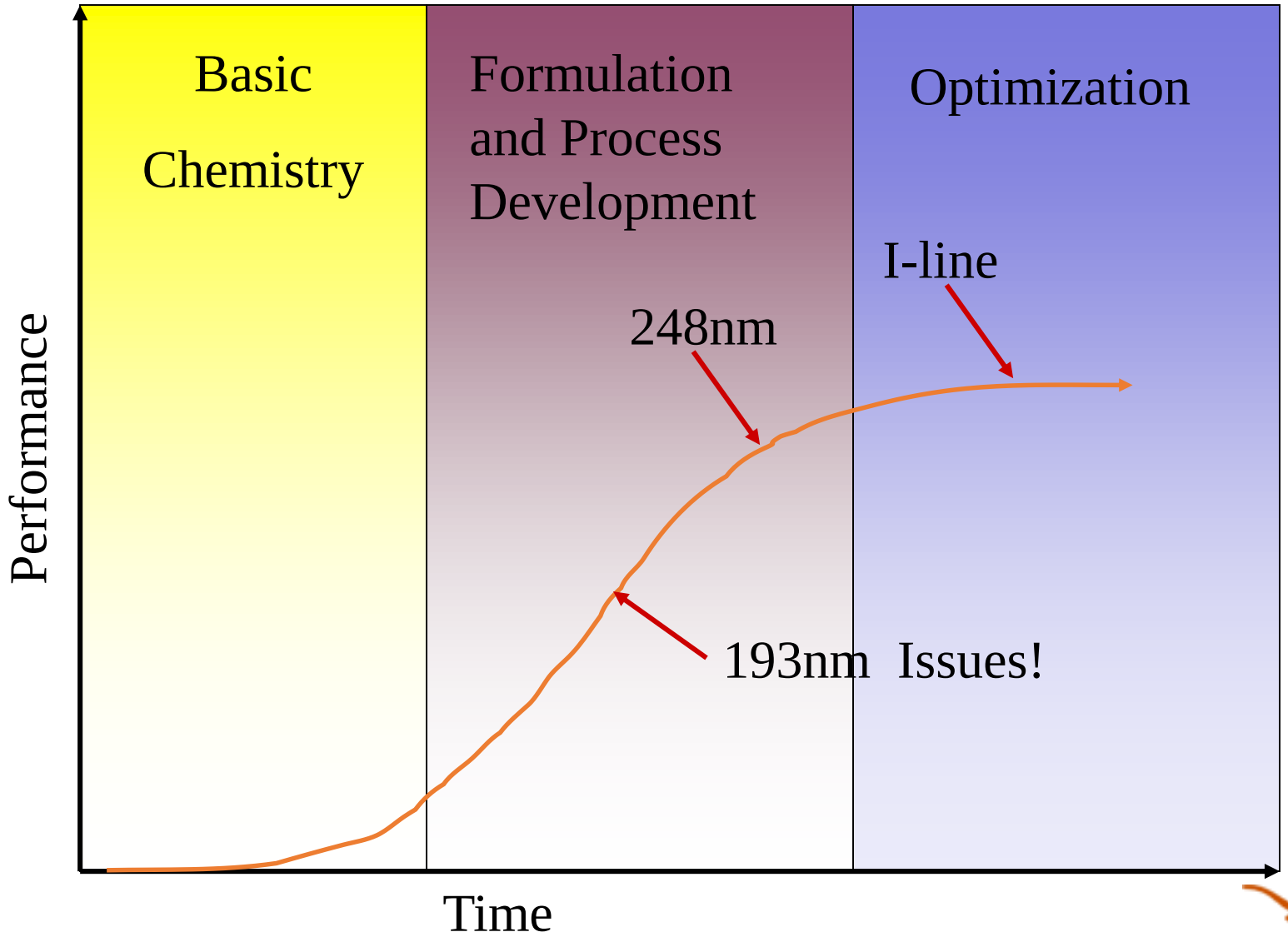
DNBC

UV Absorbance
0.44 μm^{-1}
@ 193 nm

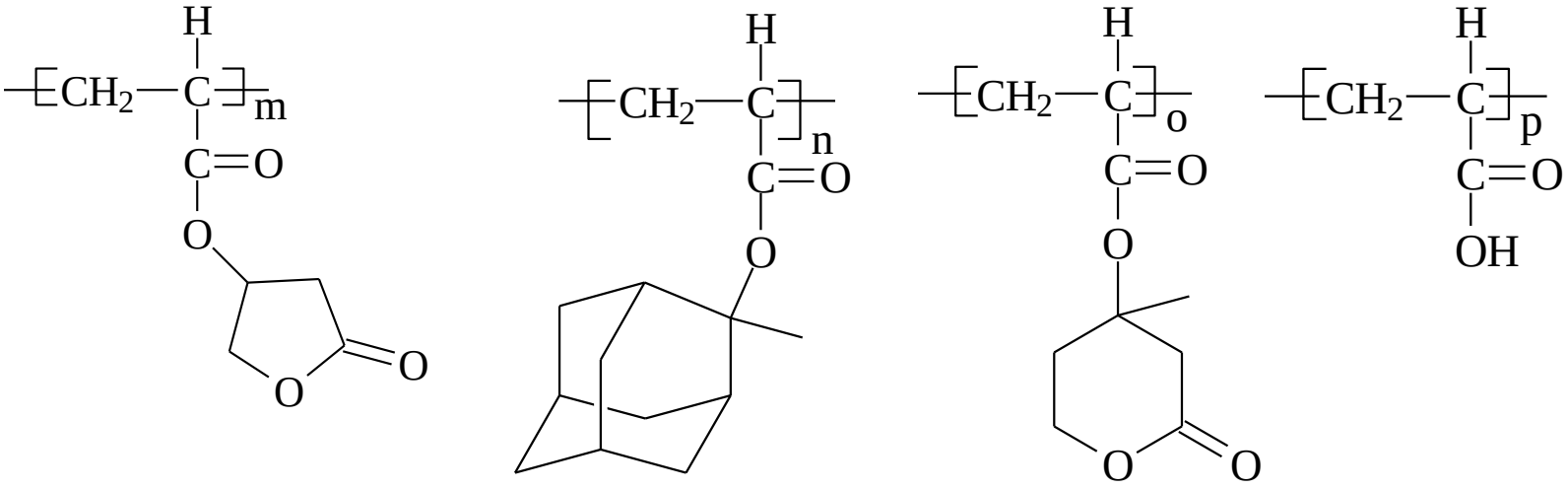
Yield : 55 %
M_n : 3,400
M_w : 4,340
Pd : 1.276

