Single Component Molecular Glass Resists for EUVL:

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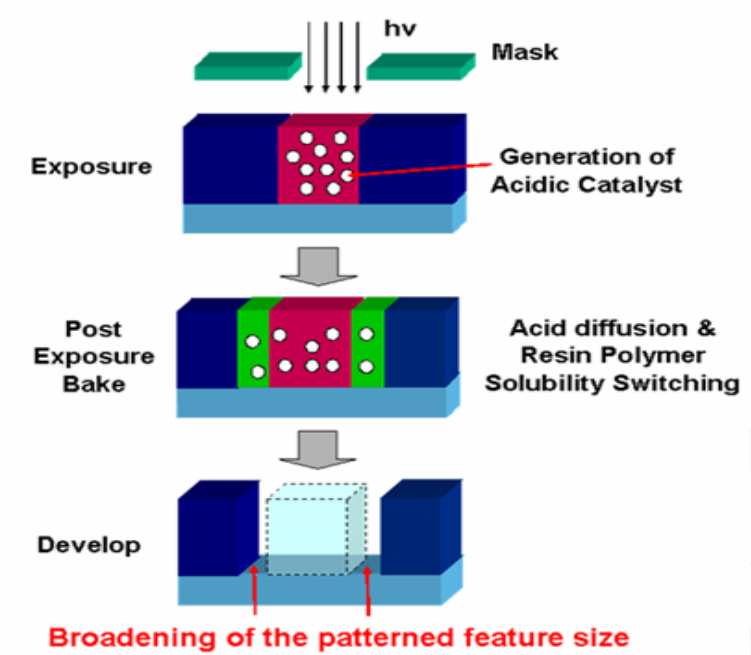
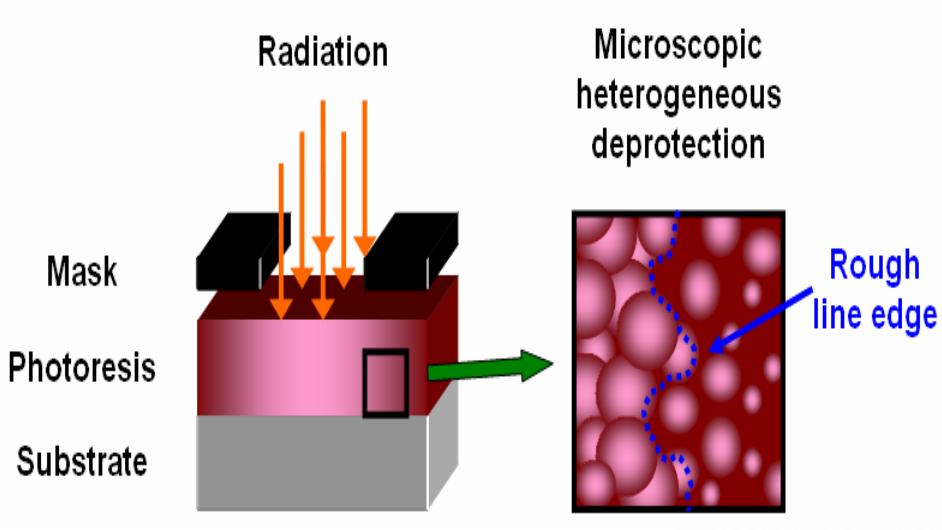
Challenges for EUV Resists

- In particular, 2005 ITRS Roadmap lists the following three criteria as major challenges for EUV resists
  - obtaining < 3 nm 3σ LWR
  - obtaining < 10 mJ/cm^2 sensitivity
  - obtaining < 40 nm ½ pitch resolution
- Outgassing is also a major concern
- Recent work on conventional CAR designs seems to indicate a trade-off between LWR, sensitivity, and resolution that will likely prevent their use
- Important factors controlling all three behaviors appear to include:
  - Photoacid diffusion
  - PAG loading
  - Inhomogeneous distribution of resist components such as PAG
  - Size of resin molecules

