Molecular Resists for Next Generation Lithography: A Rich Diversity of Possibilities

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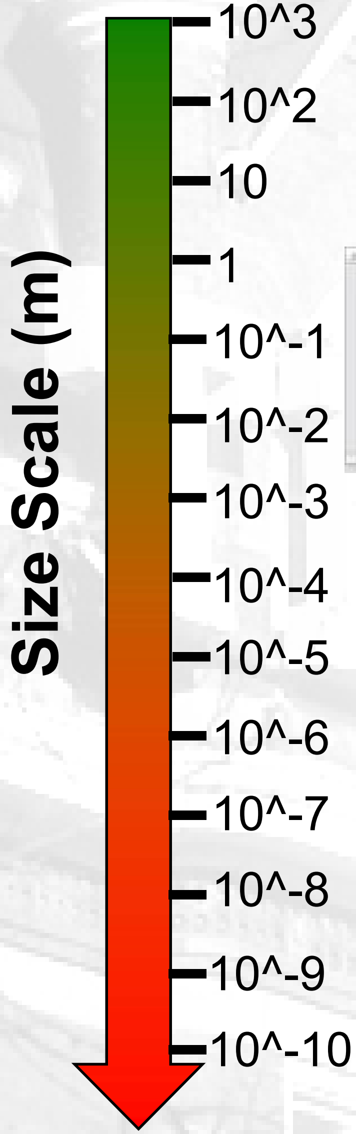
Materials Patterning:
A Diverse Challenge & Enabling Technology



Casting
Extrusion

Mechanical
Fastening

Molding

Welding

Milling

Adhesives

Micromachining

Co-deposition

Self-Assembly

Nanolithography

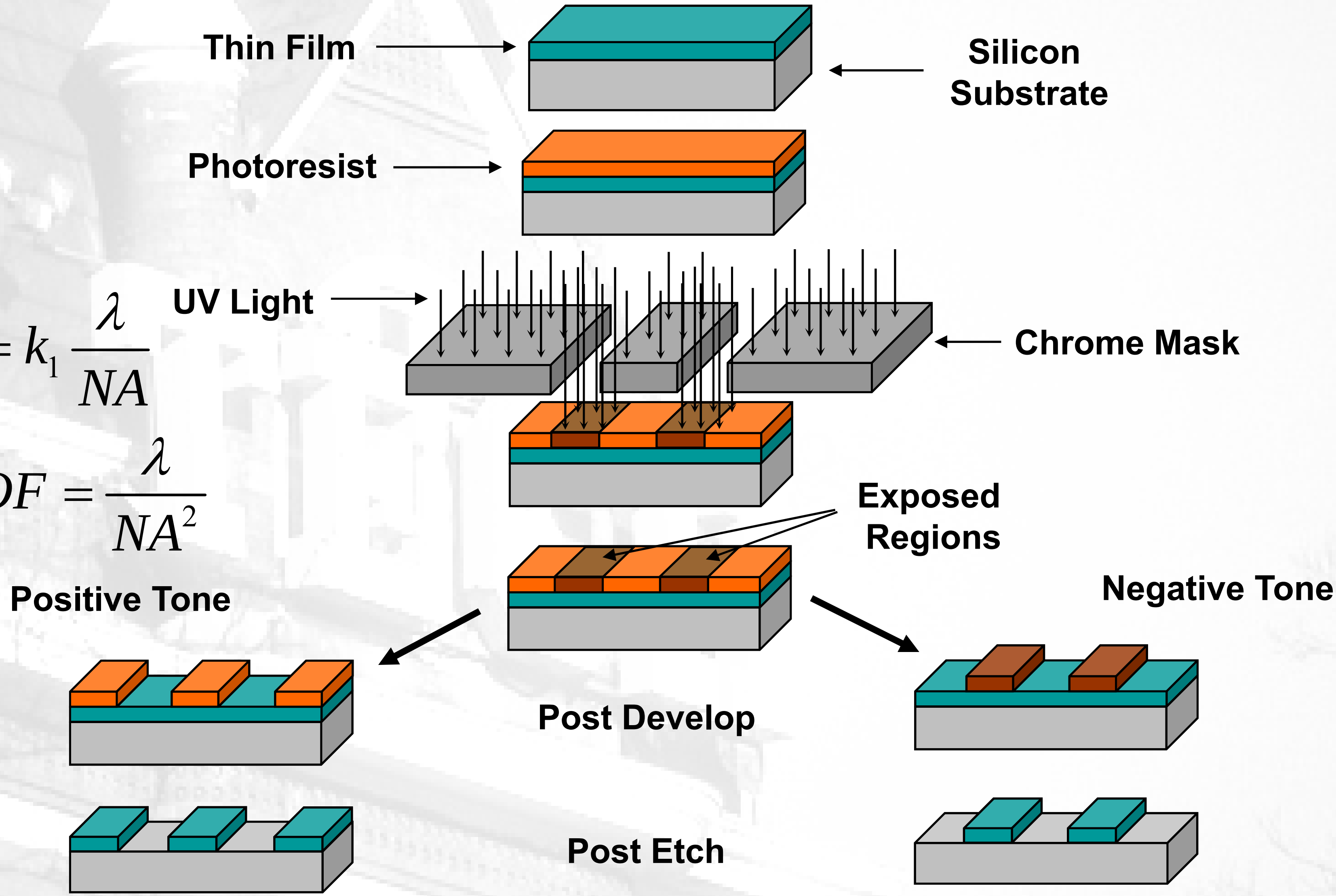
Bonding

Synthetic
Chemistry

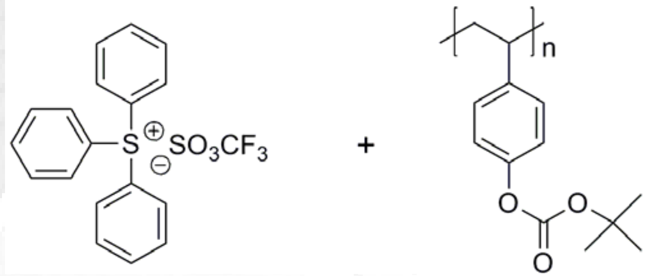
Photolithography: High Volume Champ

$$R = k_1 \frac{\lambda}{NA}$$

$$DOF = \frac{\lambda}{NA^2}$$

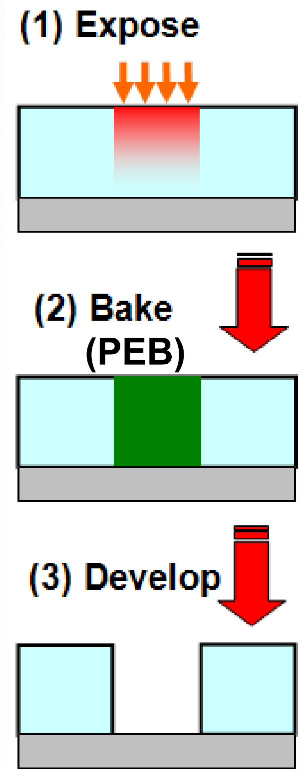


Chemically Amplified Resists (CARs): The Modern Workhorse Material

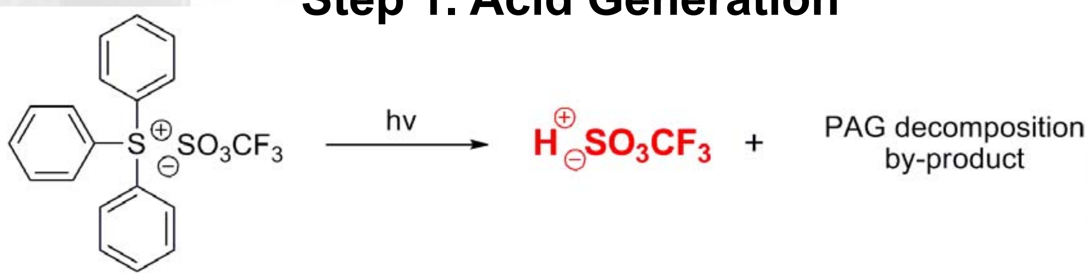


Photoacid generator (PAG), < 5 wt%

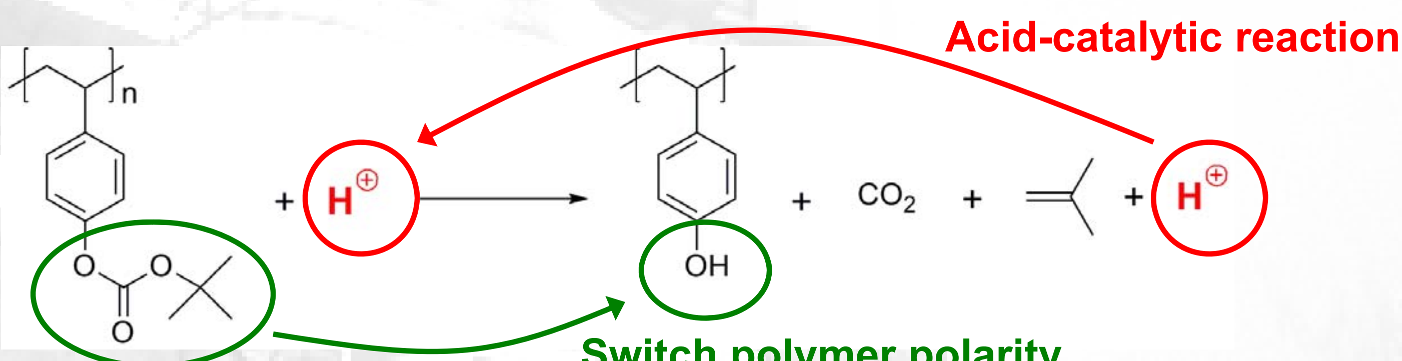
polymer resin, > 95 wt%



Step 1. Acid Generation



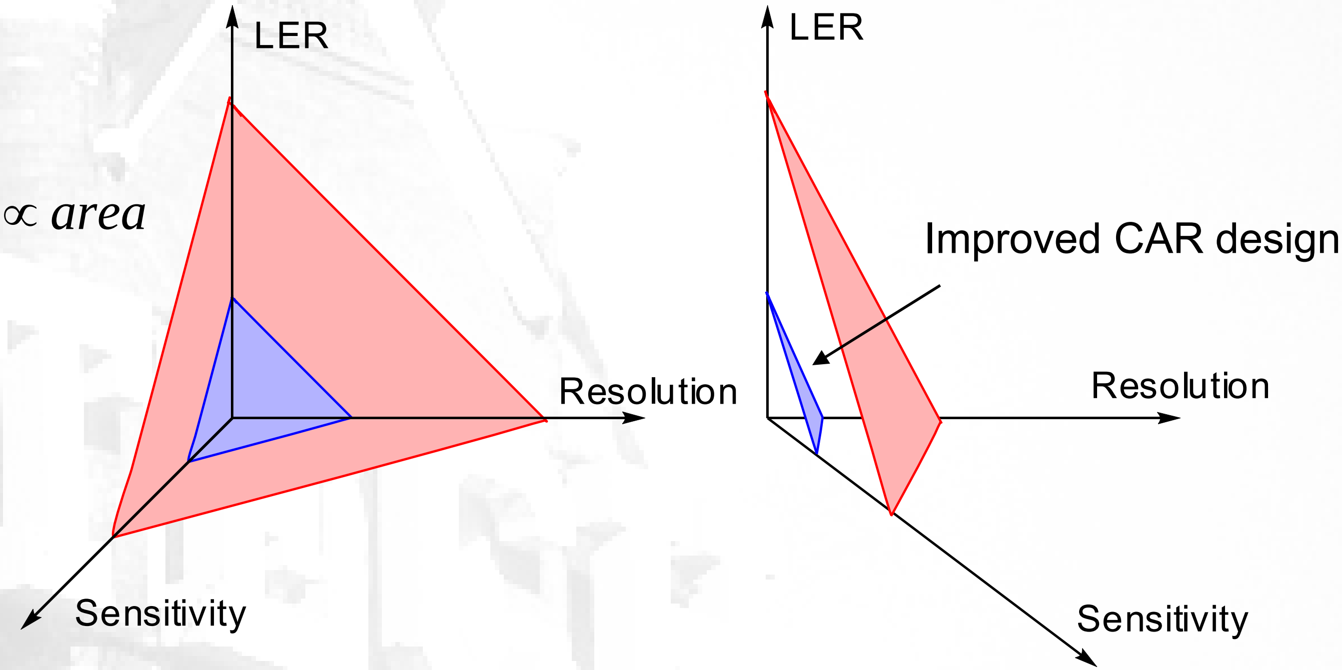
Step 2. Acid-Catalytic Deprotection



RLS Tradeoff

$$\text{Resolution}^3 \times \text{LER}^2 \times \text{Sensitivity} \approx \textit{constant}$$

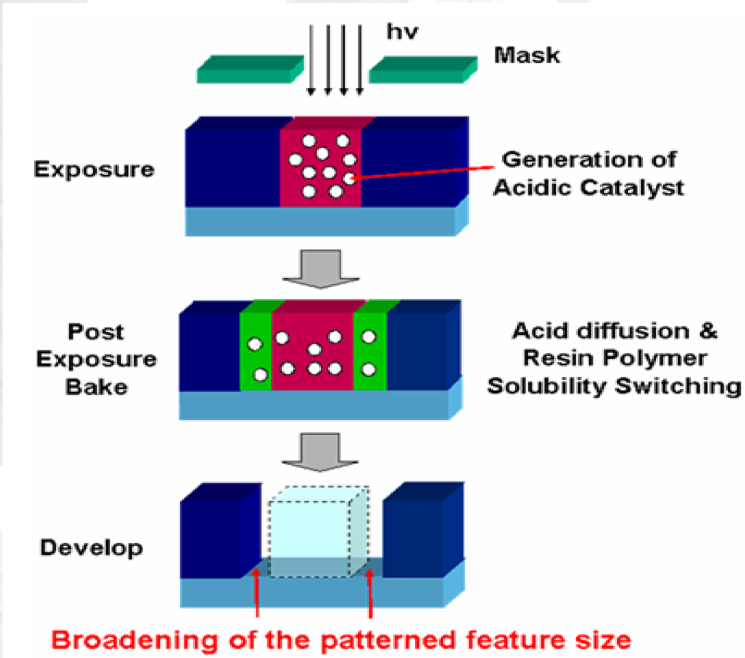
$$\textit{constant} \propto \textit{area}$$



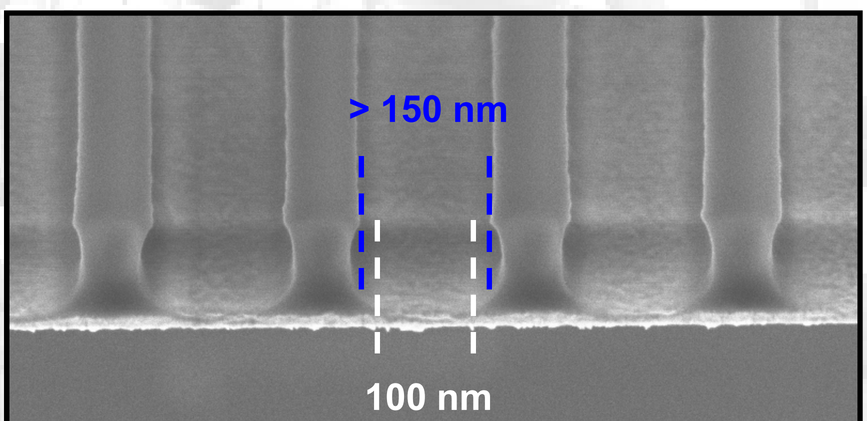
- There exists a now well known trade-off in resolution, LER, and sensitivity for chemically amplified resist materials
- RLS limitation is intrinsic to CARs → must reduce *constant*
- Modern CAR design at minimal *constant* - performance still does not meet the requirements.