With JSR

Resist and Process Development



Fujitsu's Acrylic Platform

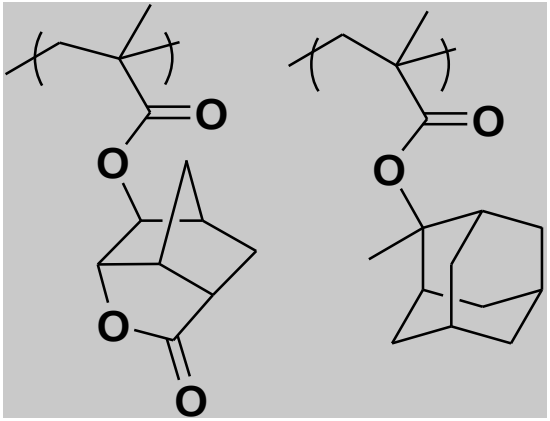


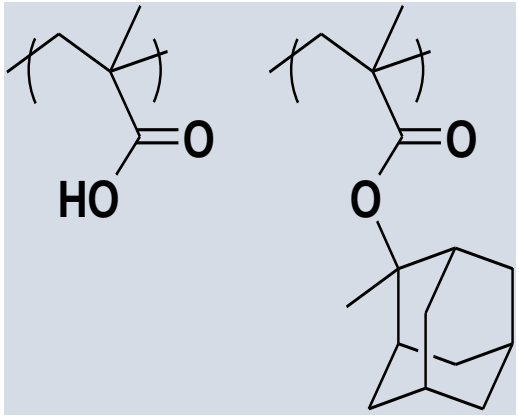
Acrylate Copolymers …

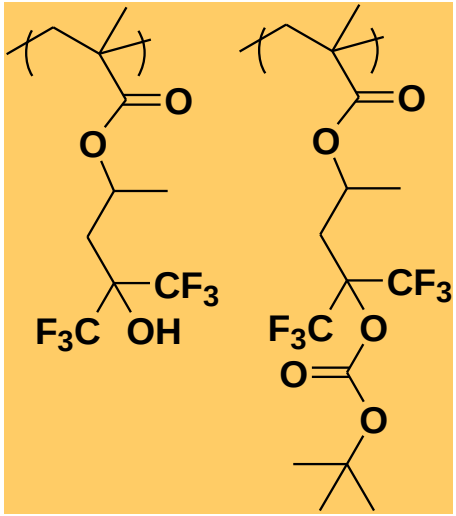
Free radical polymerizations

No metal

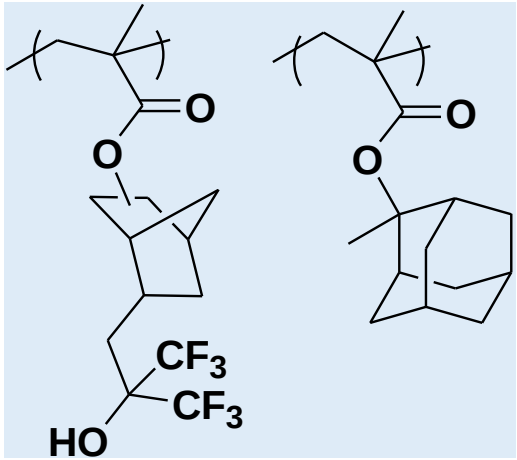
Acrylic Polymer Platform







Fujitsu

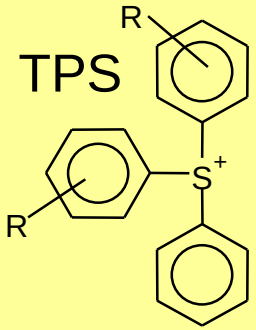


IBM,JSR, etc.

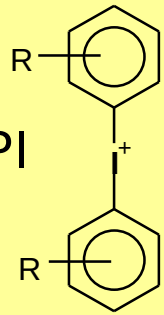
Types of PAGs Used For 193 nm Lithography

IONIC

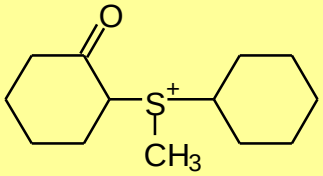
TPS



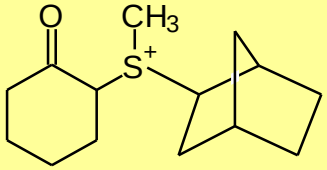
DPI



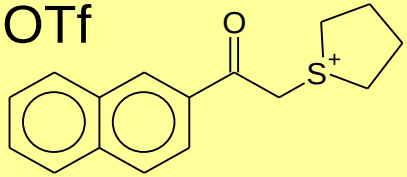
ALS



NEALS

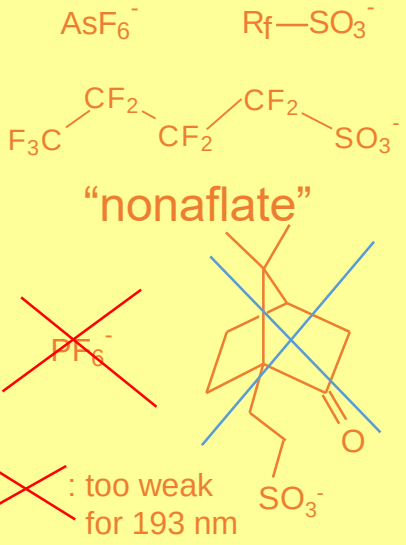


NAT·OTf



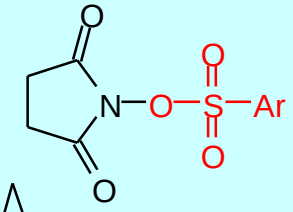
VOLATILE

NON-VOLATILE

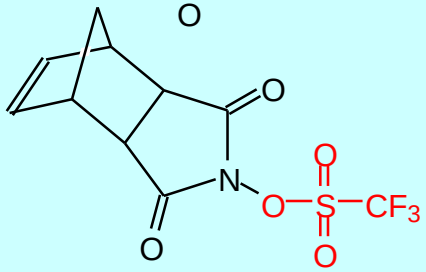


NON-IONIC

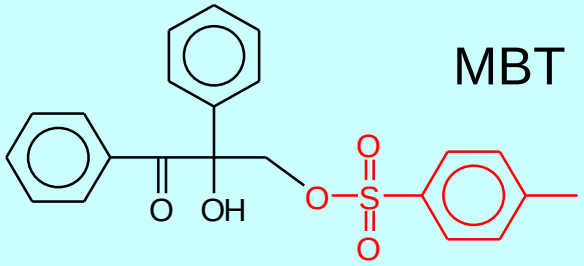
SIT



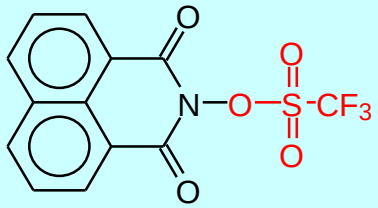
MDT



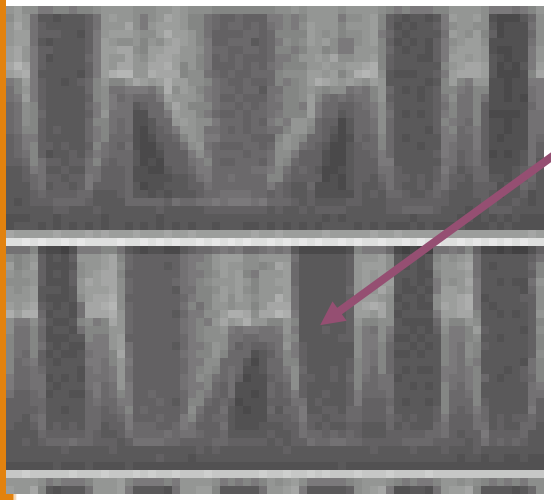
MBT



NIT

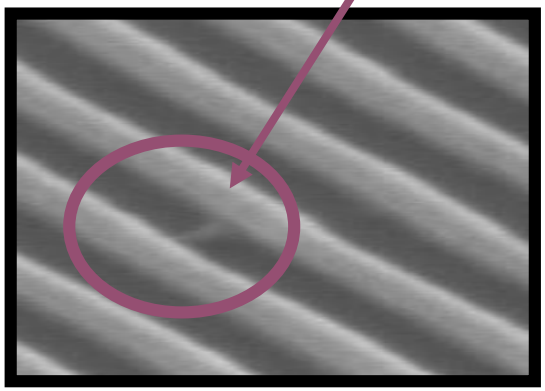


193nm Resist Challenges

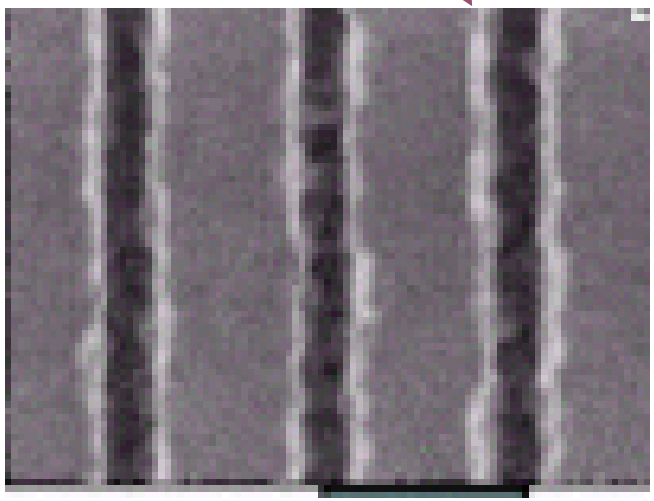


Pattern Collapse

- Pattern Collapse
- Line Edge Roughness (LER)
- Etch Resistance
- Heisenberg Principle issue
- New Defect Types