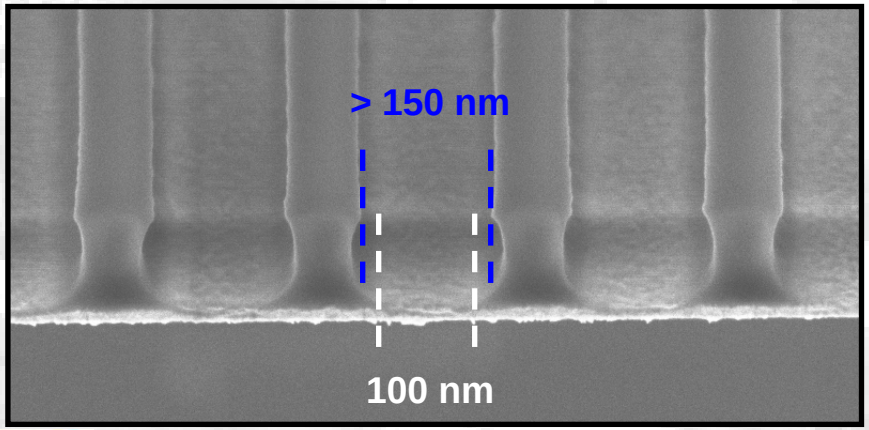
Possible Photoacid Diffusion Effects: Image Blur



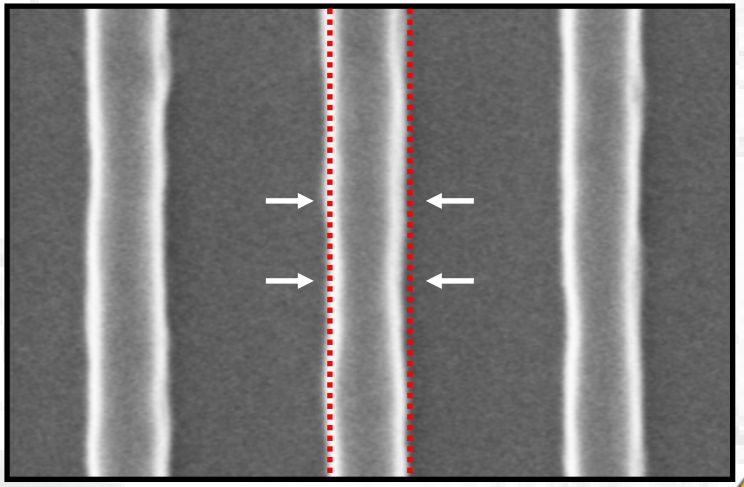
Line Edge Roughness (LER)



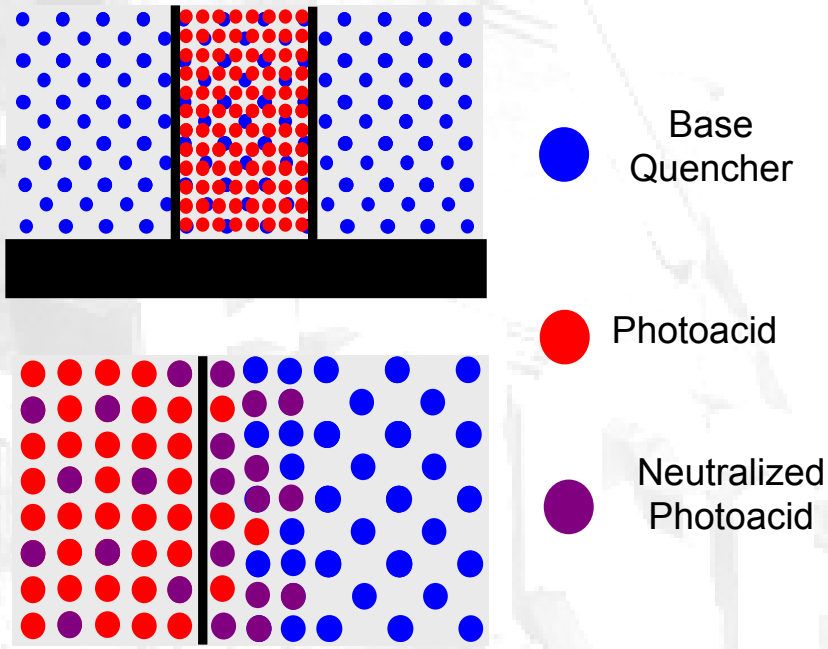
Traditional CAR photoacid diffusivity: > 5nm