Challenges with Chemical Amplification

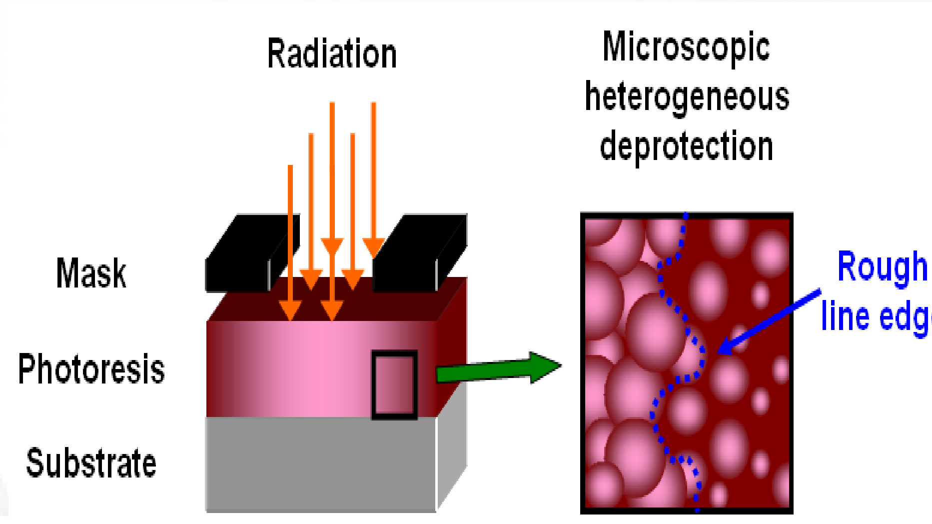
Image Blur



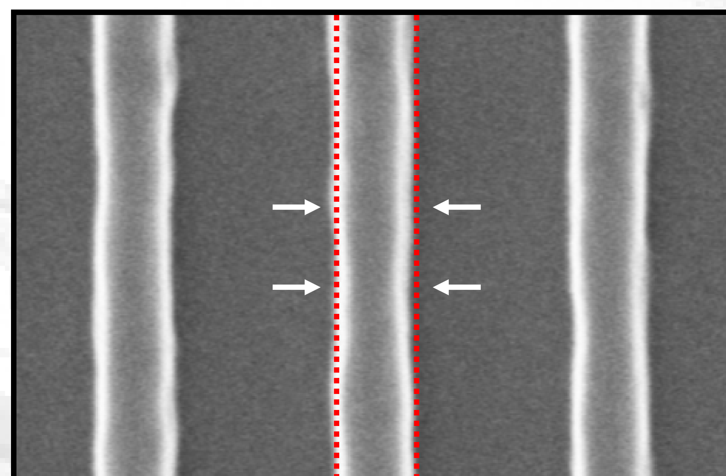
Traditional CAR photoacid diffusivity: > 10 nm



Line Edge Roughness (LER)

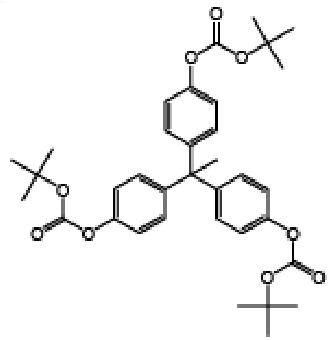


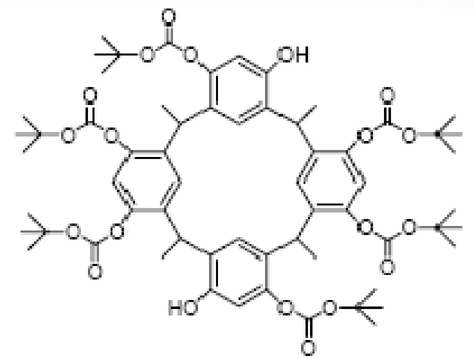
Traditional CAR 3σLER: > 5 nm



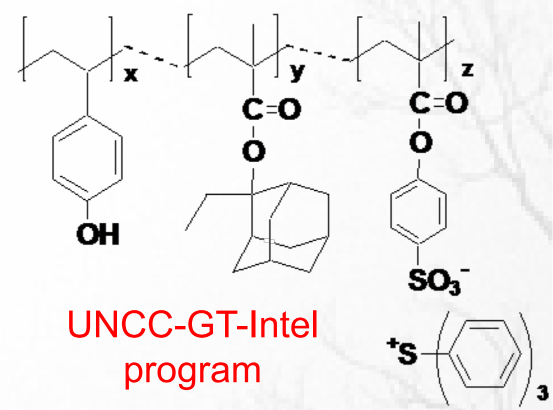
Material Designs to Solve RLS

- **Base Quencher** – shown to reduce LER and improve resolution, but at cost of sensitivity
- **Molecular Resists** – reduce pixel size to improve LER





- **Polymer-bound PAGs**
  - reduce photoacid diffusion length to improve resolution
  - has shown LER improvements
  - sensitivity penalty reduced by increased PAG loading
  - several years into development – only recently began 22 nm patterning – LER still greater than desired

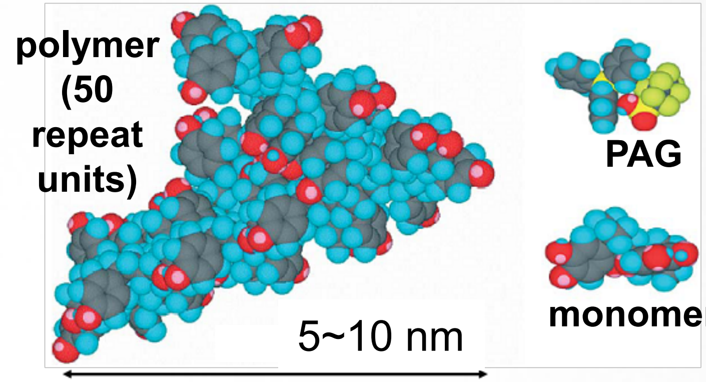


UNCC-GT-Intel program

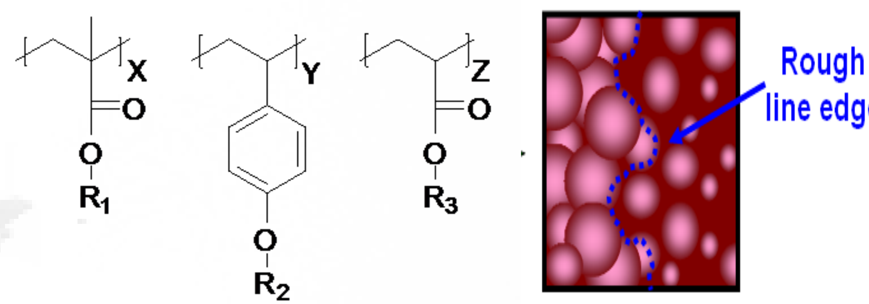
The Road to Molecular Resists

Advantages vs. Polymers

1. Reduced pixel size
2. Synthetic control
   - monodisperse
   - stereo- and regio-chemical control
3. Development
   - no microscopic heterogeneous deprotection
   - reduced swelling
   - high molecular chemical contrast

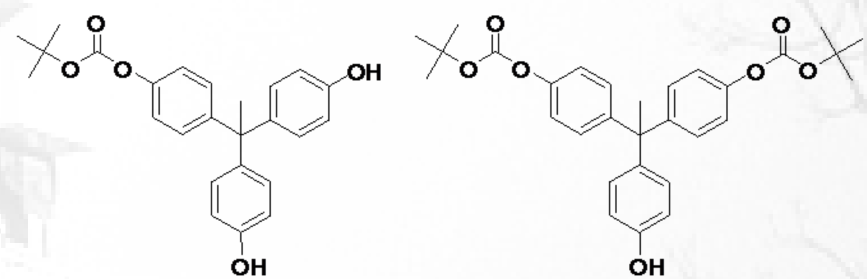


Da Yang, et. al., J. Materials Chemistry 2006



Current Molecular Resists

- Based on blending PAG and base into molecular glass matrix
- 50 nm resolution or better
- LER (3σ) of 6 nm or less



completely soluble   completely insoluble

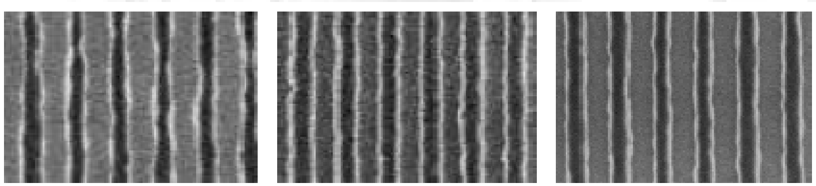
Molecular Resists: An Unfulfilled Promise?

- Most all blended molecular resists have LER (3σ) of 5 nm or more
- Inhomogenities have significant effect on LER
- Inhomogenities due to physically blended additives, polydisperse molecular weights – e.g. varying levels of protecting group
- Resolution in molecular resists also limited to due to diffusion of typically small blended acids

- Some Possible Solutions:

Single Molecule Resists

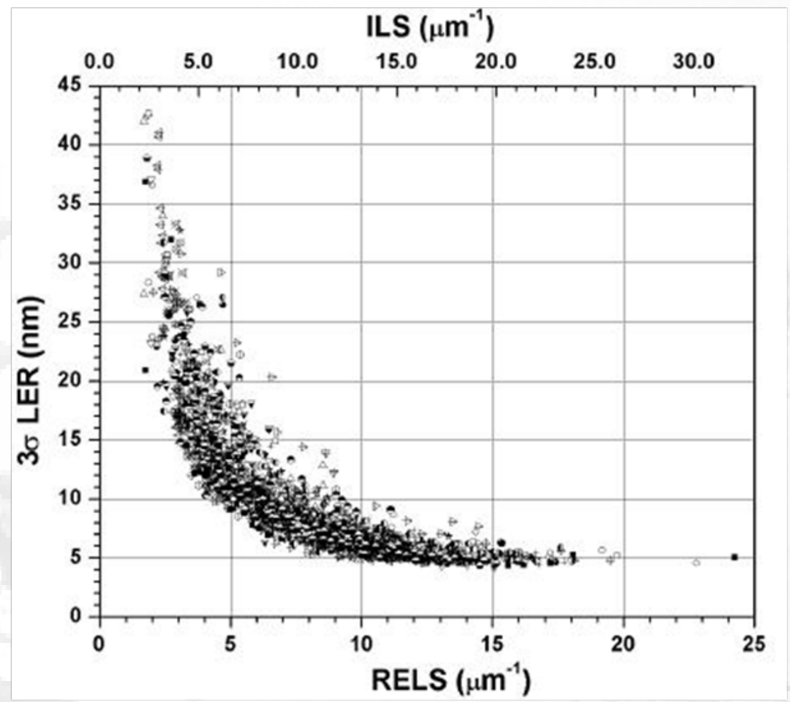
Negative Tone MRs



Increasing homogeneity

Decreasing LER

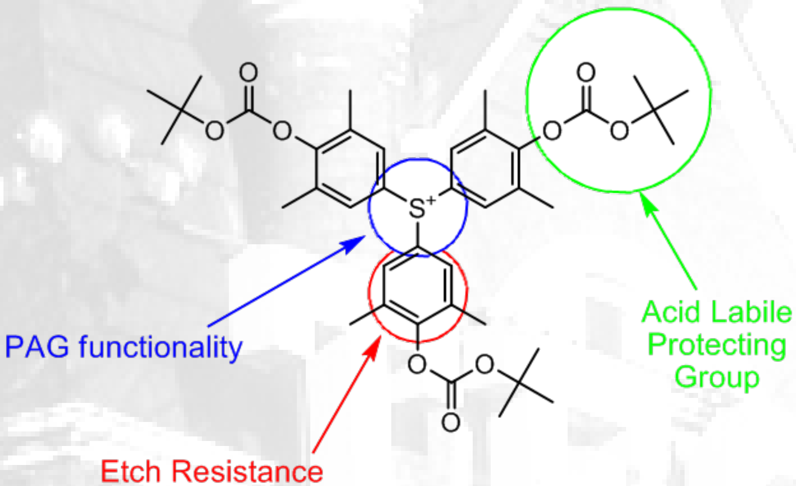
Shiono, et al. SPIE 6519, 65193U, (2007)

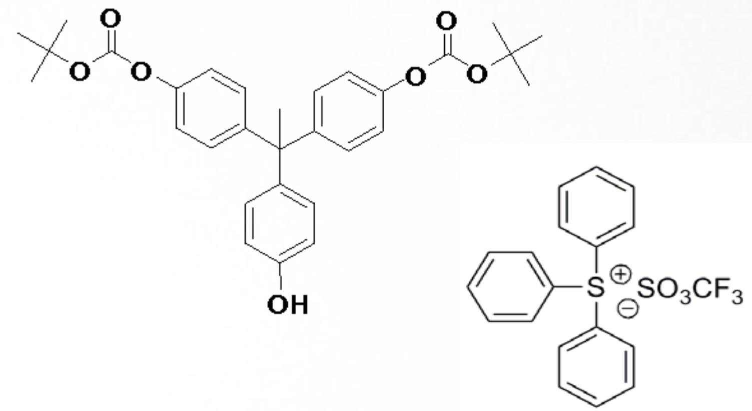


Pawloski, et al. SPIE 5376, 414, (2004)

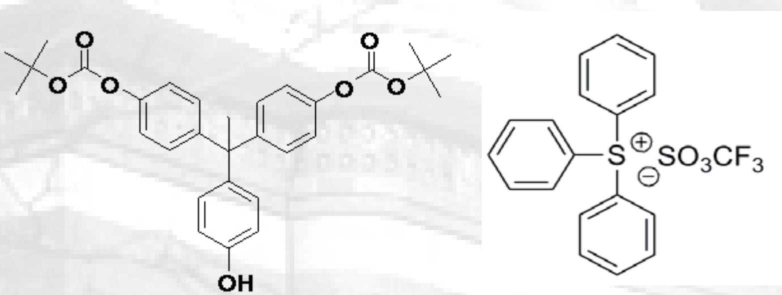
Opportunities with Molecular Resists

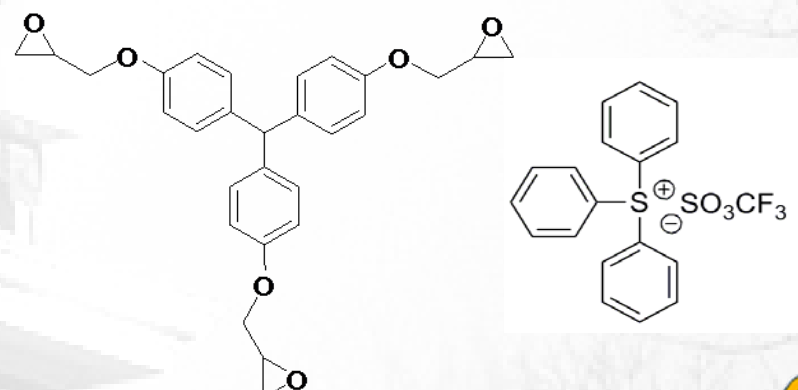
- **Single Component** **vs.** **Multi-Component**





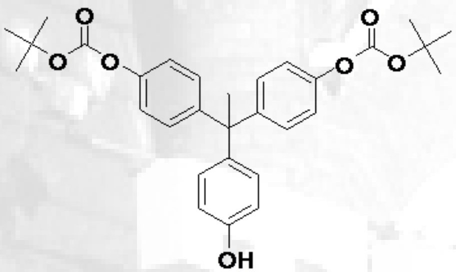
- **Positive Tone** **vs.** **Negative Tone**