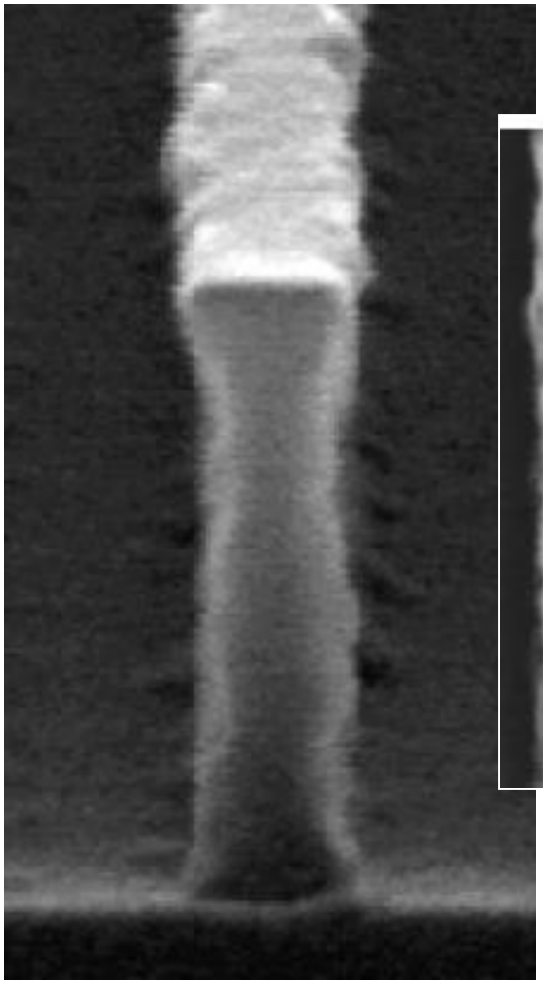


μ Bridging

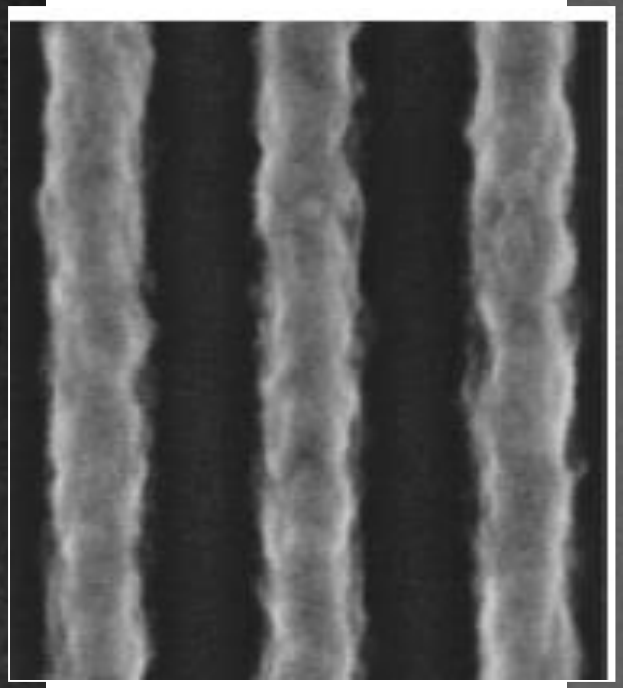


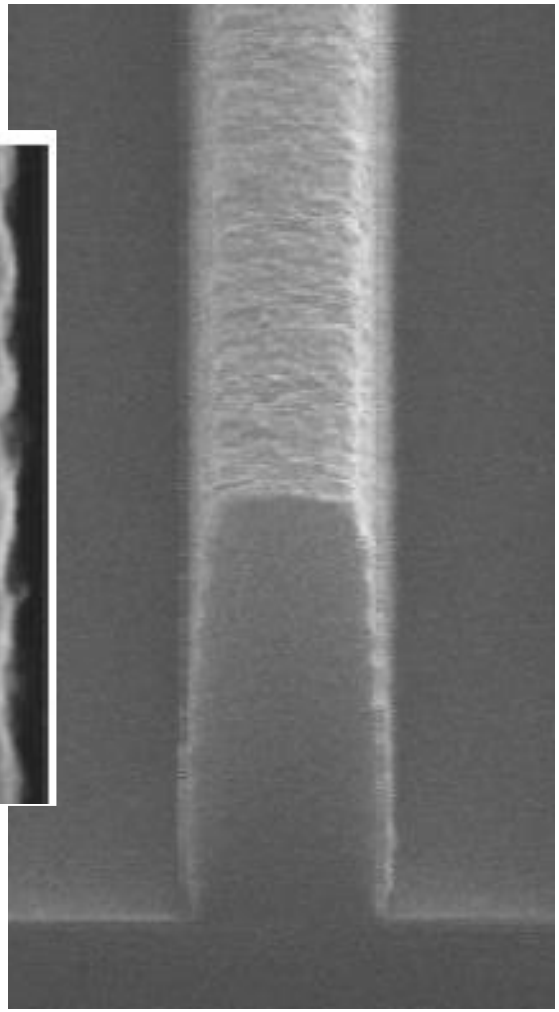
LER

Line edge Roughness



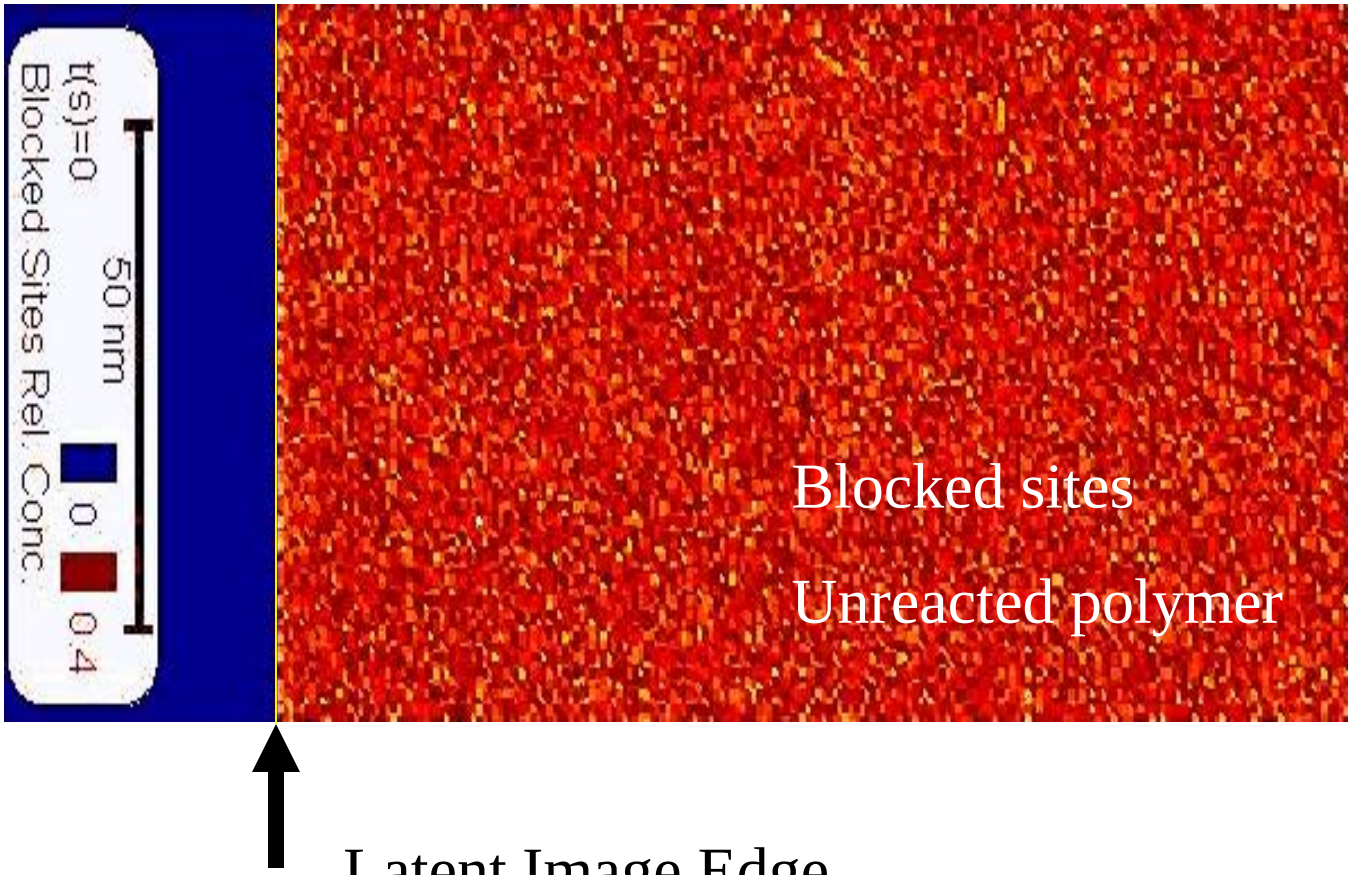
193