Traditional CAR 3σLER: > 5nm



Possible Solutions - #1: Base Quencher Additives

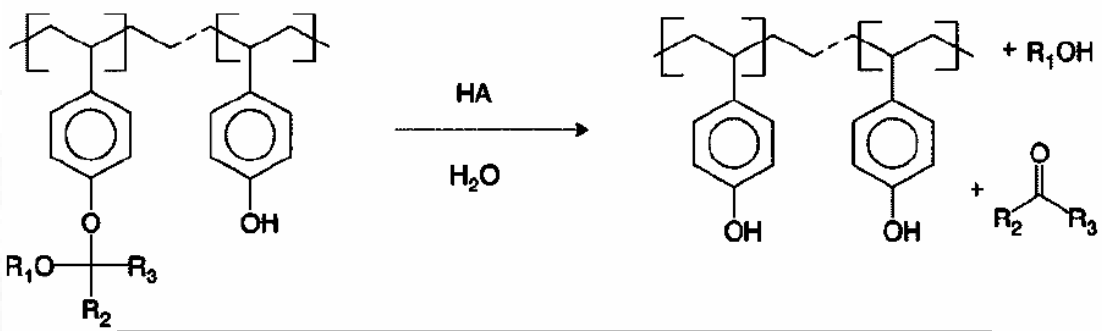


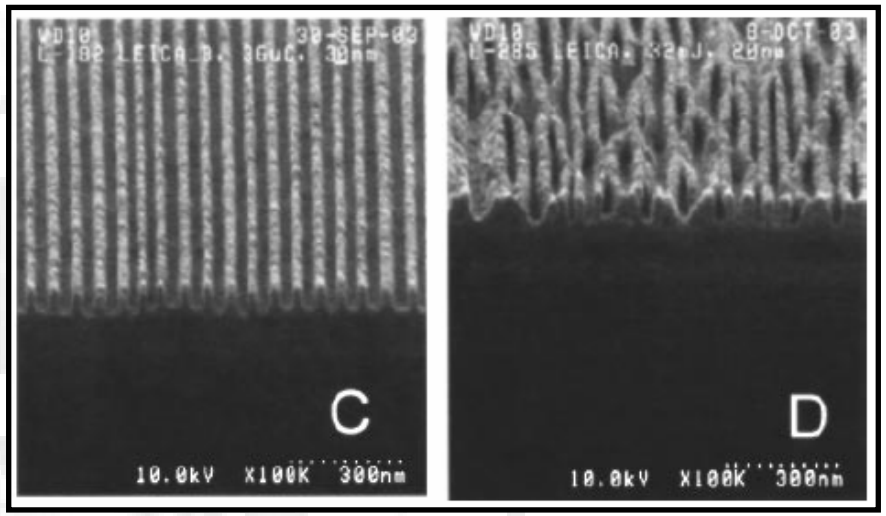
Critical Problems:

1. Acid/base molecules exhibit non-uniform distribution after spin casting.
2. Photosensitivity significantly reduced as base concentration is increased.

Base quencher molecules are added to limit the diffusion range of photoacid and improve environmental stability.

Possible Solutions - #2: Low Activation Energy Resists





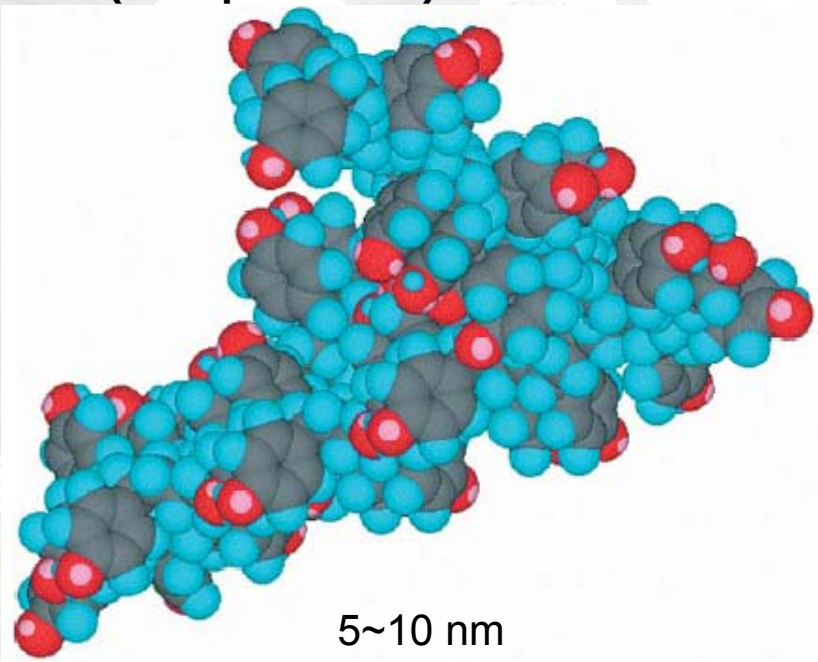
G. M. Wallraff, et. al., JVSTB 2004

Problems:

1. Studies have shown low activation energy materials exhibit more substantial outgassing.
2. Have still generally shown poor LER/LWR performance.