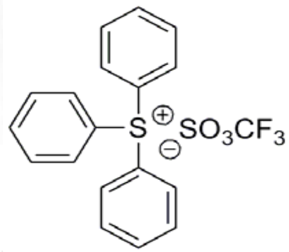


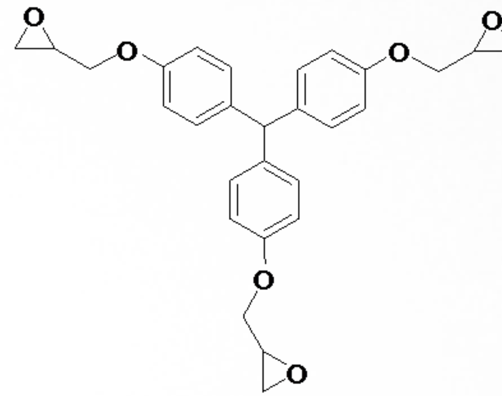


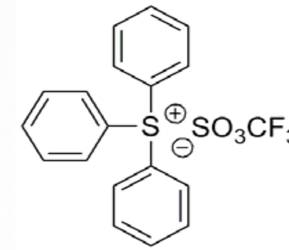
Opportunities with Molecular Resists

- **Aqueous Development** vs. **Solvent Development**

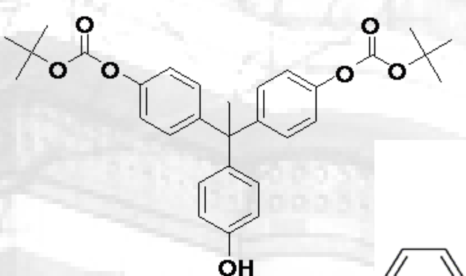


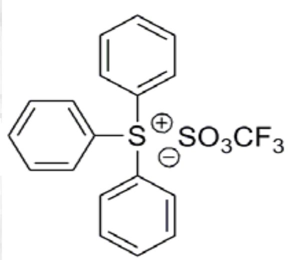


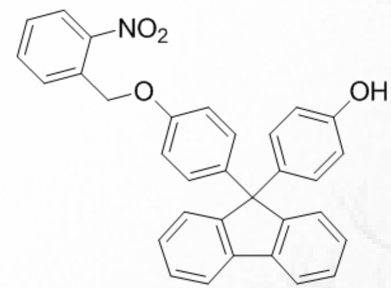




- **Chemically Amplified** vs. **Non-Amplified (Inhibited)**

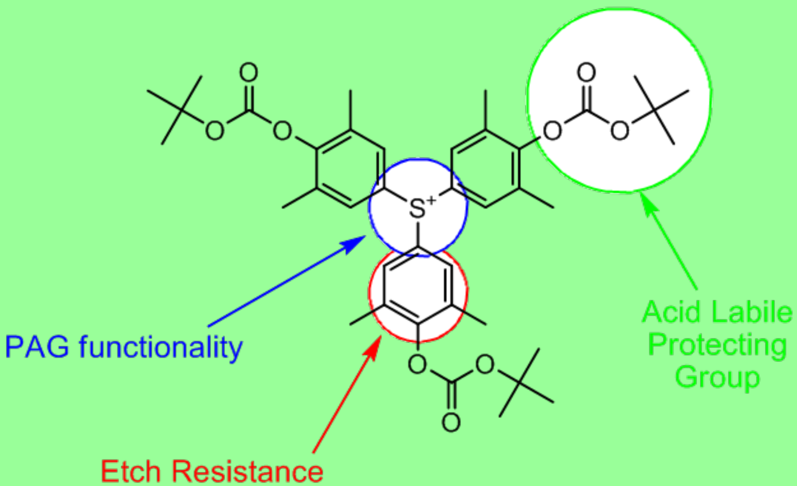


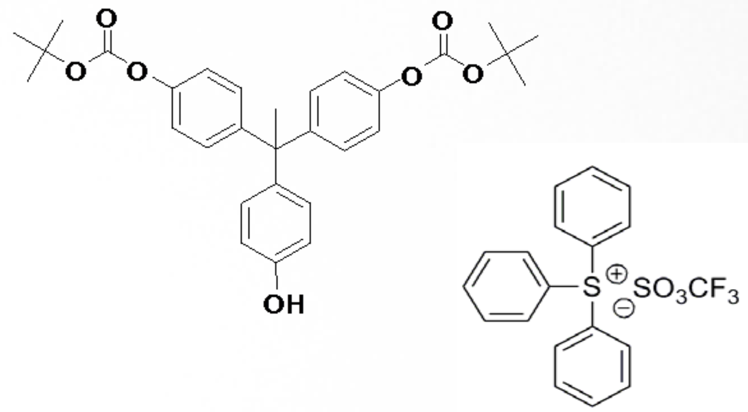




Opportunities with Molecular Resists

- **Single Component** **vs.** **Multi-Component**





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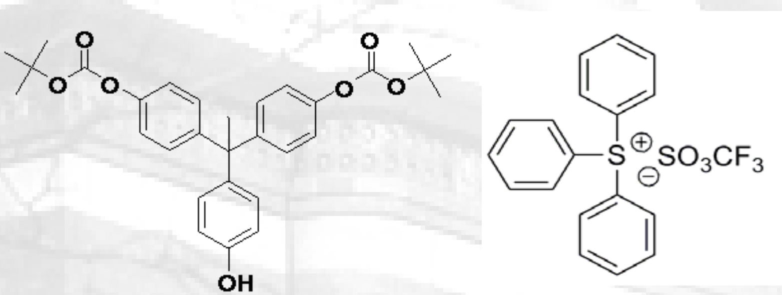
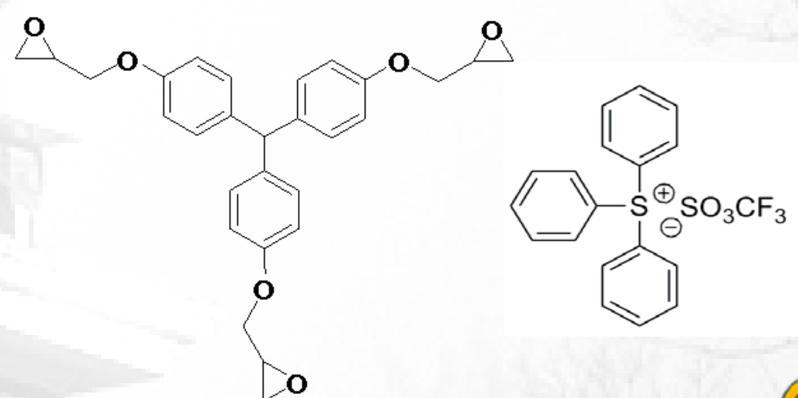
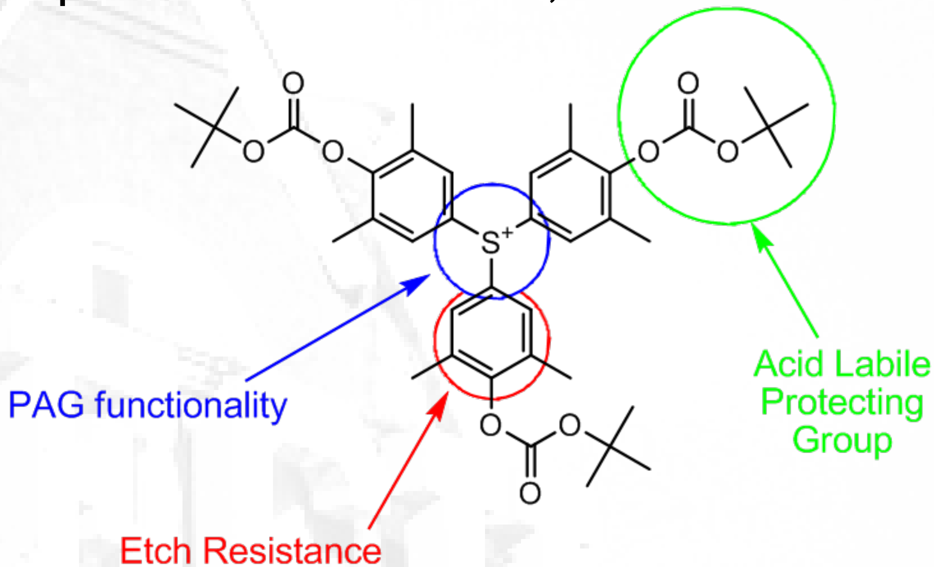




Single Molecule CARs

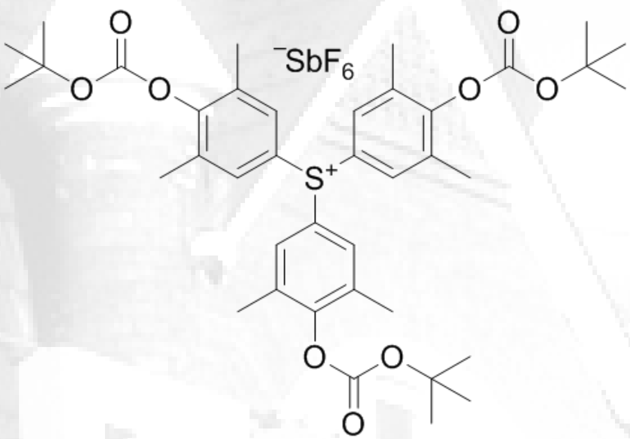
- A molecular resist that contains PAG functionality and acid labile protecting groups on a base soluble, etch resistant molecular glass core.

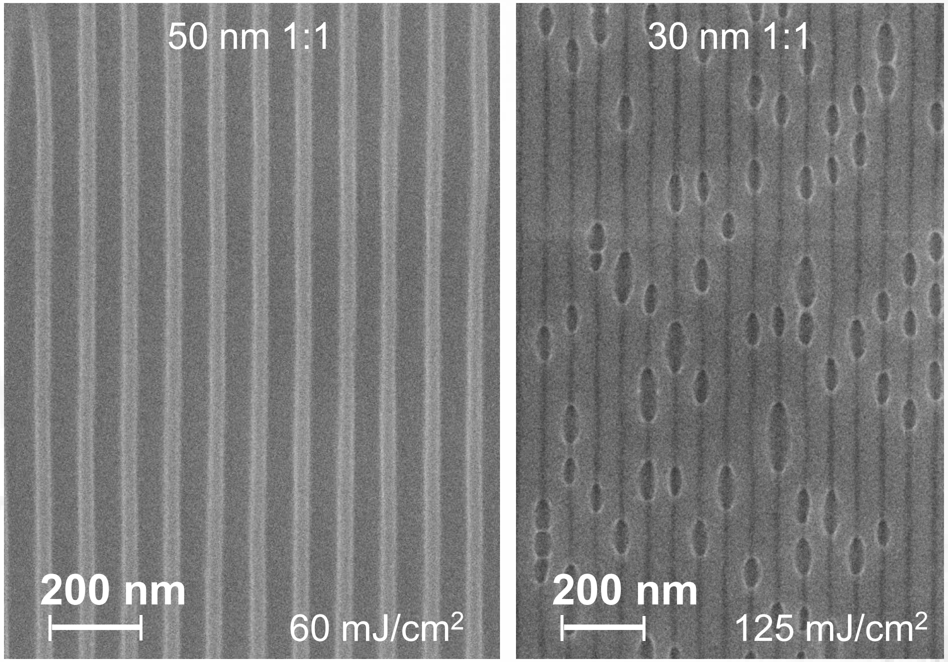


Advantages:

1. Molecularly homogeneous resist film
2. Highest PAG loading possible with no PAG segregation
3. Binding photoacid to molecular glass allows control of acid diffusion
   - resolution and LER improved
   - loss of photospeed offset by high PAG loading.

TAS-tBoc-SbF_6 EUV Results

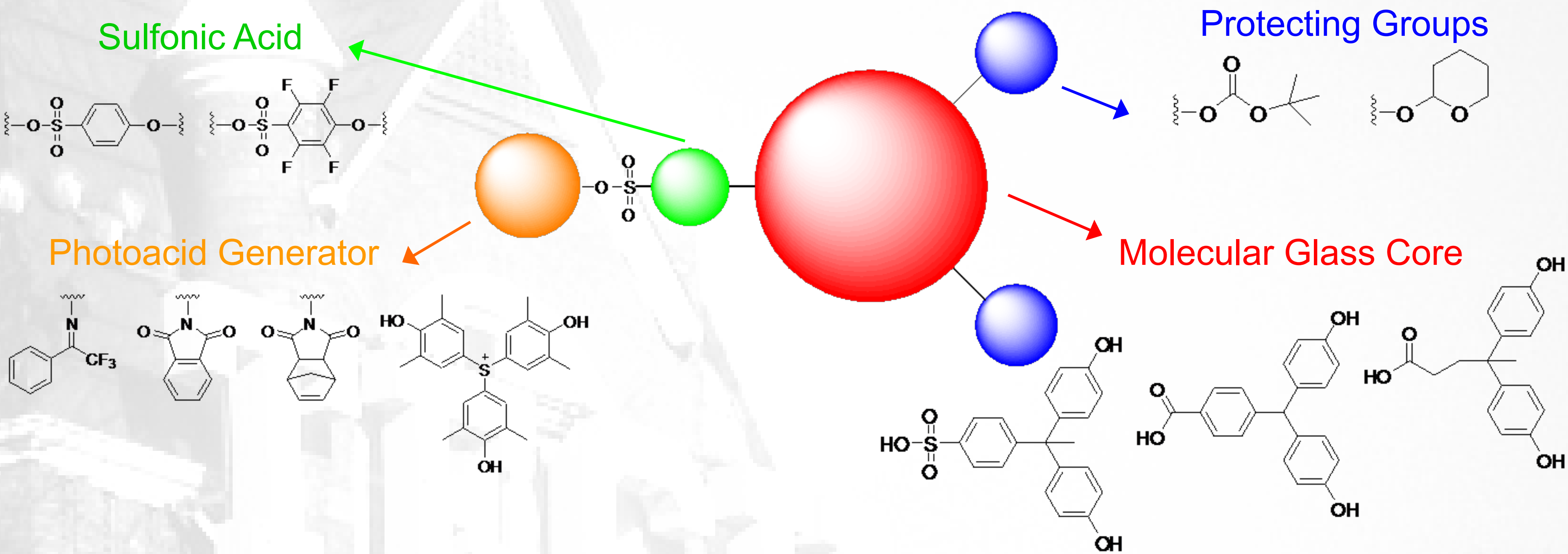




LER (3σ) = 4.9 nm

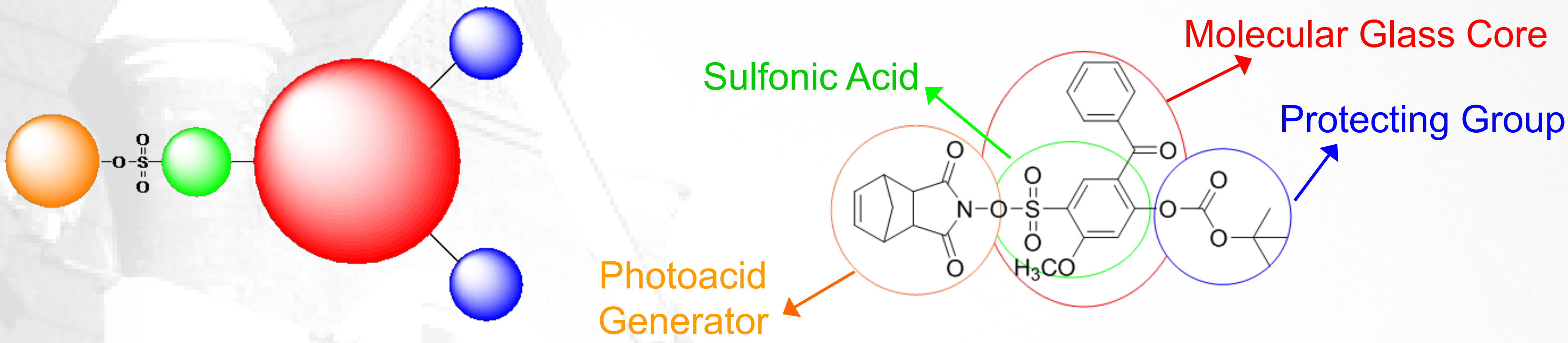
- EUV exposures done on PSI tool in Switzerland
- 50 nm 1:1 lines resolved with low LER of 4.9 nm
- 30 nm 1:1 lines open only att very high dose
- Failure not due to acid blur, but due to pattern collapse/diffusion limitations

Single Molecule Bound Sulfonic Acids

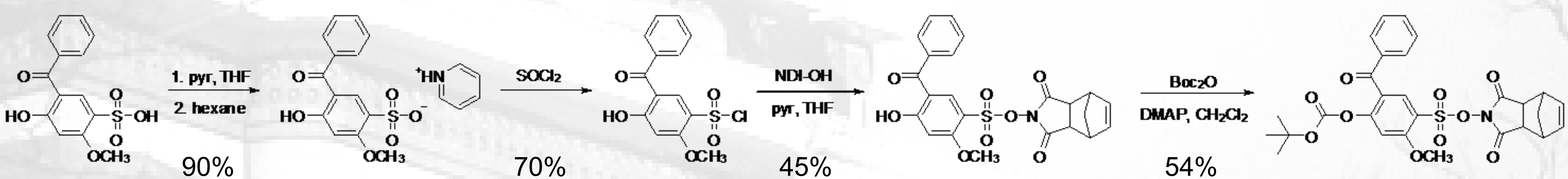


- Design covalently binds sulfonic acid moiety directly to larger molecular glass core to control photoacid diffusion - improving both resolution and LER
- Next generation evolution of molecular resists and polymer-bound PAG resists
- Resist design space greatly increased compared to TAS allowing for systematic variation of each component
- Multi-functional cores allow selective attachment of acid and PAG, maintaining high homogeneity in a complex molecule
- Acid can be selectively attached to core or designed directly on the core
- Non-ionic PAGs now available to improve solubility issues with TAS

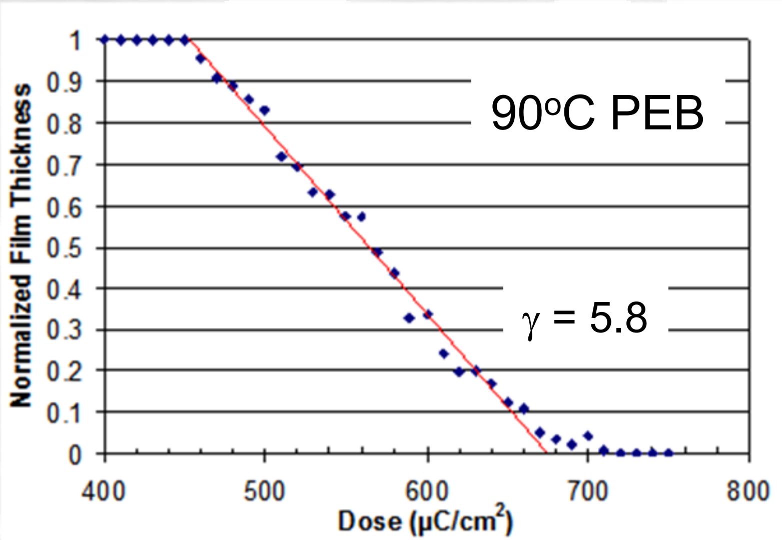
NBB : NDI-BHMOBS-Boc



- NBB first example of non-ionic bound sulfonic acid molecule resist
- Sulfonic acid is directly part of molecular glass core
- Norbornene dicarboximide PAG
- Superior solubility in casting solvent as compared to TAS compounds
- Has good adhesion and forms excellent films
- Zero dark loss over 30 sec. development in 0.261N TMAH