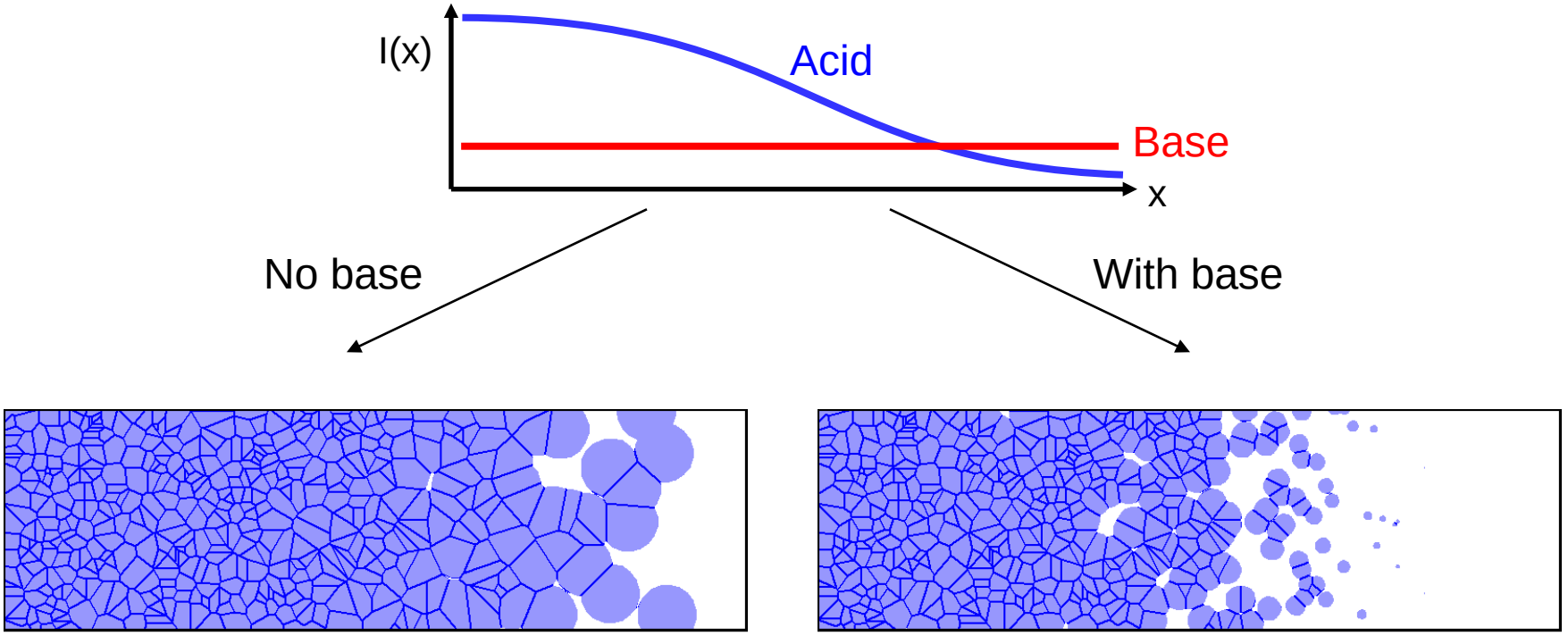
248

Simulation of a PE Bake



Influence of Base on LER

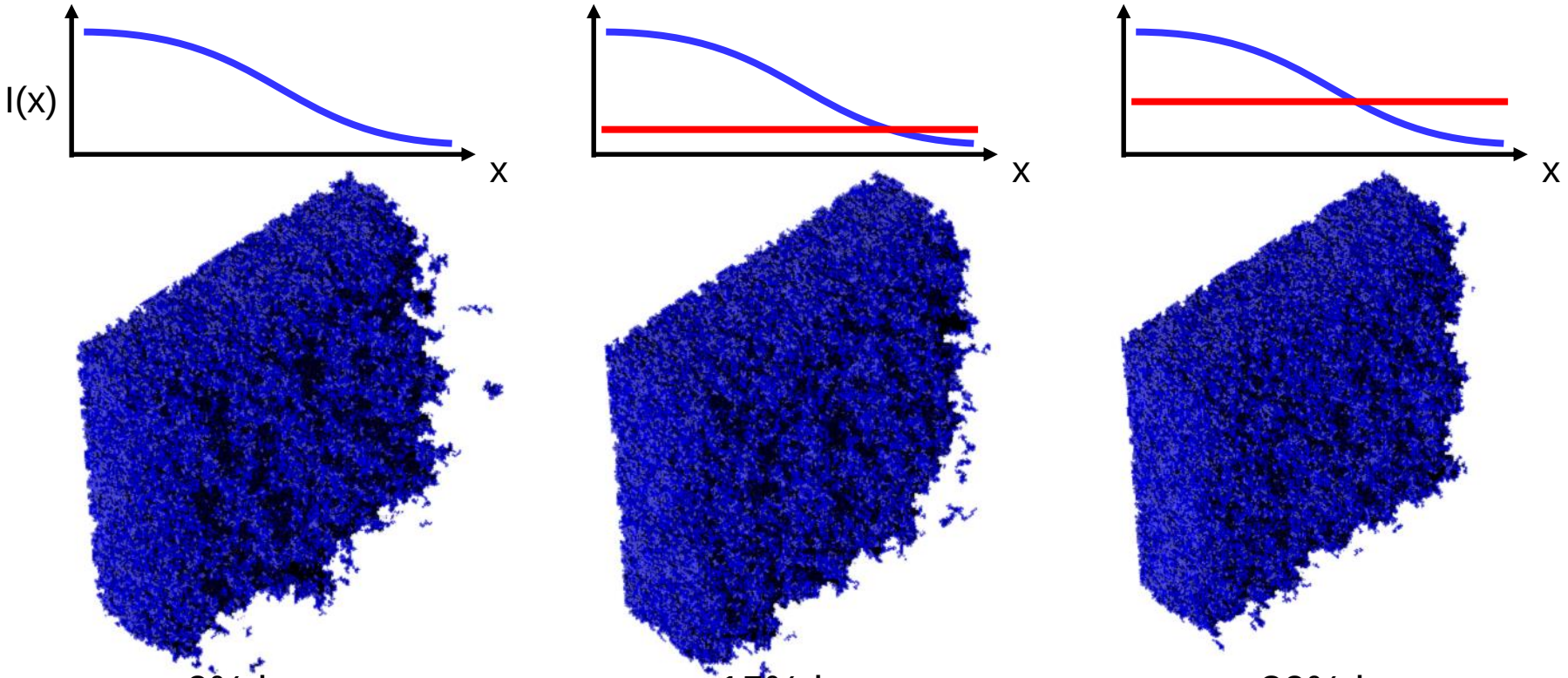
- Base quencher can decrease the acid sphere of influence in low contrast regions, thereby reducing LER.