Possible Solutions - #3: Molecular Glass Resists

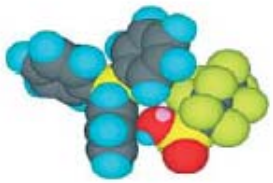
Polyhydroxystyrene (50 repeat units)

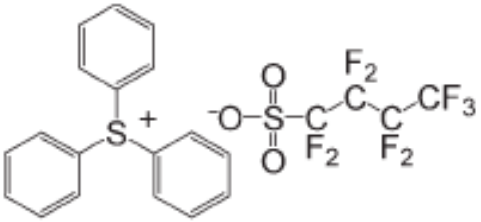


5~10 nm

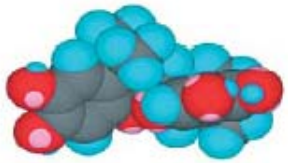
Da Yang, et. al., J. Materials Chemistry 2006

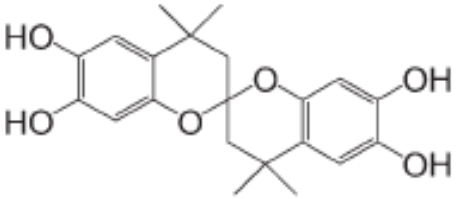
TPS.Nonaflate

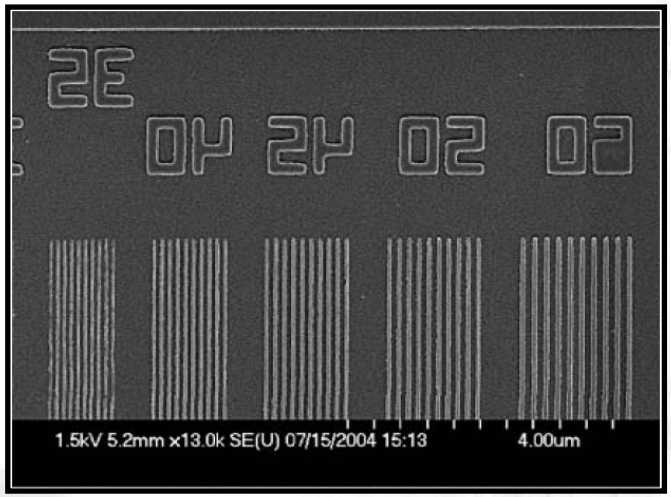




Resist monomer







Advantages:

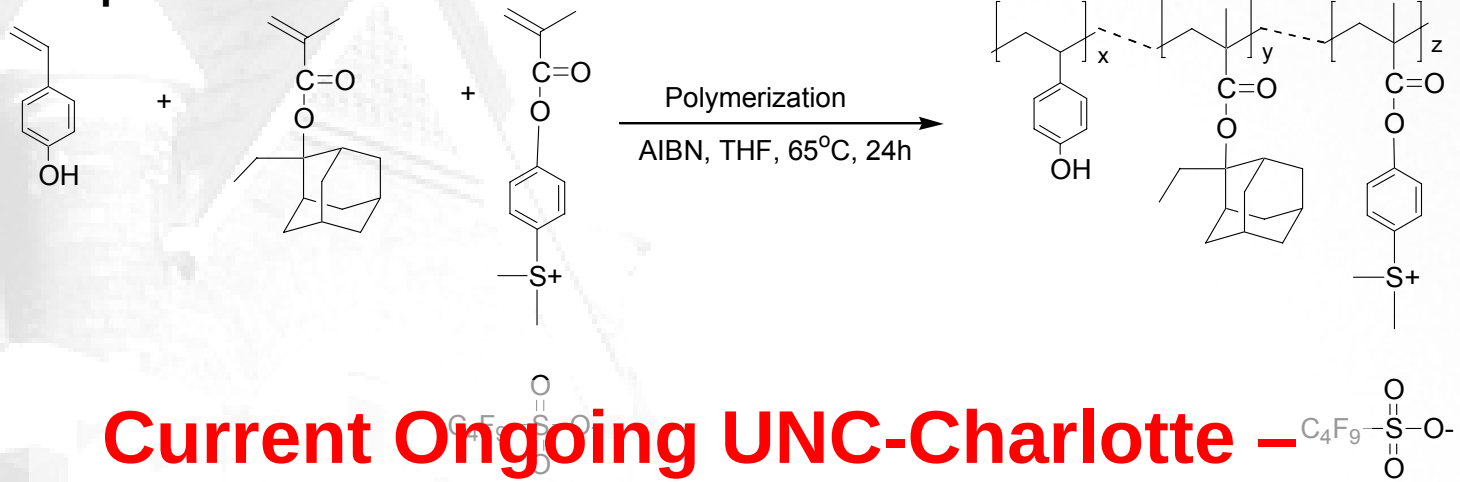
1. Reported low LER (3σ LER ~5 nm).
2. Better phase compatibility with PAGs.