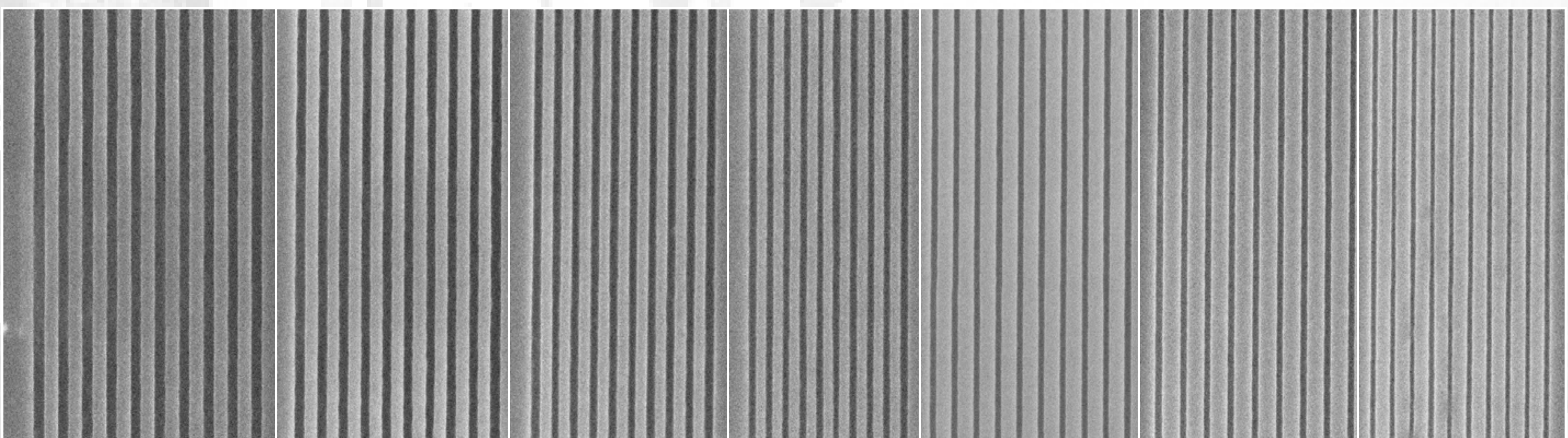


NDI-BHMOBS-tBoc E-beam Litho



- NDI-BHMOBS-tBoc shows poor sensitivity under 100 keV e-beam ~ 3x of TAS
- Excellent image quality and resolution, down to at least 40 nm 1:3 lines/space
- No appreciable acid blur, even at 90°C PEB, above Tg
- Excellent LER (3σ) = 4.8 nm
- Suffers from pattern collapse starting at 60 nm 1:1 lines (aspect ratio > 2) using current developer and rinse protocols

100 nm 1:1 90 nm 1:1 80 nm 1:1 70 nm 1:1 60 nm 1:2 50 nm 1:3 40 nm 1:3



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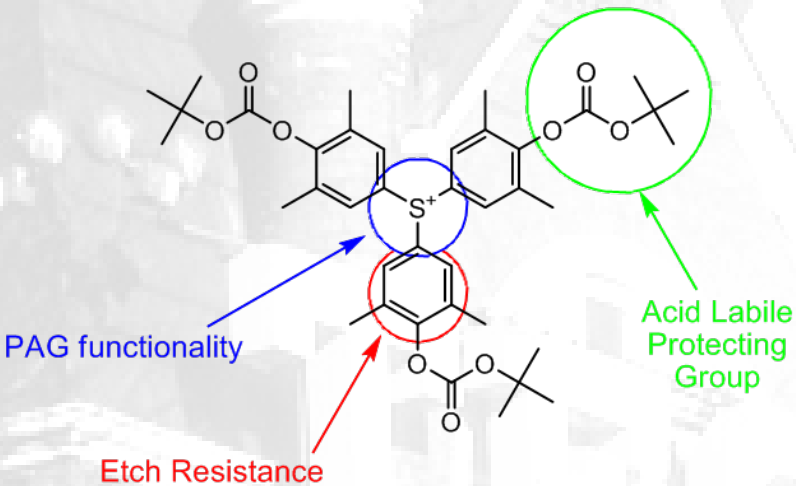
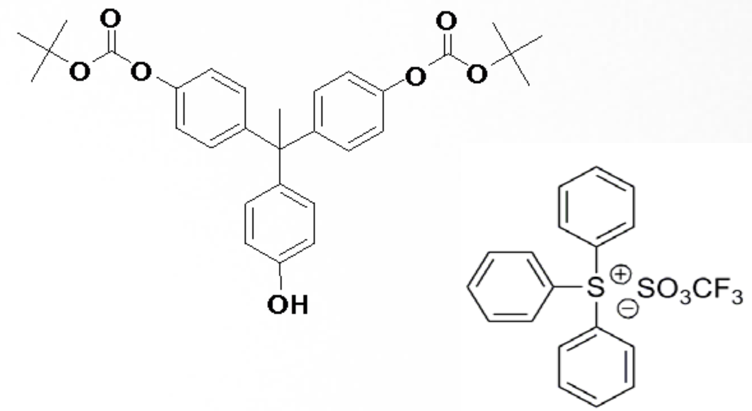
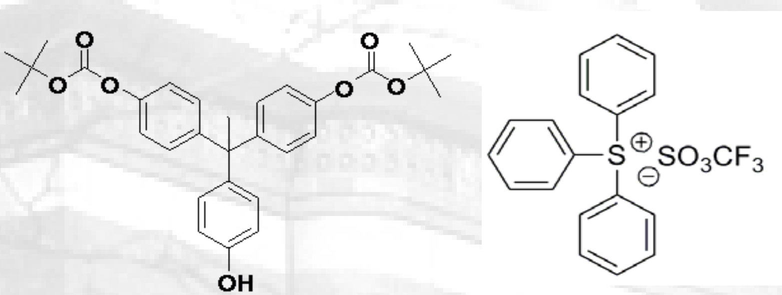
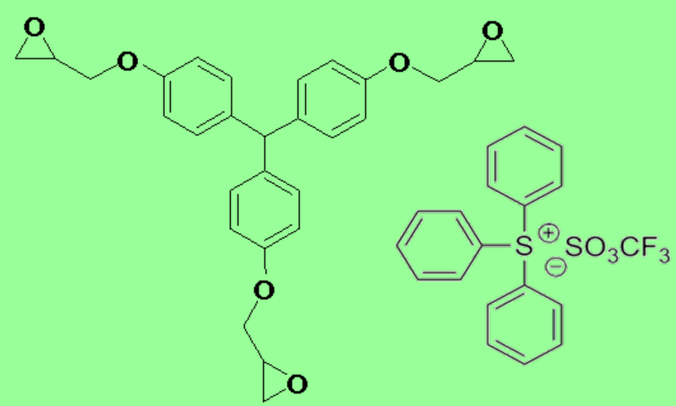


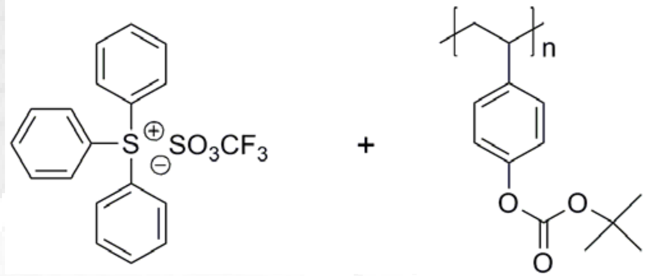


- **Positive Tone** **vs.** **Negative Tone**





Chemical Amplification & Acid Diffusion: A Necessary Curse?



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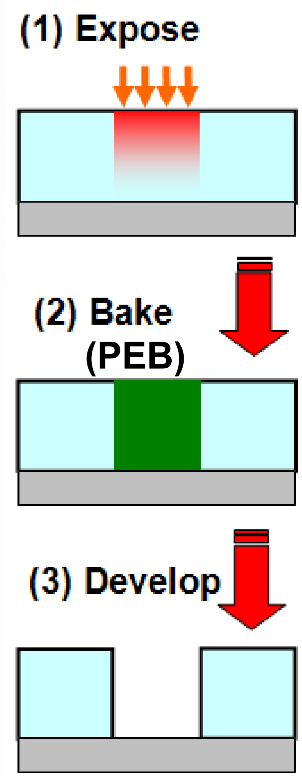
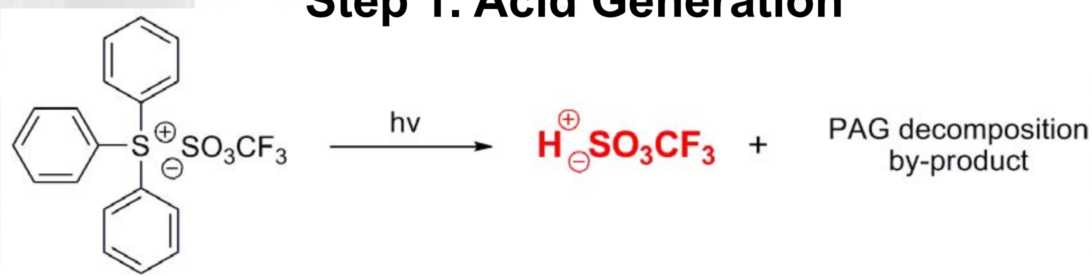


Step 1. Acid Generation



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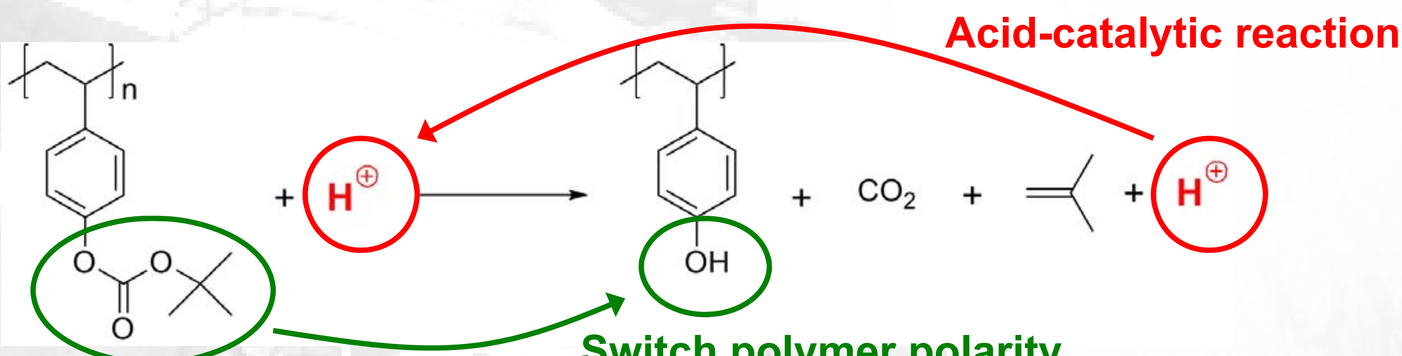
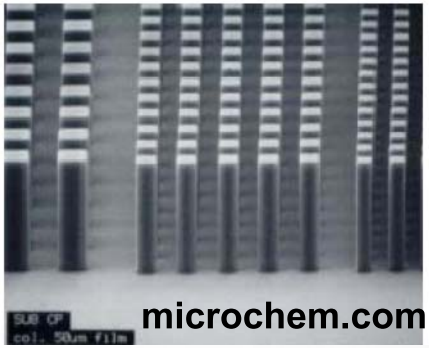
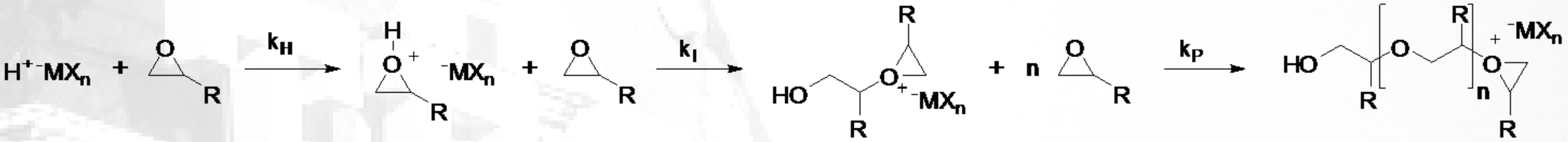


Advantages of Cationic Polymerization

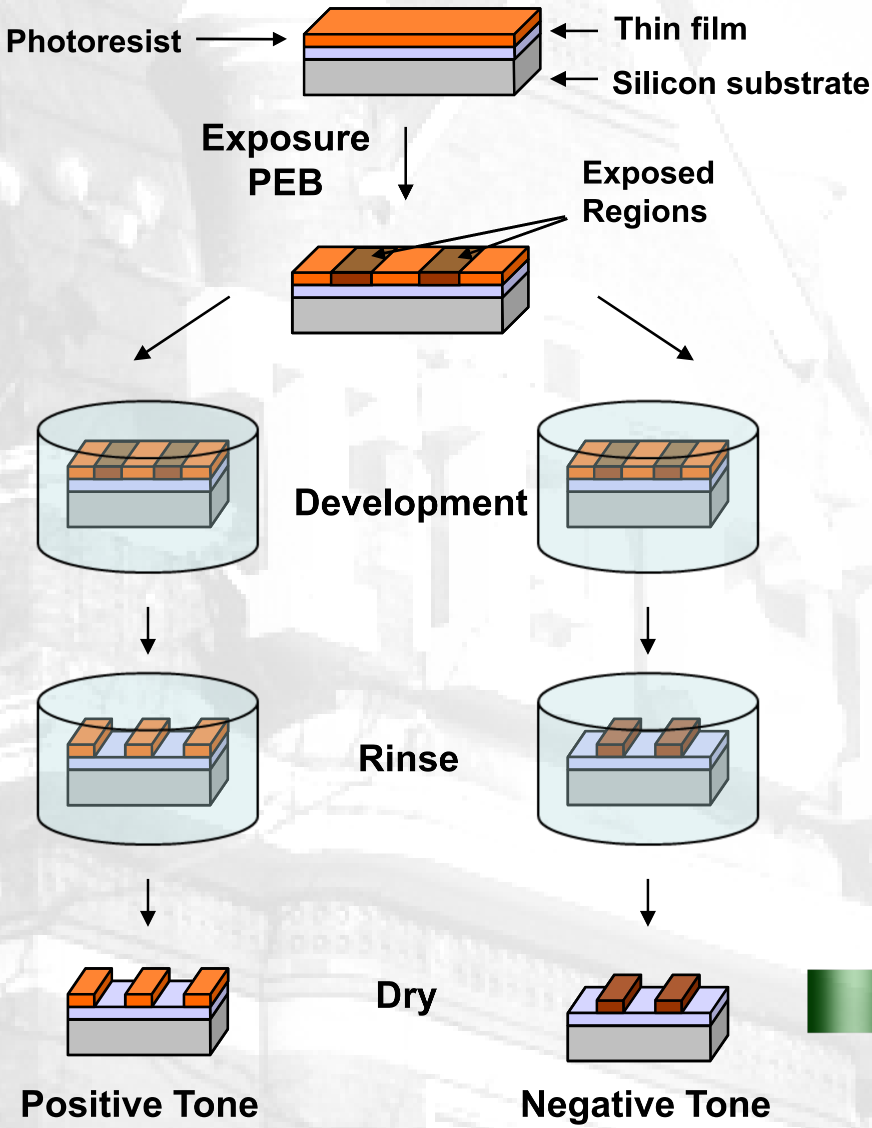


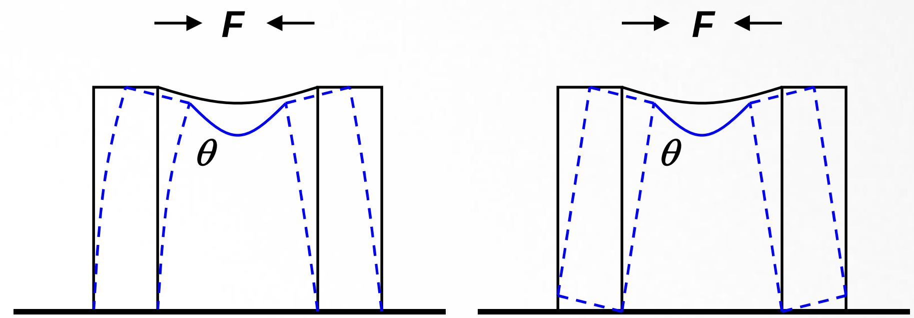
- Most high resolution CARs are based on photoacid catalyzed deprotection of protecting groups
- CARs based on cationic polymerization have been used for many years for micropatterning – SU-8

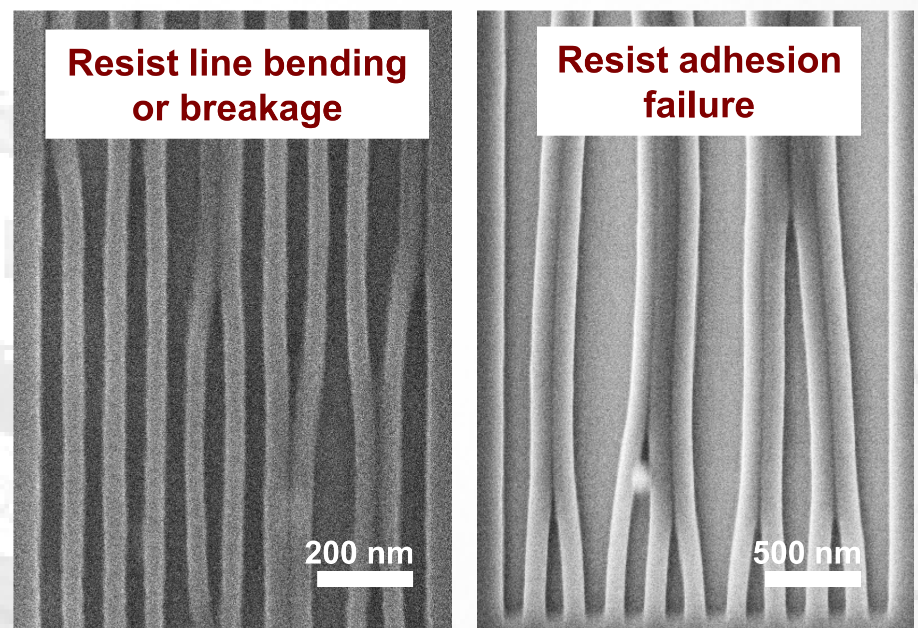


- Potential advantages of cationic polymerization CARs
  - superior mechanical strength – high MW cross-linked film
  - superior environmental stability – highly stable cationic chain propagation controls conversion
  - intrinsic diffusion control – active cation directly attached to exponentially growing chain/network
  - no outgassing – zero mass loss process