J. E. Meiring, T. B. Michaelson, G. M. Schmid and C. G. Willson, *Proc. SPIE*, **5753**(2005), to be published

Exploring Base Effects

- To add base quencher seems to make the contrast higher, thereby LER reducing.



0% base
6.61 nm RMS

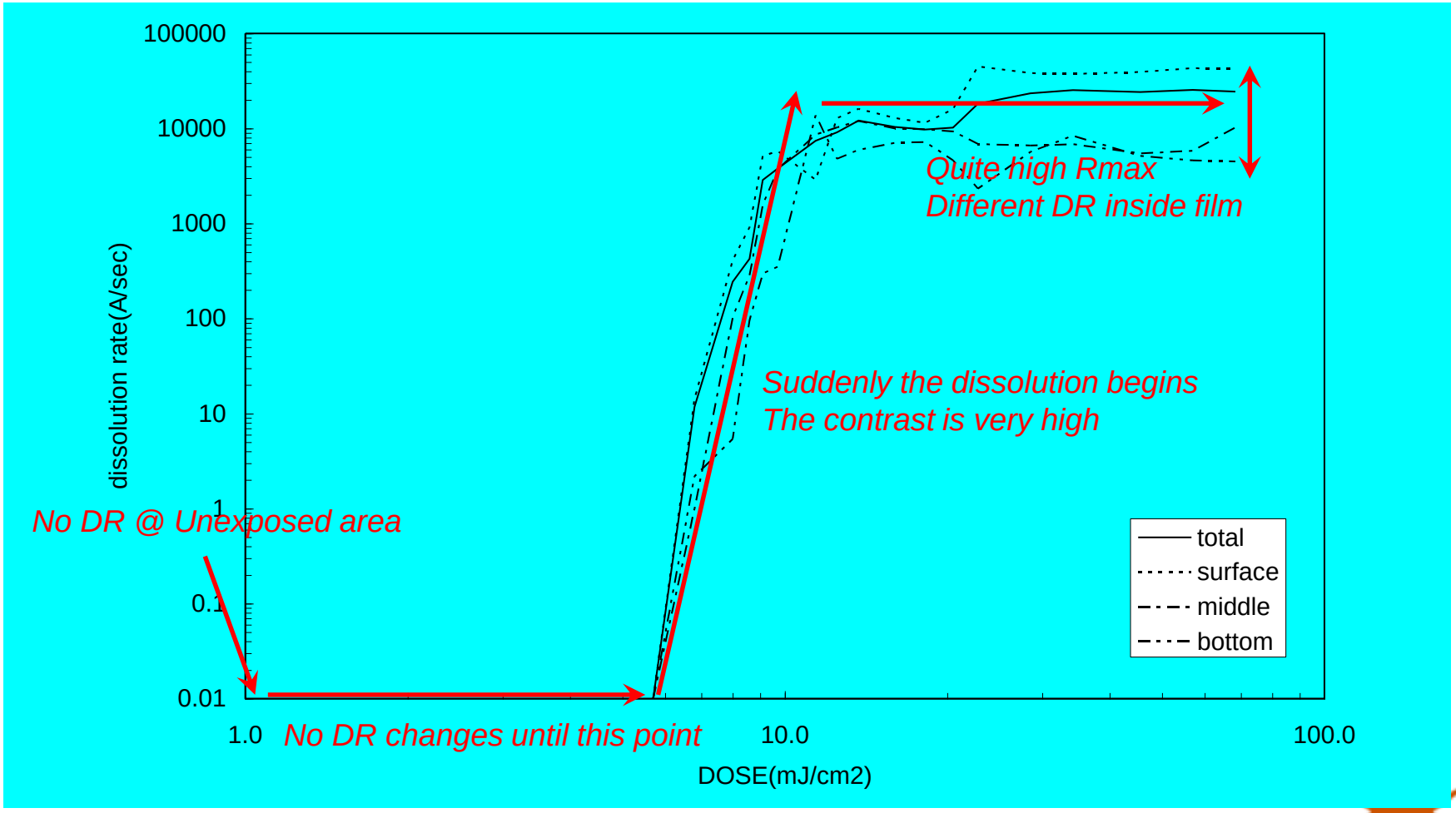
15% base
5.47 nm RMS

30% base
3.89 nm RMS

J. E. Meiring, T. B. Michaelson, G. M. Schmid and C. G. Willson, *Proc. SPIE*, **5753**(2005), to be published

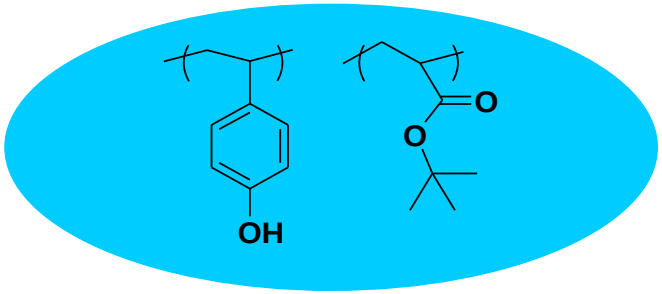
Comparison of ArF and KrF

- Typical KrF system always shows moderate variation of DR……

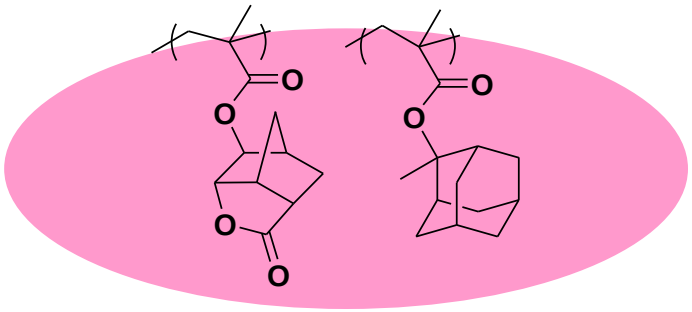


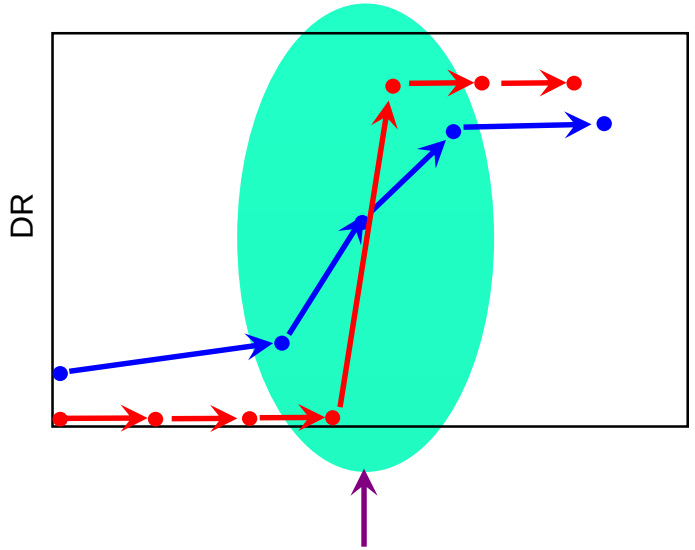
Dissolution behavior

KrF System



ArF System

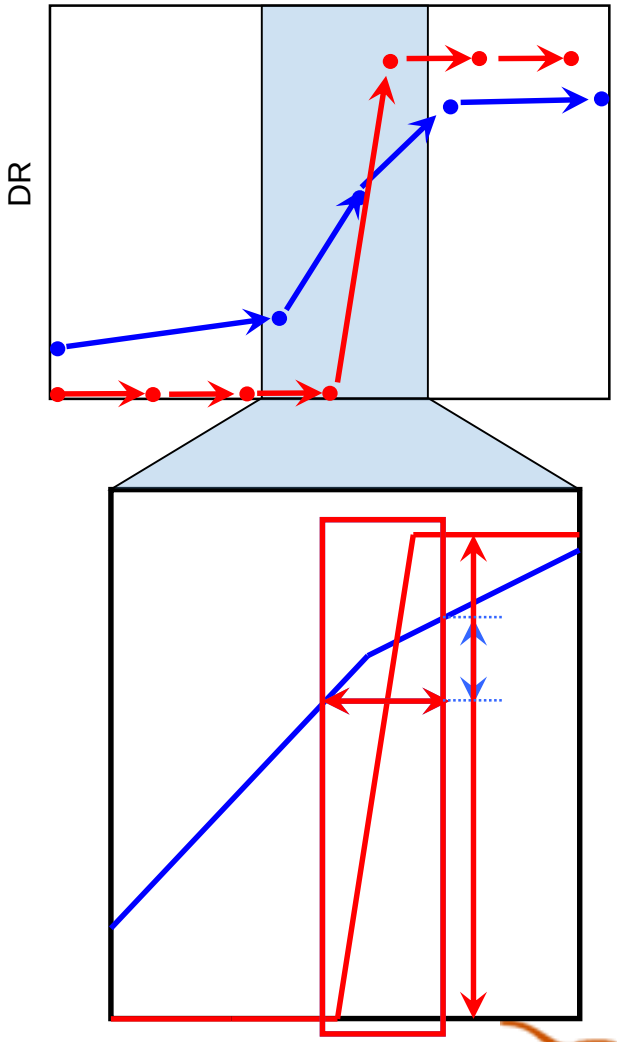




This difference in the contrast amplifies small variations in the blend region. “Digital” On/Off switching phenomenon makes the line edge rough.

Is there such a thing as too much contrast?