Still More Problems:
Resist Pattern Collapse







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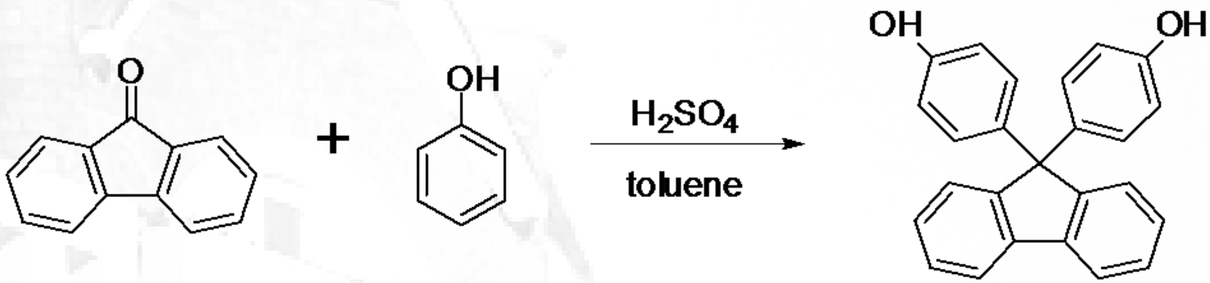
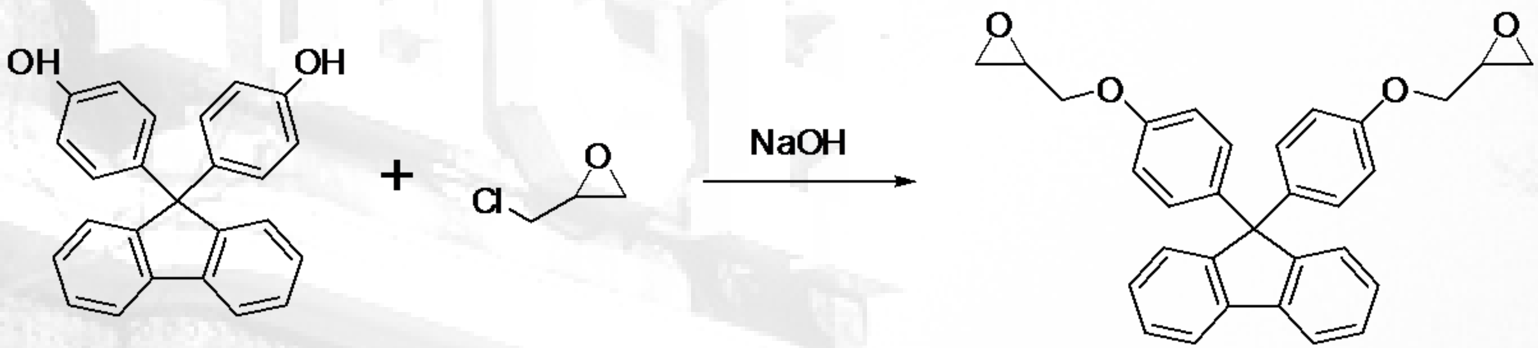
Synthesis of Resists

- Molecular resist core made by acid-catalyzed condensation of phenol with a ketone or aldehyde



- Core functionalized by reaction with epichlorohydrin in the presence of base



- Final product purified by recrystallization or column chromatography

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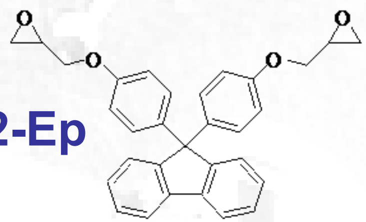
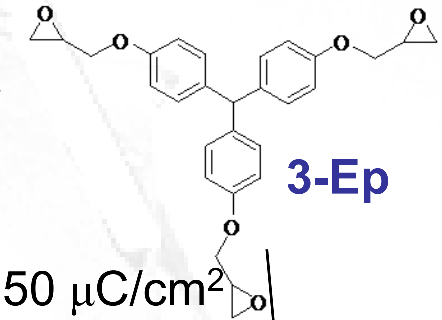
Comparison of Epoxide MR E-beam

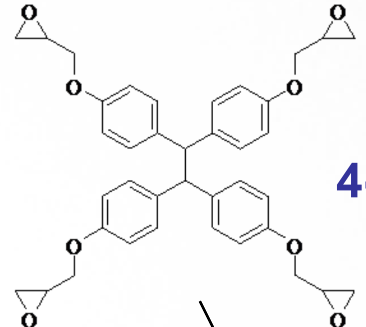
- Resolution increases as functionality decreases
- Maximum aspect ratio increases as functionality increases



2-Ep

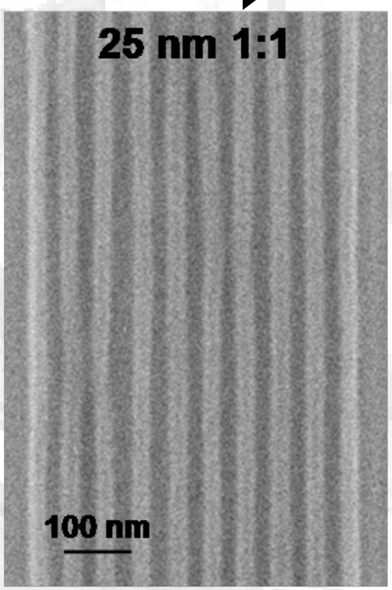


3-Ep

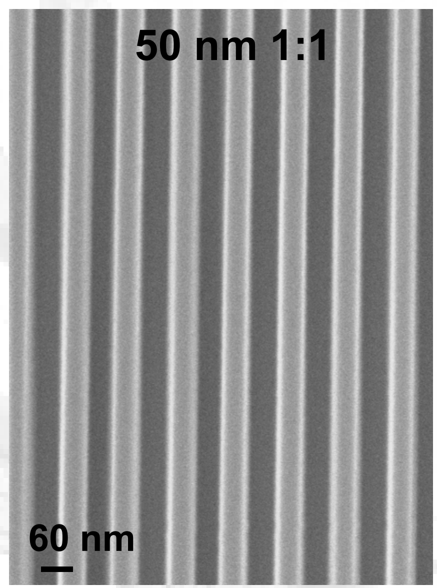


4-Ep

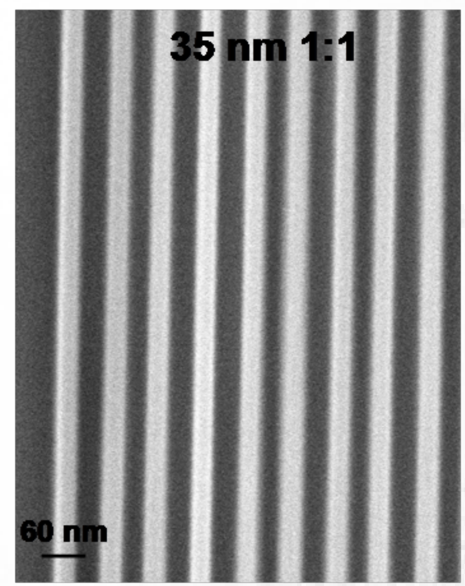
75 μC/cm^2 (100keV)
t = 50 nm
LER = 2.8 nm



50 μC/cm^2
t = 110 nm
LER = 2.3 nm

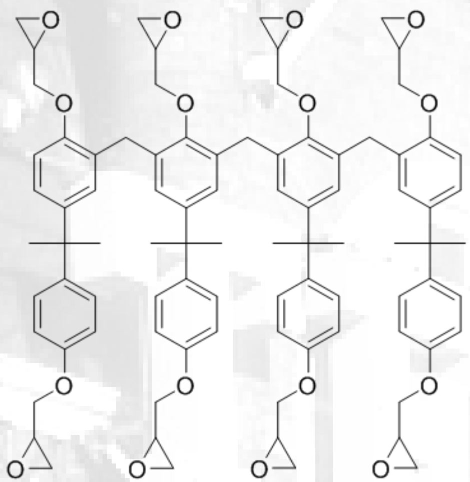


50 μC/cm^2
t = 70 nm
LER = 2.3 nm

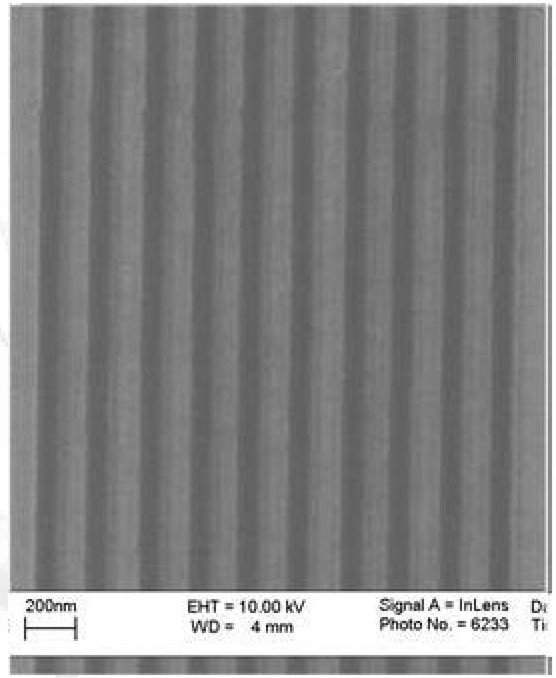


SU-8 E-beam Litho

SU-8



100 nm 1:1

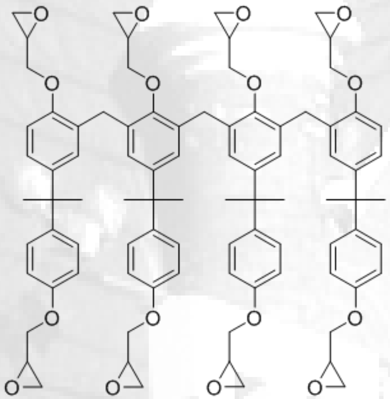


70 nm 1:1

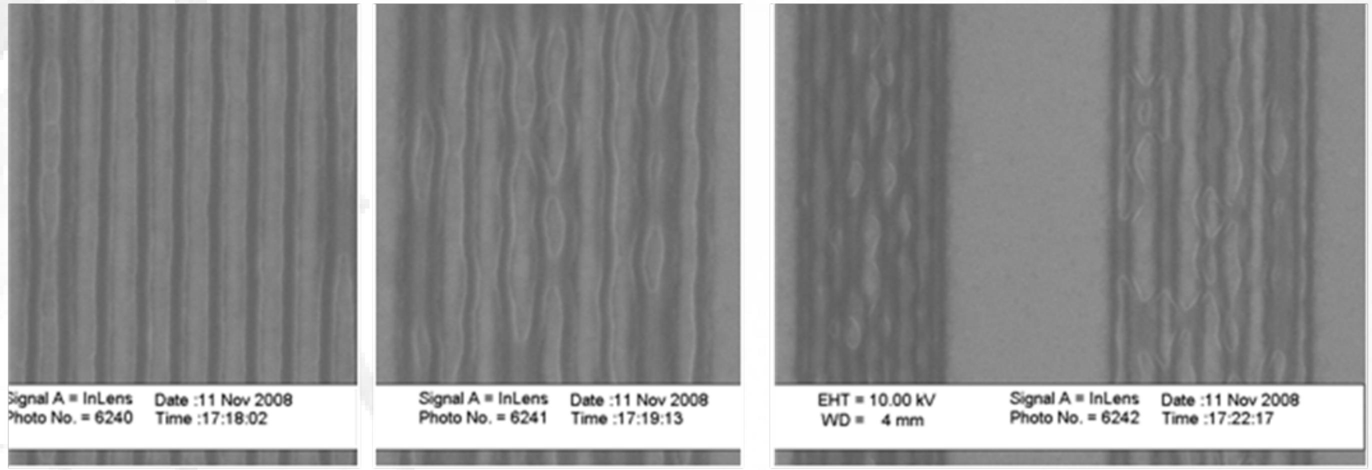
- SU-8 is a well-known CA epoxide resist
- SU-8 shown in literature to produce isolated lines down to sub-30 nm
- SU-8 2000 used after dilution in PGMEA to form thin films, 60 C PEB
- 70 nm 1:1 begins to show bridging and line “wobble”

SU-8 vs. Epoxide Molecular Resist

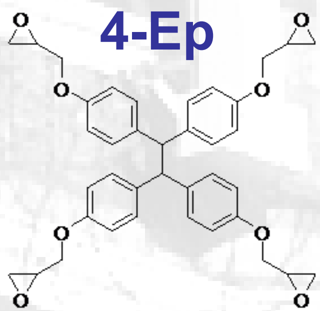
SU-8

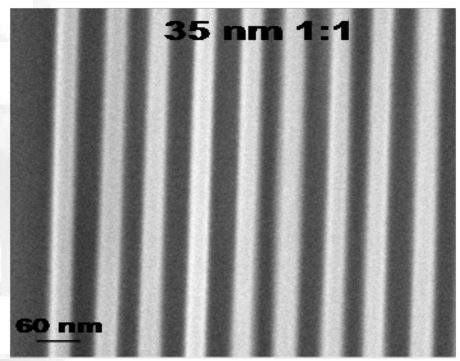


55 nm 1:2 | 50 nm 1:2 | 35 nm 1:2 | 35nm 1:3



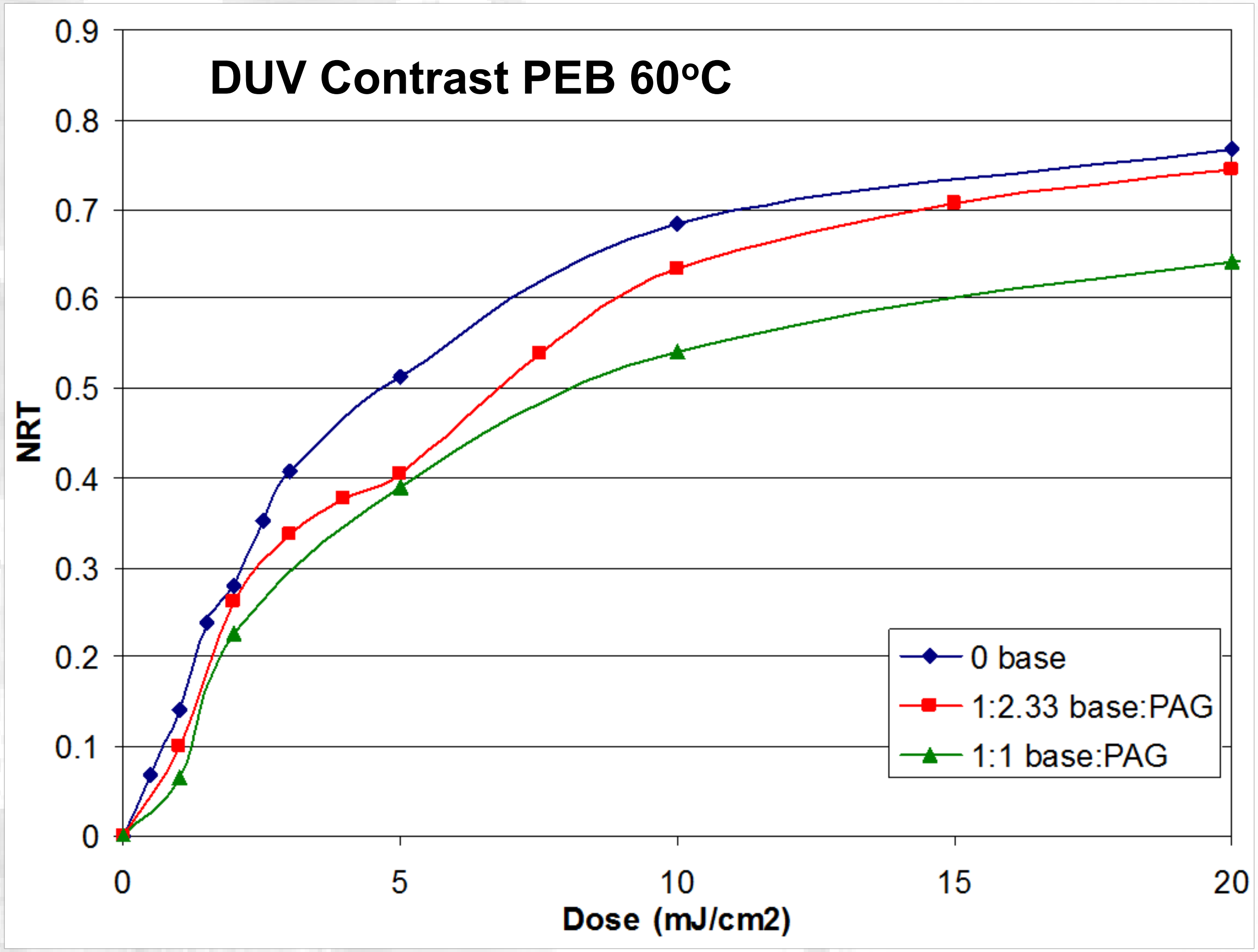
4-Ep



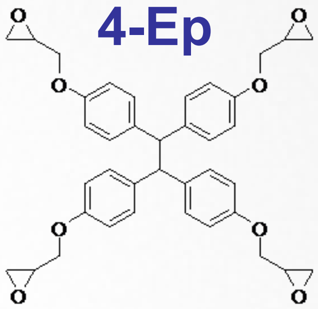


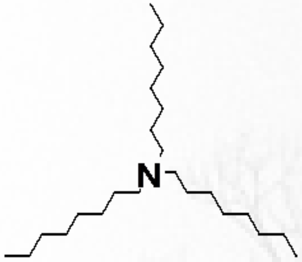
- SU-8 shows inferior resolution and LER to 4-Ep
- Swelling appears to be main failure for SU-8
- Differences likely due to extent of cross-linking in molecular resist 4-Ep compared to oligomeric SU-8

Further Improvements: Quenchers?



4-Ep

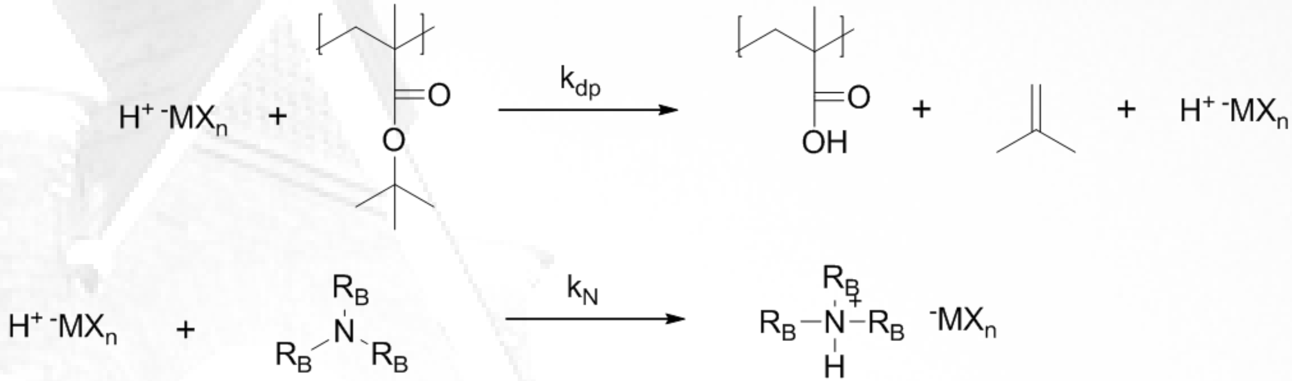




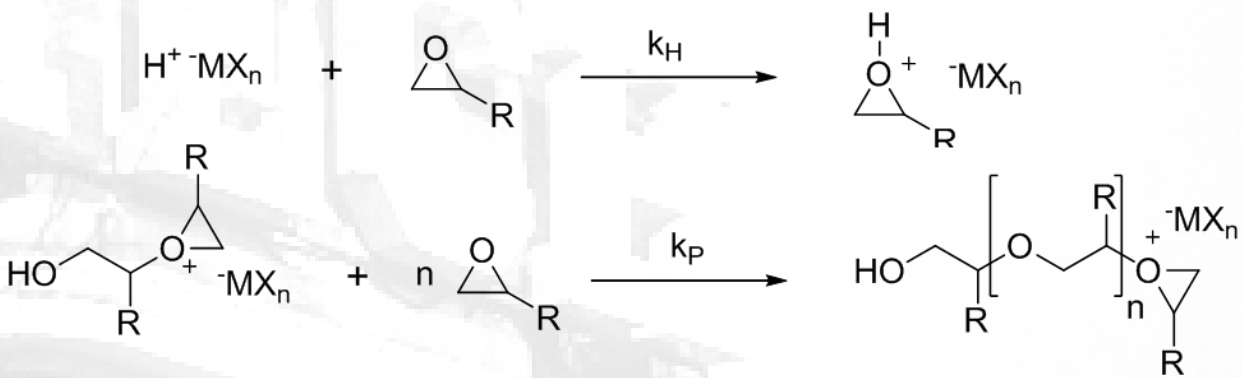
TOA

- Even up to very high base loadings (1:1 PAG:base), the base has little effect on the cross-linking

Base Quencher Ineffective in Epoxide Resists



- In standard CARs, the photoacid is regenerated after each reaction. The base acts to quench the acid and reduce catalytic chain length.

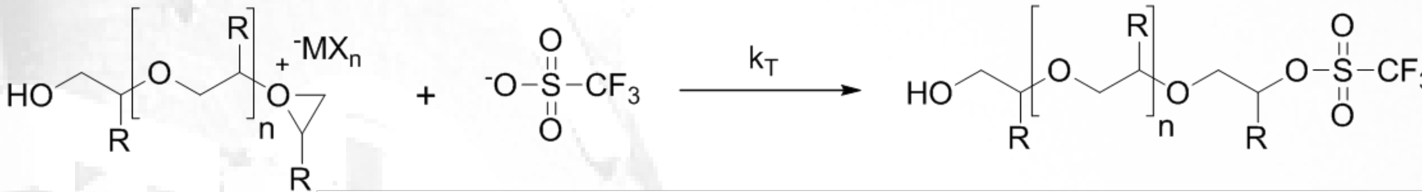


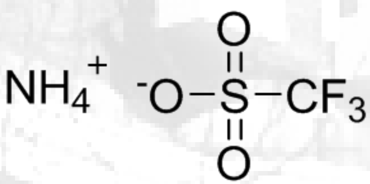
- In cationic polymerization CARS, the photoacid reacts only once. The active cation is the species that gets regenerated after each reaction. Base has less effect on the active cation.

Nucleophilic Quenchers

- What will act to quench a cationic polymerization?

  A strong nucleophile such as a triflate anion.





Added to 4-Ep

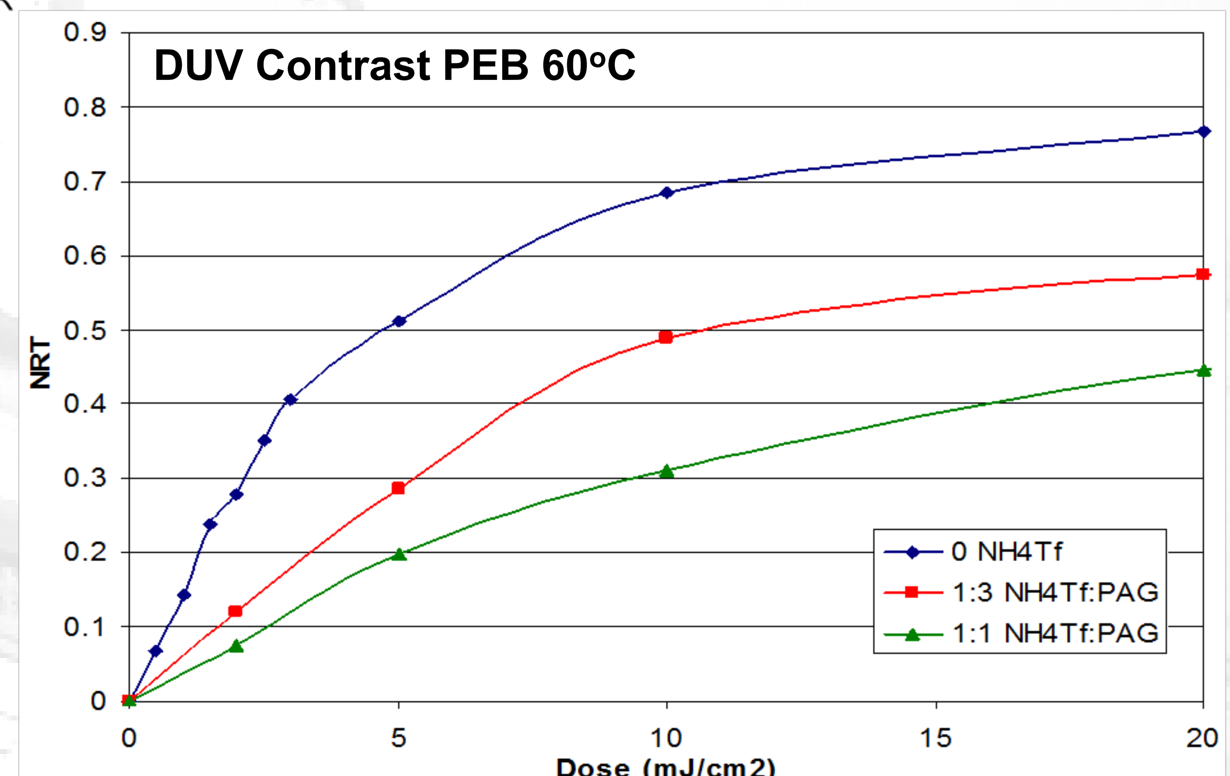
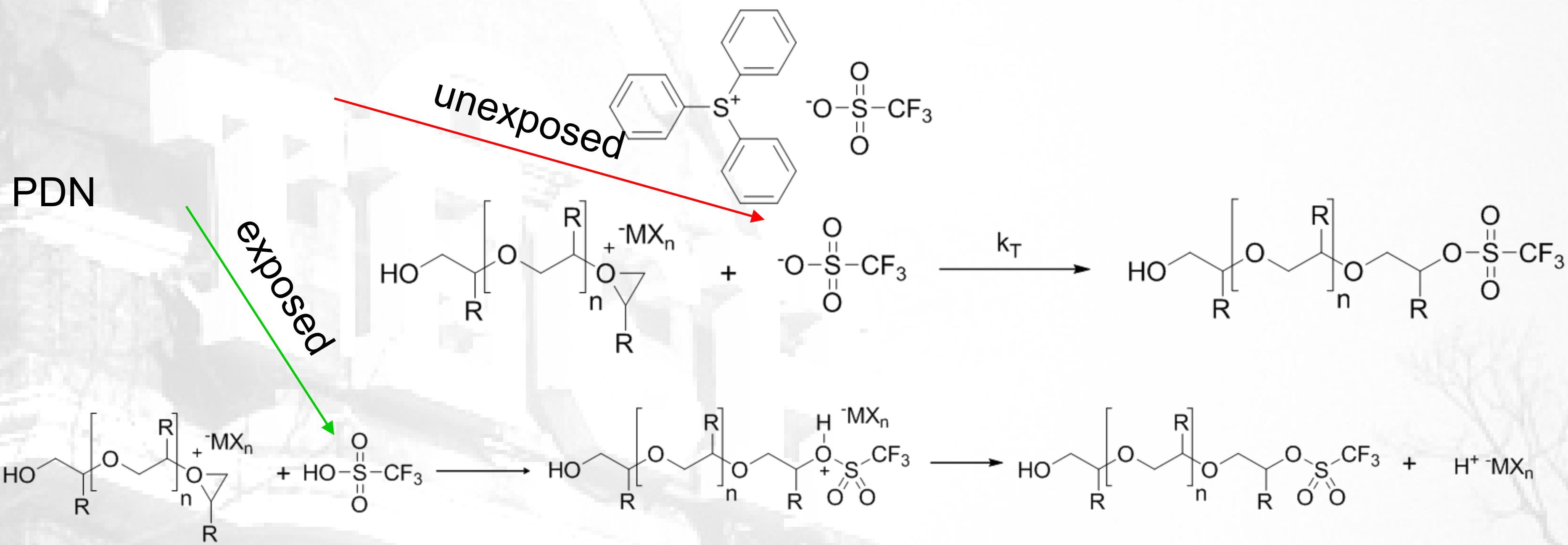


Photo-Decomposable Nucleophile (PDN)

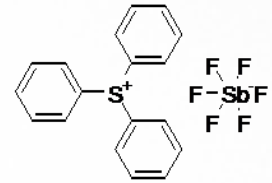
- Addition of strong nucleophile shows significant effect in quenching
- Only needs to terminate polymerization outside the exposed region
- What type of chemical can achieve this??



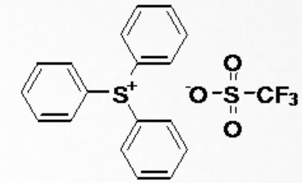
- TPS-Tf added to 4-Ep formulation
- Triflic acid acts like chain transfer agent – regenerating the initial photoacid

Photo-Decomposable Quencher – TPS-Tf

- Behavior looks like reduced PAG loading at low dose, but can obtain the same performance as no additive
- Has benefits of nucleophilic quencher with less drawbacks
- Contrast improved (γ_0 = 0.49, $\gamma_{1:4}$ = 1.14, $\gamma_{1:2}$ = 1.13)