- The KrF system has lower contrast
- Small fluctiuations cause small changes in dissolution rate..



- The ArF system changes from insoluble to soluble over a very narrow dose range
- Small fluctuations are amplified and cause huge changes in dissolution rate.
- Stochastic process noise becomes line edge roughness

Could have been

Can "it" be done again at 157nm???

Perhaps….but

This time it would have been <u>really</u> hard!!

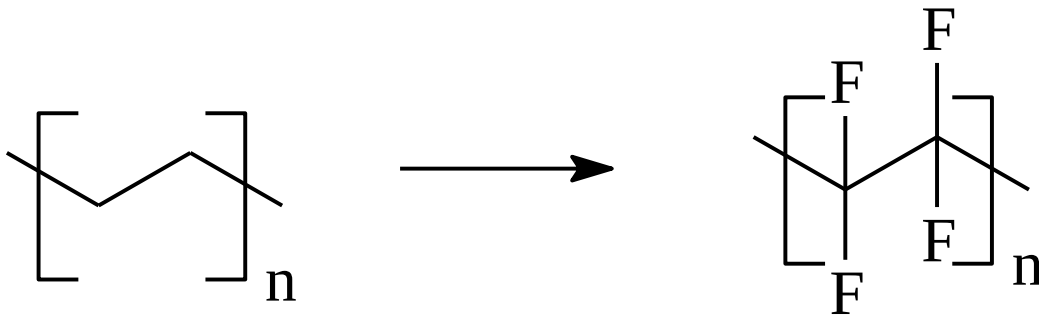
Absorption (μm^{-1}) of Common Polymers

Transmission 0.00001%!!!	Wavelength (nm)		
	157.6	**193**	**248**
248 resist	6.84		**0.37**
193 resist	6.86	**0.47**	
Polystyrene*	6.20		
Polynorbornene*	6.10		
PMMA*	5.69		
Fluorocarbon*	0.70		

- Vacuum UV
- O_2, H_2O absorbs at this wavelength
- Even hydrocarbons like butane and polyethylene absorb strongly

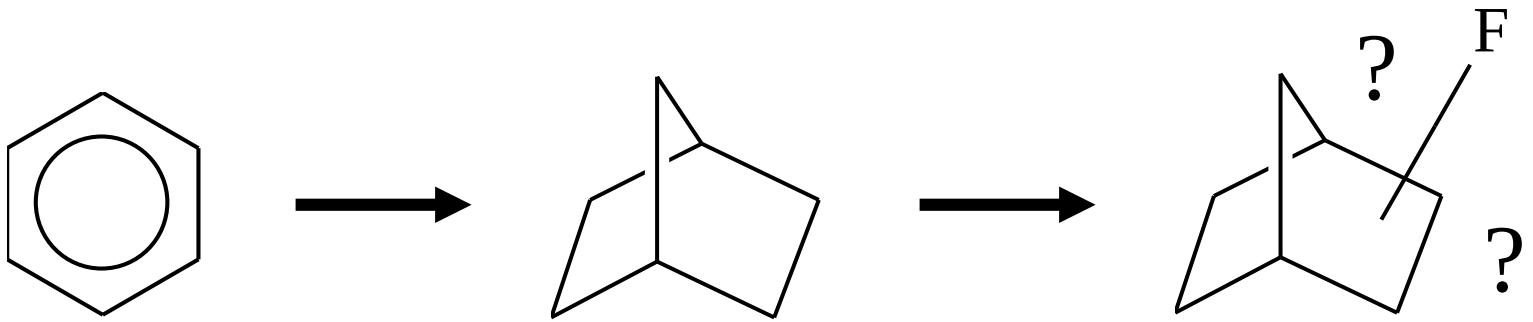
* R.R.Kunz,et al., Proc. SPIE 3678, 13 (1999).