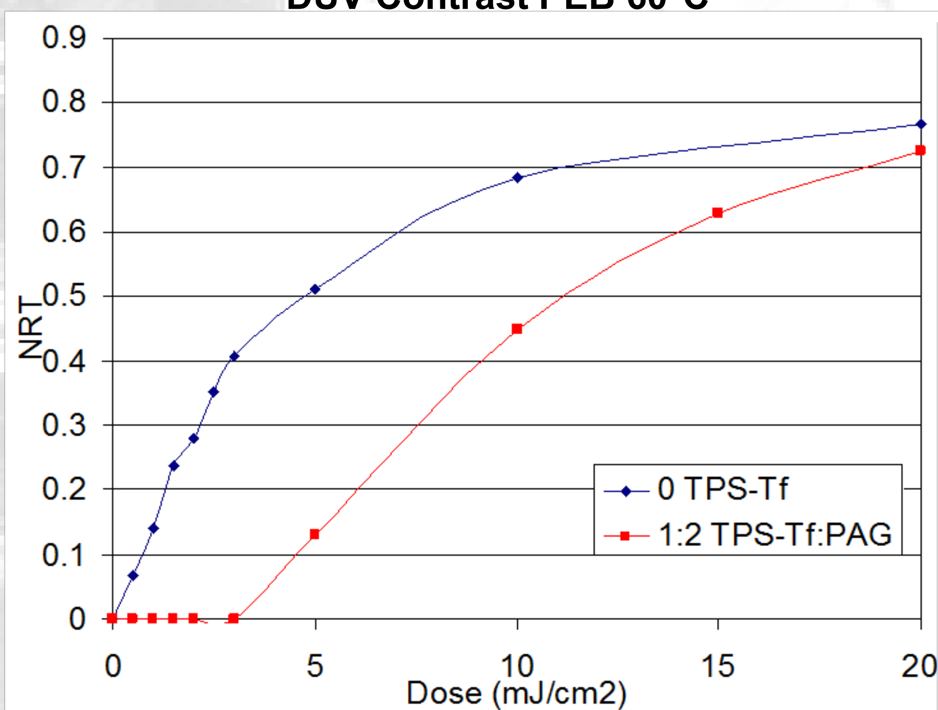


TPS-SbF_6

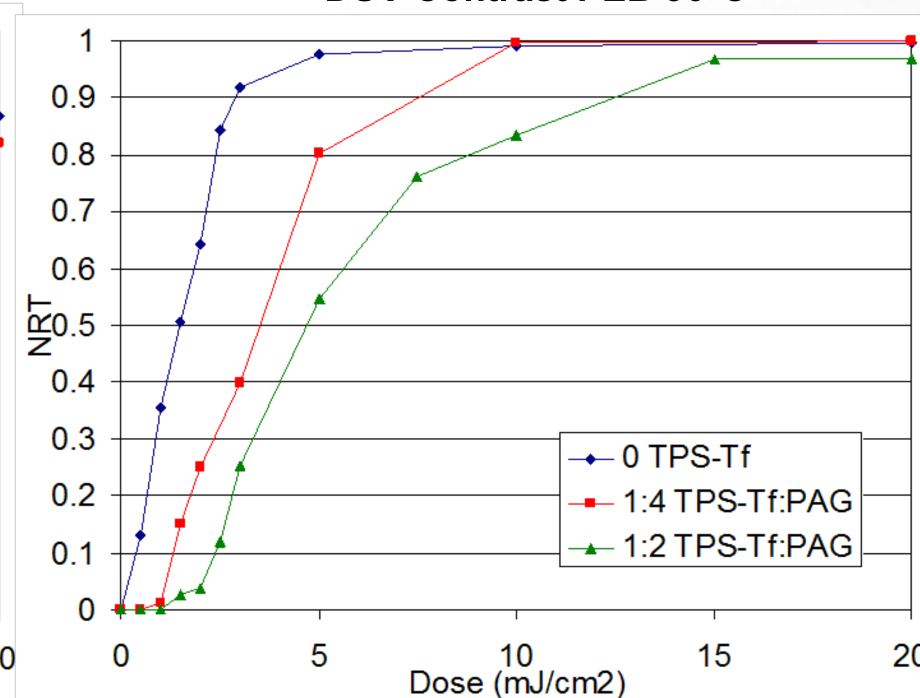


TPS-Tf

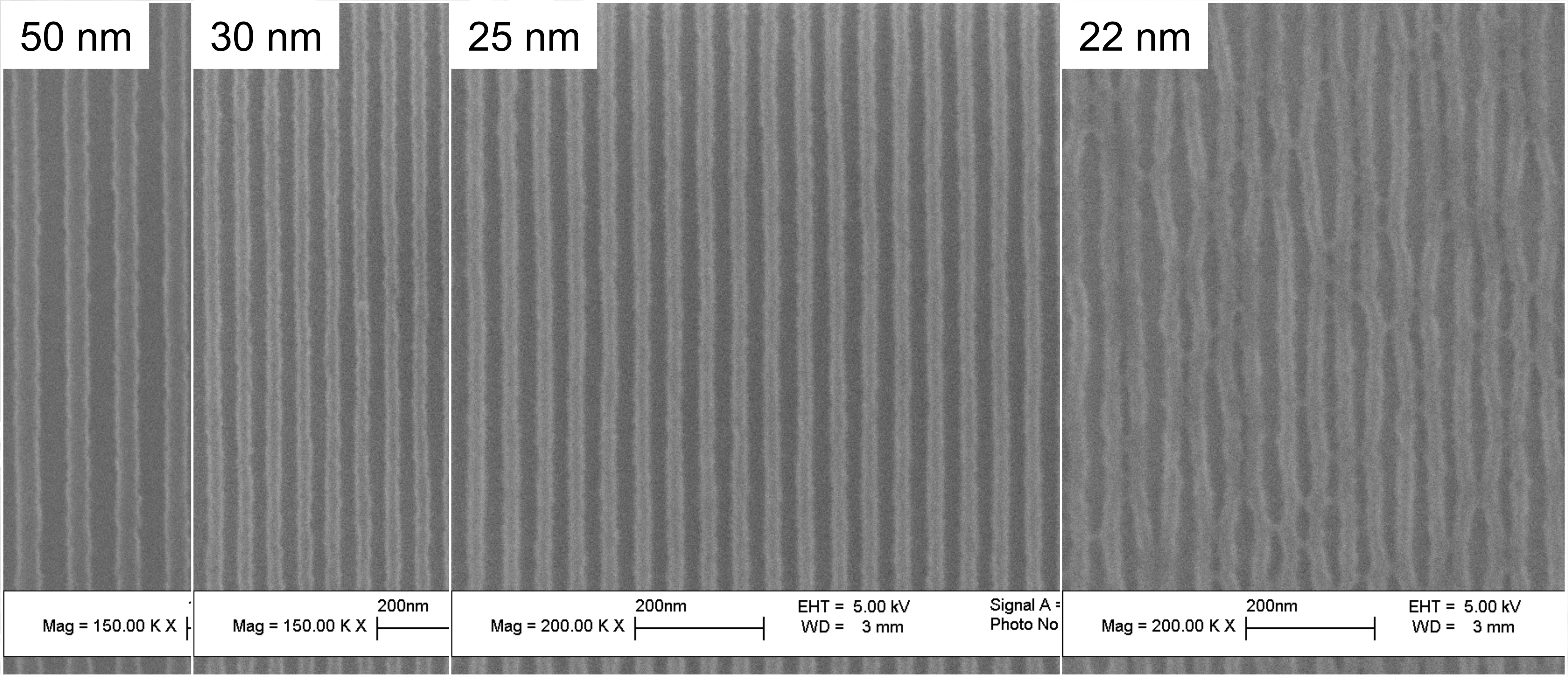
DUV Contrast PEB 60°C



DUV Contrast PEB 90°C



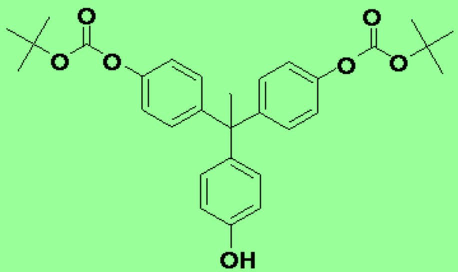
4Ep EUV at PSI PEB 60°C with TPS-SbF_6/TPS-Tf

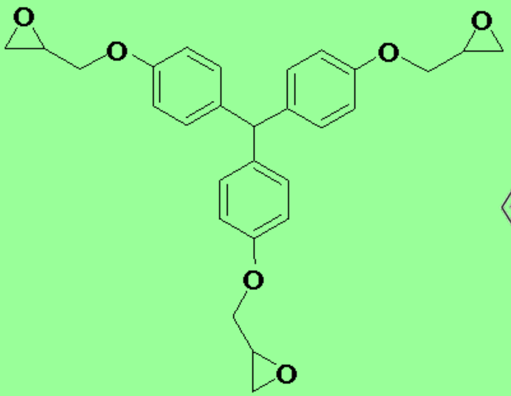


- Modified resist formulation, 1:2 TPS-Tf:TPS-SbF_6
- Dose-to-size = 15 mJ/cm^2 (Dose-to-Mask = 45 mJ/cm^2 July 08)
- LER (3σ) = 4.0 nm for 50 nm lines
- LER (3σ) = 4.5 nm for 25 nm lines

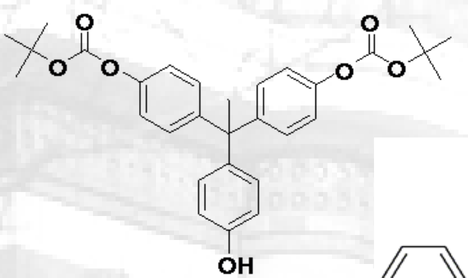
Opportunities with Molecular Resists

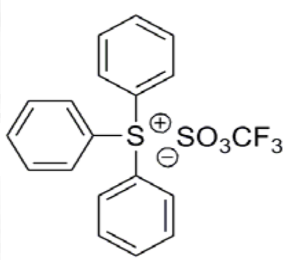
- **Aqueous Development vs. Solvent Development**

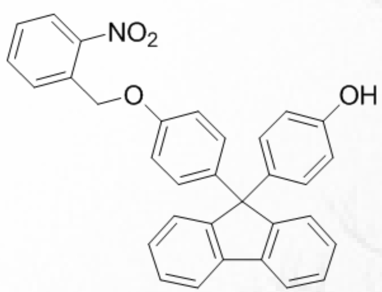




- **Chemically Amplified vs. Non-Amplified (Inhibited)**

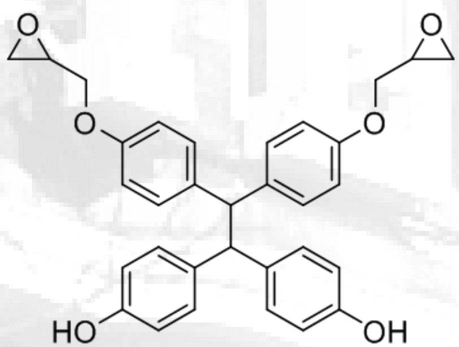




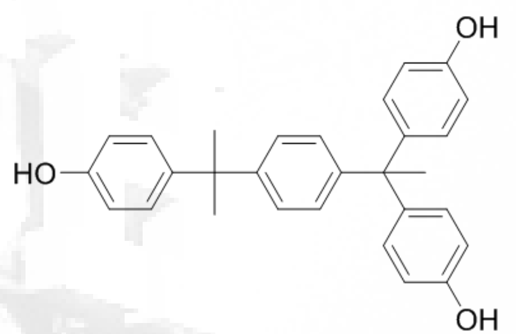


TMAH Developed Epoxides

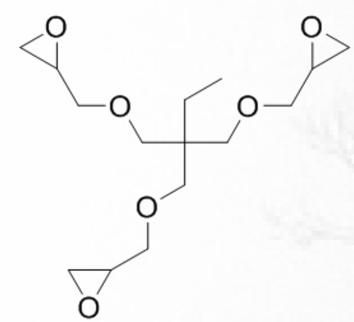
- These systems have excellent performance under both e-beam and EUV, but they are developed in organic solvents.
- The industry standard for development is aqueous base solutions of 0.26N TMAH.
- This concept is extendable to aqueous base development with the design of new resist molecules and blends.



Non-Blended Designs



THPIB

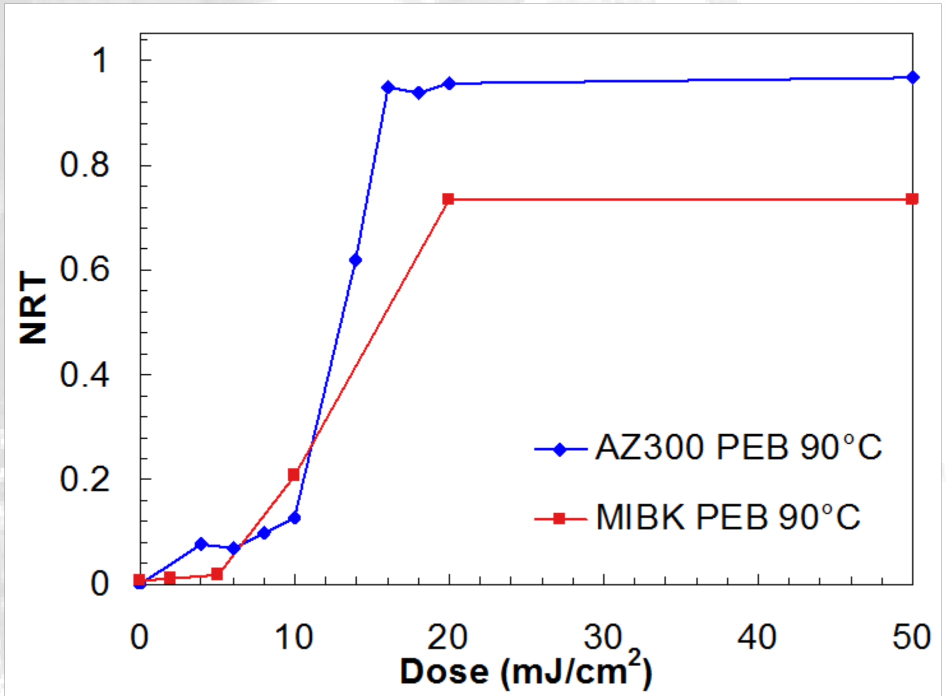


TMP-3Ep

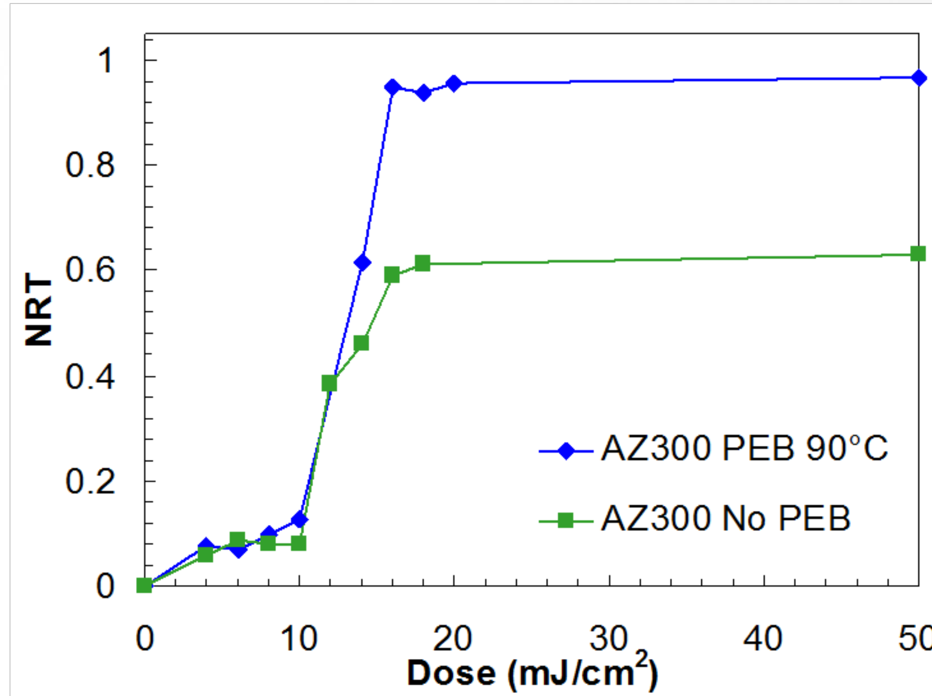
Blended Designs

Base Developed Epoxides – Blended Resists

Base vs. Solvent Developed



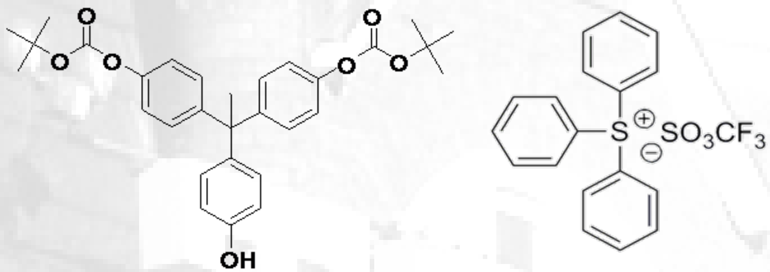
Effect of PEB

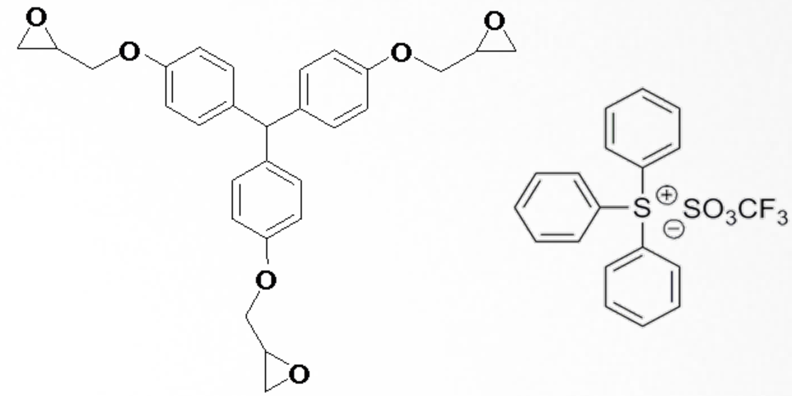


- Shows similar behavior in solvent and base
- $\gamma = 4.2$ in AZ300
- Can be reasonably imaged with no PEB – due to additional etherification mechanism
- High resolution imaging currently underway

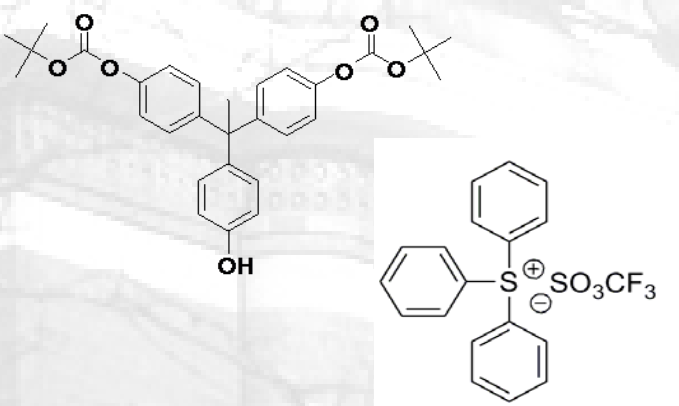
Opportunities with Molecular Resists

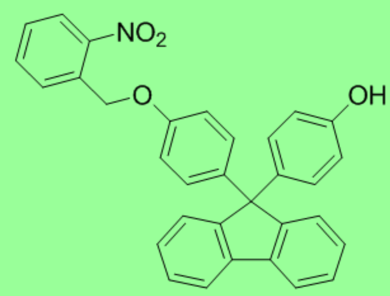
- **Aqueous Development** **vs.** **Solvent Development**





- **Chemically Amplified** **vs.** **Non-Amplified (Inhibited)**





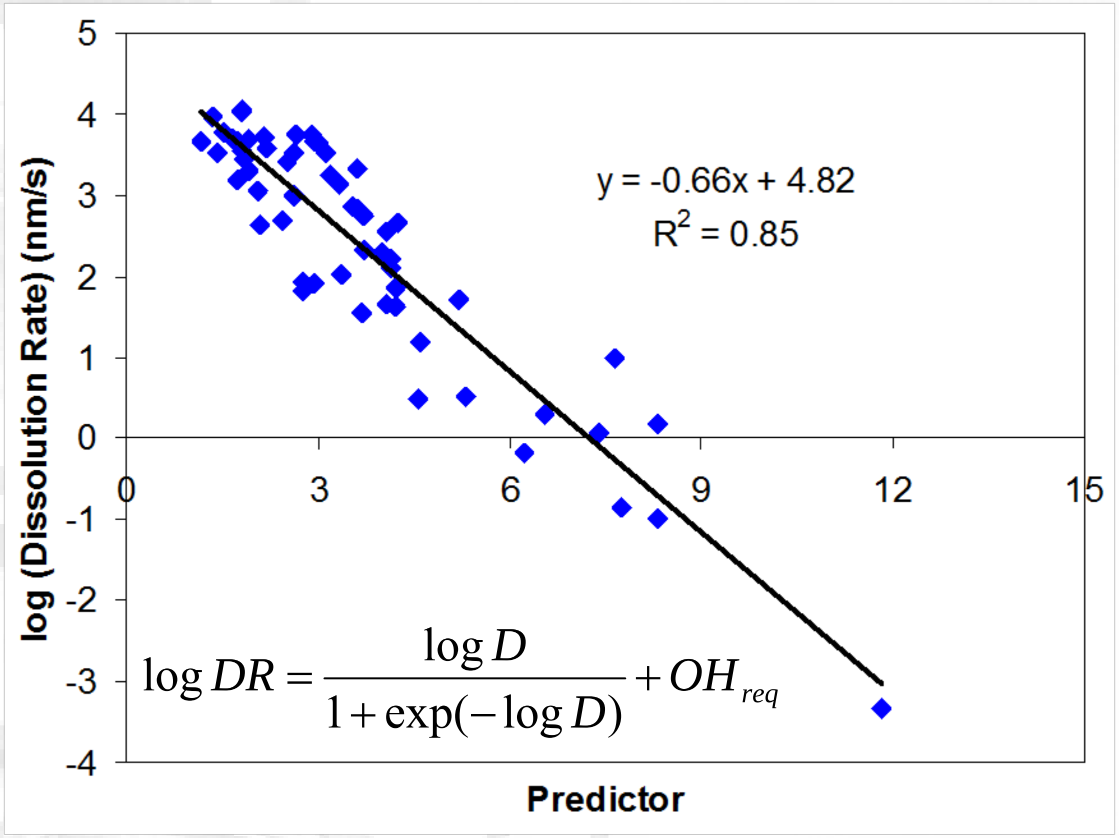
Non-Amplified Resists

- Positive Tone
  - DNQ/Novalac – DNQ inhibits dissolution of novalac, undergoes Wolff rearrangement to become dissolution promoter – requires water during exposure to operate in positive tone mode
  - PMMA – chain scission – reduction in MW leads to solubility difference – electronics/absorbance of chain can be altered to improve photosensitivity, but still limited
- Negative Tone
  - HSQ/Acetyl or Chlorobenzyl Calixarenes – photoinduced radical generation which induces cross-linking – high resolution, but relatively large number of cross-links required to render insoluble – low sensitivity

Non-Amplified Resists

- These designs have minimal ways to improve sensitivity
- The dissolution inhibitor (DI) resists can be potentially be made very sensitive (but not with DNQ).
- DIs using photosensitive protecting groups were investigated in early 1980s (pre-CARs).
- Huge amount of literature on photosensitive protecting groups in total synthesis – most non-ionic PAG chromophores can be applied as photosensitive protecting groups.
- Molecular resists provide precise control of functionality needed for high resolution non-amplified resists.
- Molecular resist dissolution behavior means that very high amounts of DI are required to render the film insoluble.