Fluorination of Norbornane Skeleton



Opaque

Transparent



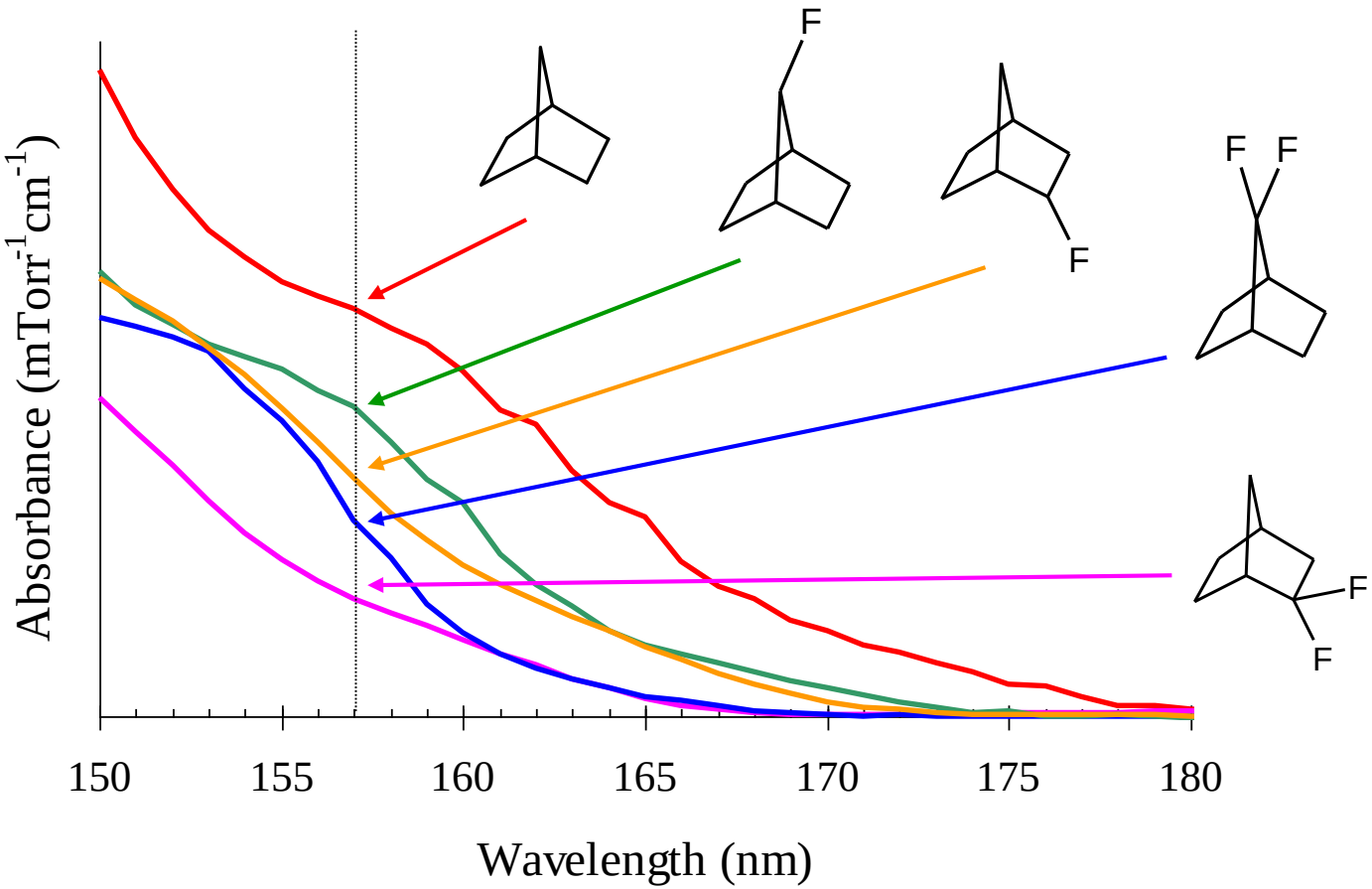
248 nm

193 nm

157 nm

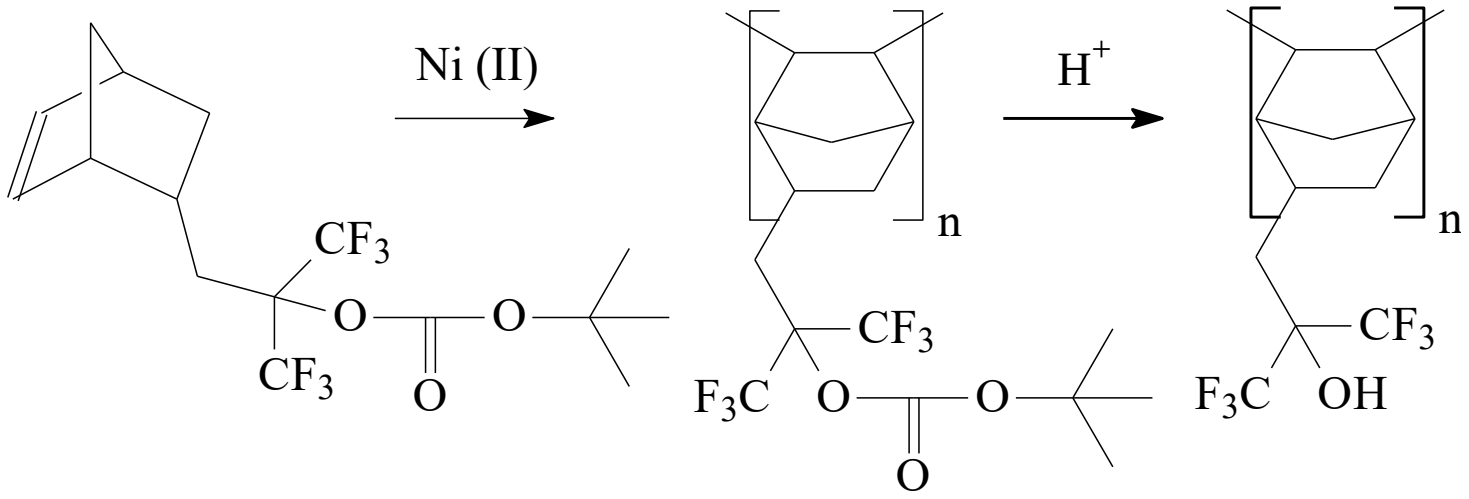
How many fluorines and where to fluorinate?

Selective Fluorination of Norbornane



Geminal substitution at the two carbon bridge is the most effective fluorination pattern → α-CF_3 acrylates

Surprising Serendipitous Discovery



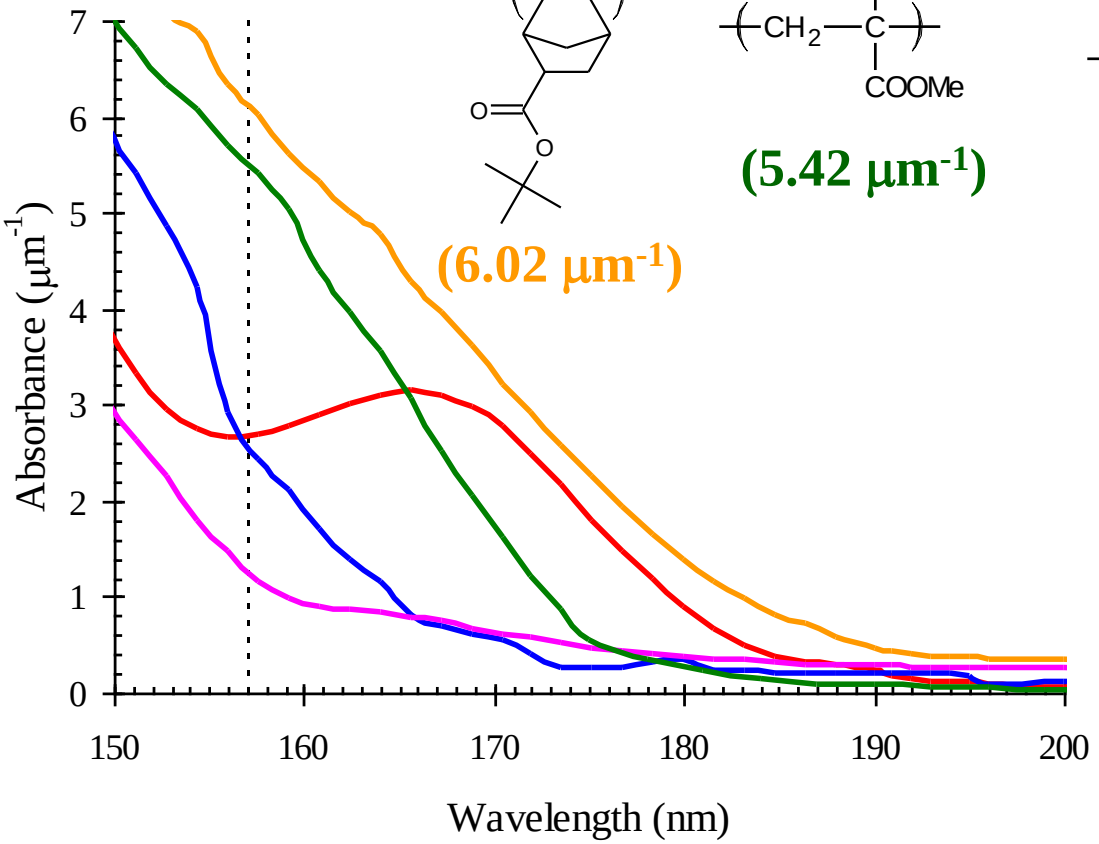
$A_{157} = 2.57\ \mu m^{-1}$

$A_{157} = 1.15\ \mu m^{-1}$

NBHFABOC and NBHFA are surprisingly transparent

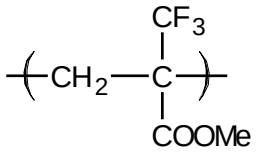
T. Chiba, et. al., J. Photopolym. Sci. Technol **,** *13 (2000) 657-664*

Absorbance of Fluorinated Polymers

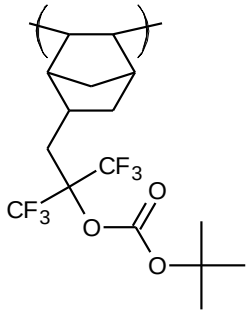


(6.02 μm-1)

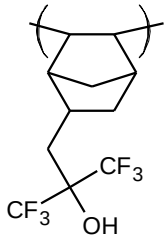
(5.42 μm-1)



(2.68 μm-1)



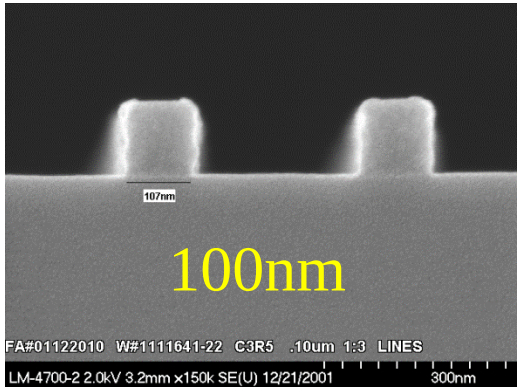
(2.44 μm-1)

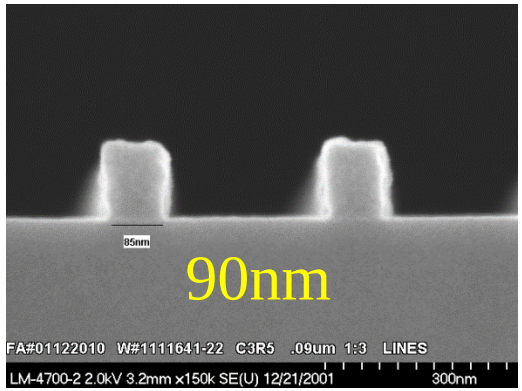


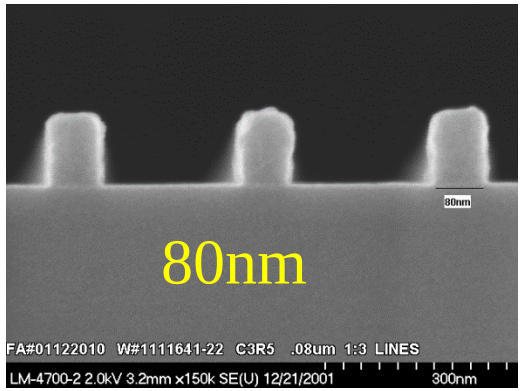
(1.15 μm-1)

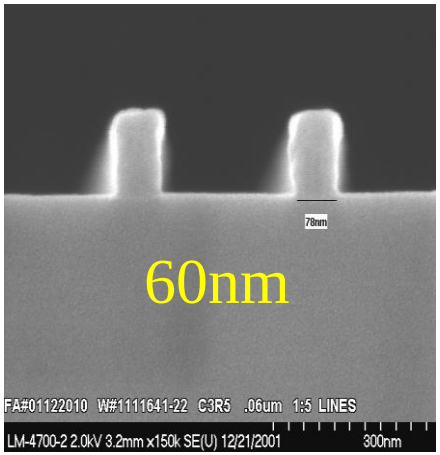
Hexafluoroisopropyl and α-trifluoromethylcarboxylic acid are groups surprisingly transparent!

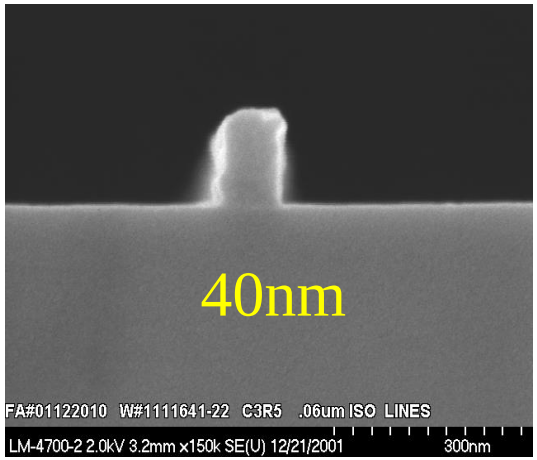
Some Imaging Results



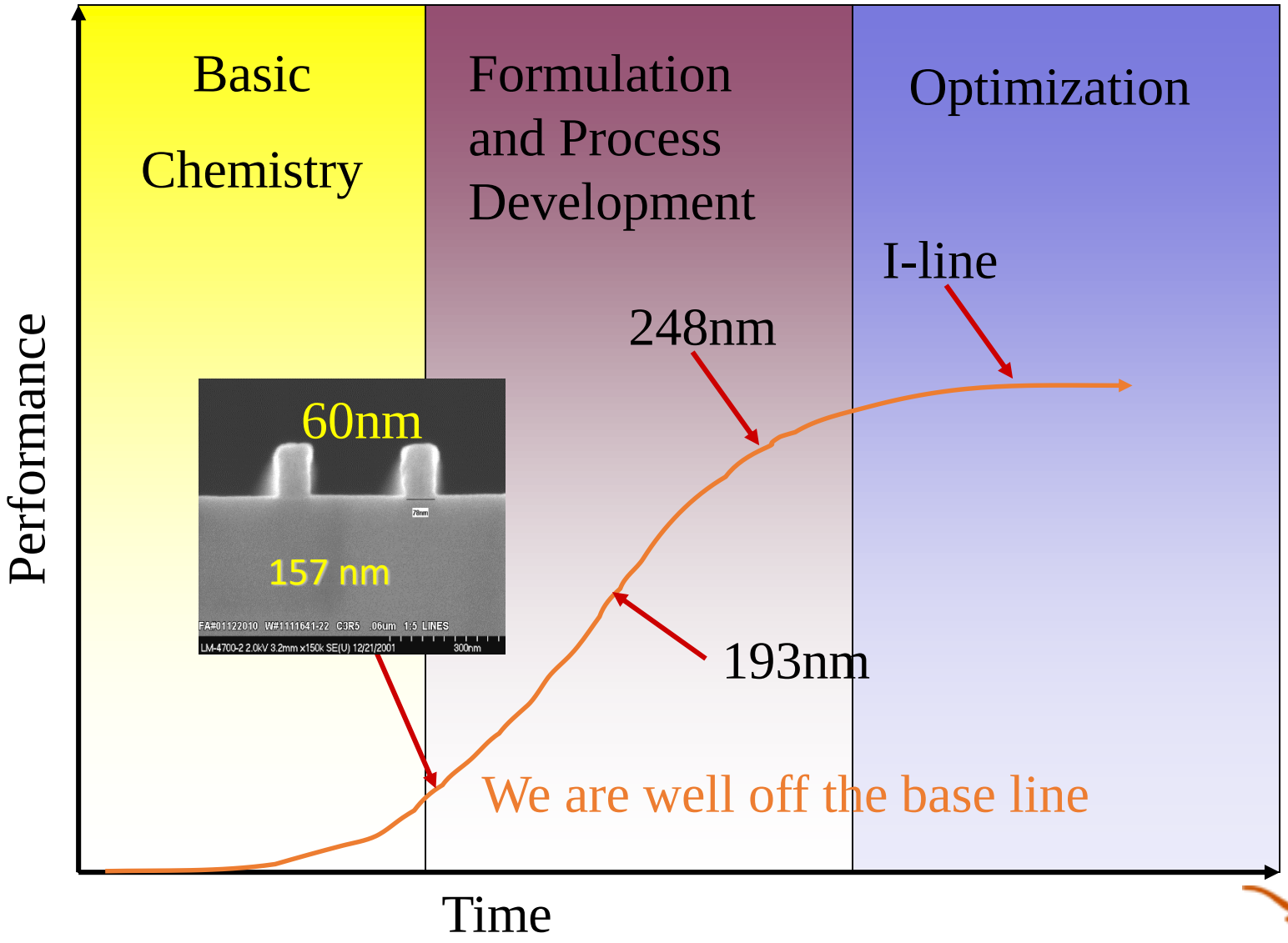








Resist and Process Development



Images in UT 157nm Resists