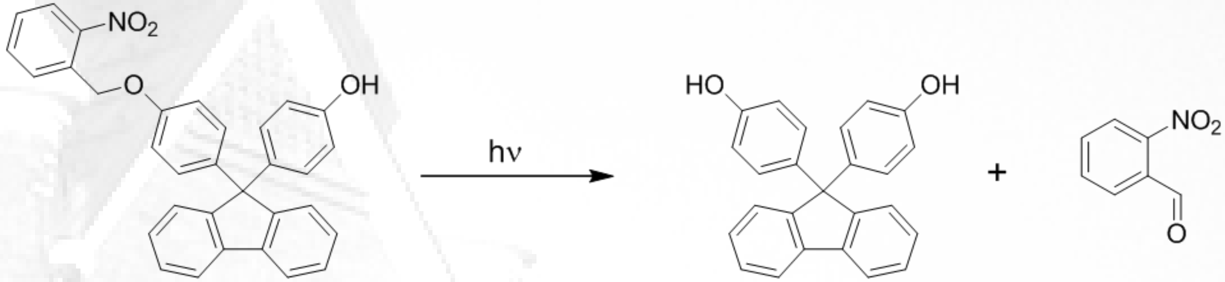
Predictive Modeling Is Possible in MRs



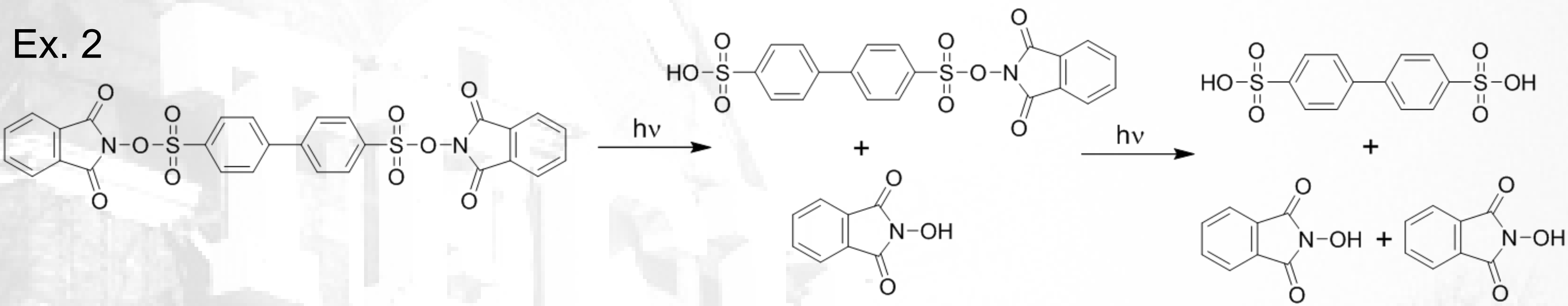
- We have greatly improved the understanding of the dissolution behavior of molecular resists
- The previous work has only been done for pure components, but an actual resist consists of a mixture of soluble and insoluble species.
- A study has been carried out to understand this effect on the dissolution of actual molecular resists.

1st Gen Non-Amplified MRs

Ex. 1

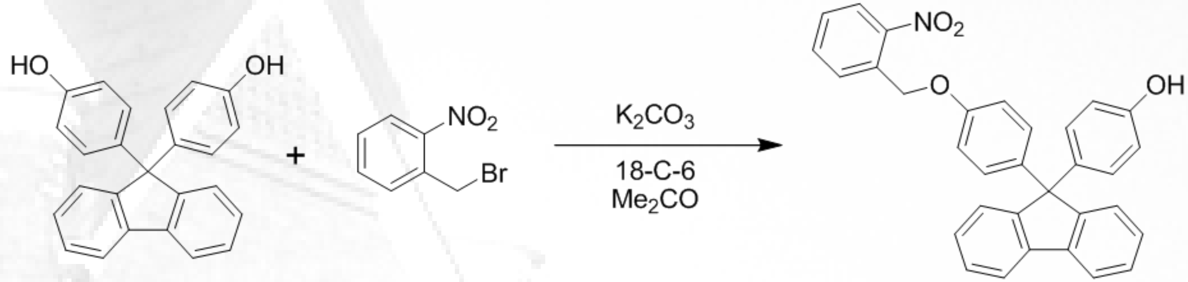


Ex. 2



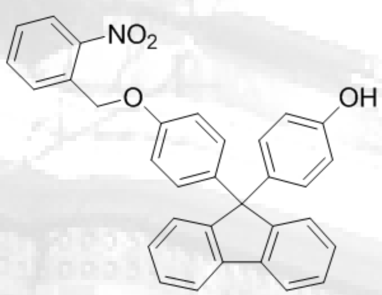
- Desire to investigate ultimate tradeoffs in non-amplified vs. CA resists
- No high sensitivity positive tone non-CA resists reported for high resolution imaging
- DNQ cannot be used because Wolff rearrangement requires in-situ water – DNQ in vacuum leads to cross-linking
- Designs based on dissolution inhibition by compounds with photosensitive functional groups
- Should provide some learning on future single component systems

NBnHPF



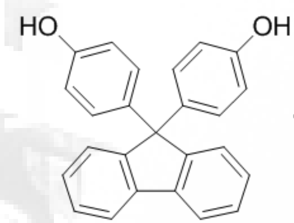
- Synthesized by Williamson etherification, purified by simple column
- Can be imaged as single component system or imaged as blended system (with BHPF)

Single Component

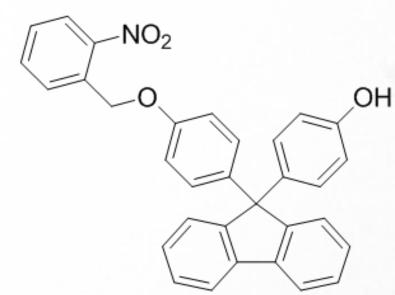


100%

Blended System



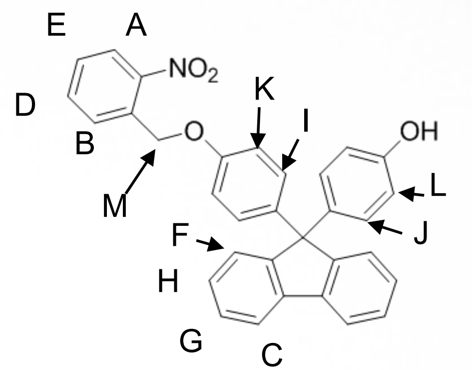
25-50%

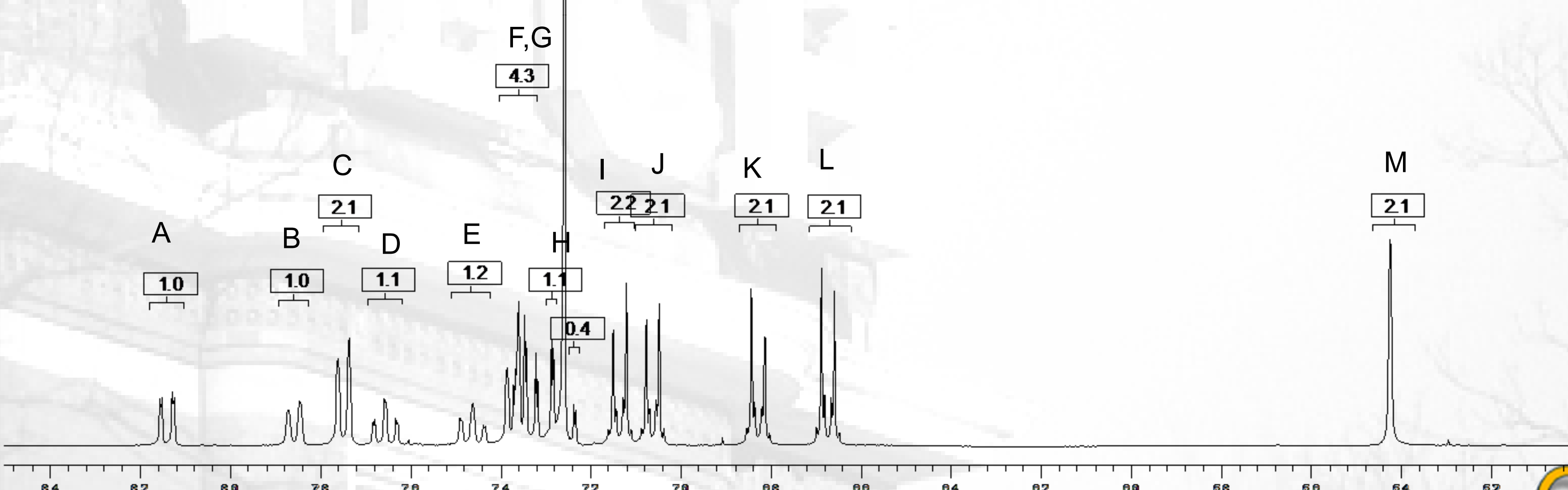


50-75%

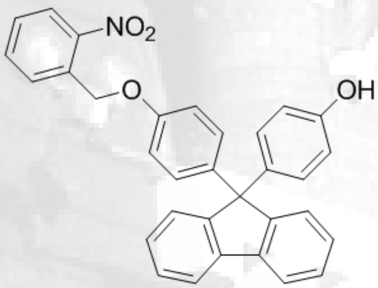
NMR of NBnHPF

Materials can be isolated as clean pure compounds!

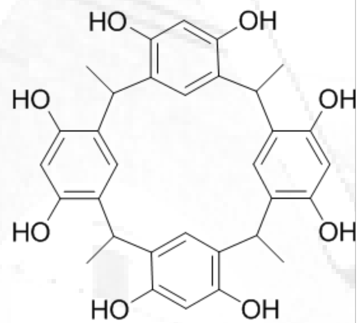




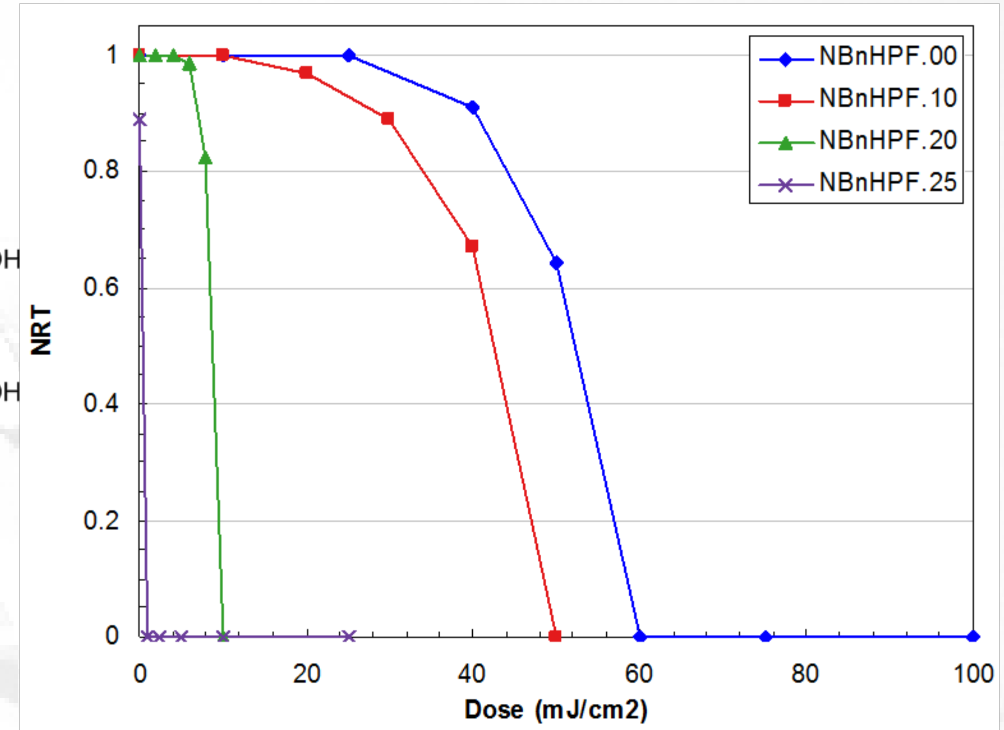
NBnHPF/C4MR Blends



NBnHPF



C4MR



- 55 nm thick film
- Processed with **No PEB**
- Cleanly dissolves in 0.26N TMAH – no apparent delamination on HMDS primed surfaces
- Sensitivity adjustable by formulation - 0, 10, 20, 25% C4MR in NBnHPF – down to 1 mJ/cm2 at 248 nm exposures
- 20% C4MR has senstivity of 10 mJ/cm2 with contrast of 8.26 under DUV
- Might be faster under EUV due to potentially improved photoreaction rate constant of NBn PPG (photoactive protecting group).

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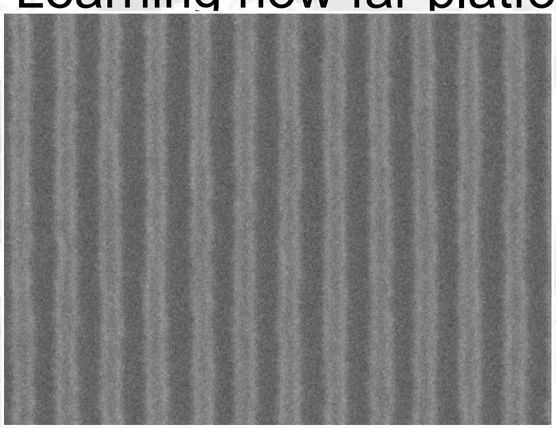
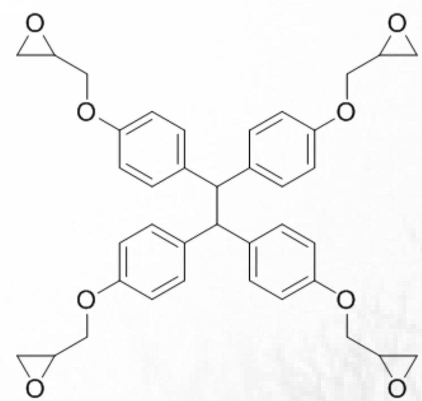
Summary

- Molecular resists offer a rich class of materials for next generation resists
  - Ability to synthesize and isolate pure, single species an inherent advantage
- Predictive materials design modeling tools have been developed
  - Predict Tg, solubility, dissolution rate,…
- Outstanding results have been demonstrated in early negative tone materials
  - Low LER, very high sensitivity, very high resolution
- A new method for "diffusion control" has been developed and demonstrated in negative tone MRs using PDNs
- Single component MRs have been demonstrated
- Highly sensitive non-amplified MRs have been developed
- Learning how far platforms can be pushed…



4-Ep
PSI
25 nm 1:1
15 mJ/cm^2
LWR: 5-6 nm



Acknowledgements

- Intel Corporation for funding support
- Todd Younkin, Steve Putna, Jeanette Roberts, and Wang Yueh at Intel for helpful discussions.
- Harun Solak, Vaida Auzelyte, and Anja Weber at PSI for EUV exposures

EUV 25 nm 1:1