Potential Problems:

1. Does not directly address acid diffusion and may in fact make it worse.

Possible Solutions - #4: Polymer-bound PAG Resists

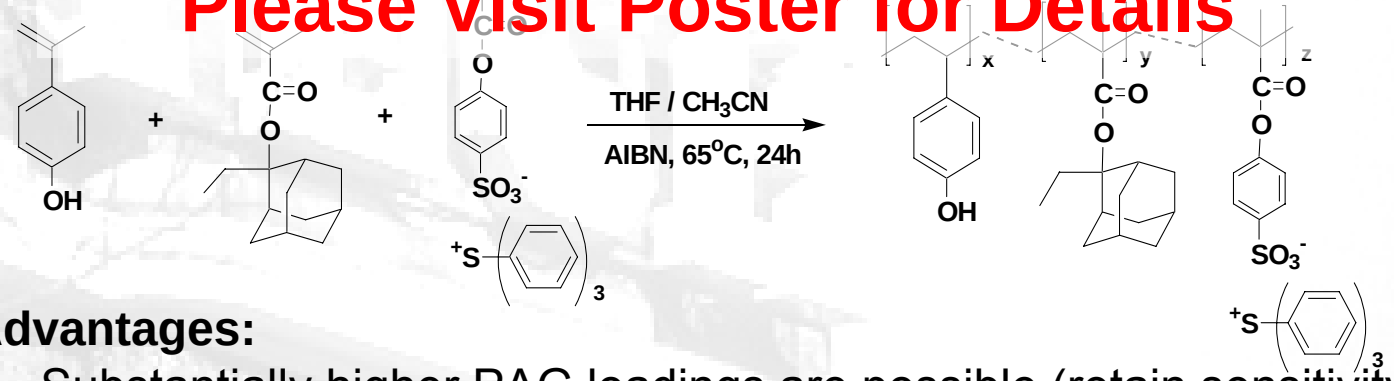
Example cation-bound PAG resist



Current Ongoing UNC-Charlotte – Georgia Tech – Intel Program

Please Visit Poster for Details

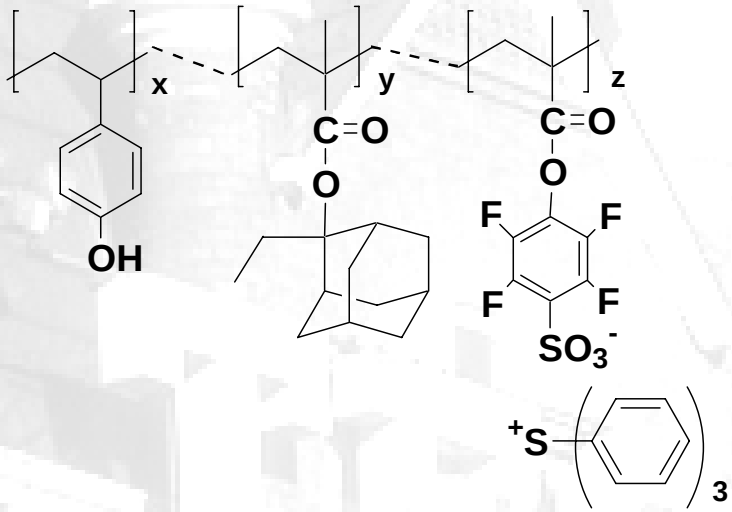
Example anion-bound PAG resist



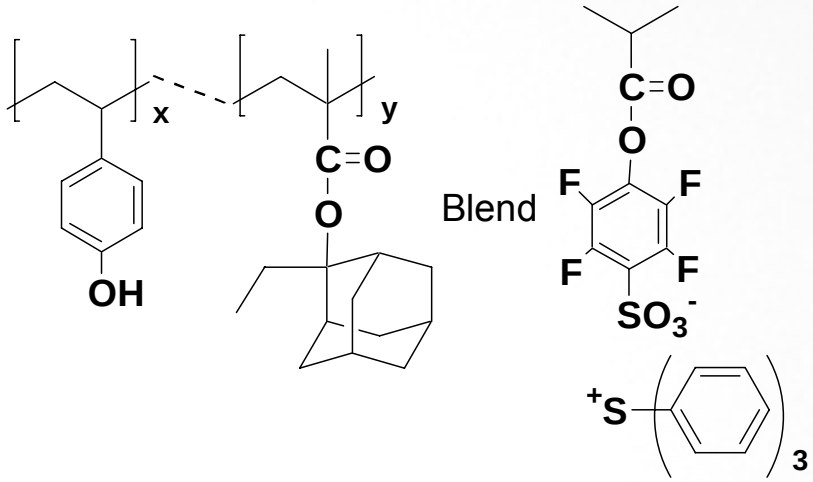
Advantages:

1. Substantially higher PAG loadings are possible (retain sensitivity with reduced acid diffusion).
2. Eliminates segregation and inhomogenous PAG distribution.
3. Permits direct acid diffusion control.

Characterization of bound and blend resists



HOST-EAMA-F4-MBS.TPS



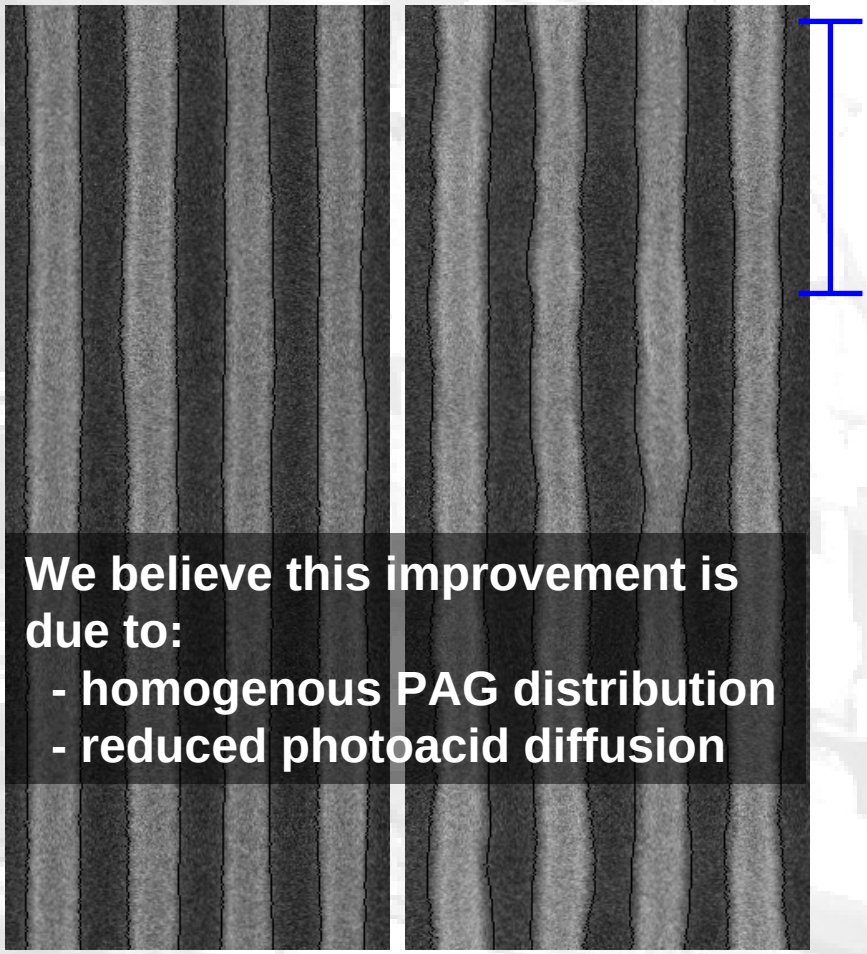
HOST-EAMA Blend F4-IBBS.TPS

Polymer	Mole Feed Ratio			Polymer Composition			Yield / %	Mw (PDI)	Stability / °C	Tg / °C
	HOST	EAMA	PAG	HOST	EAMA	PAG				
HOST-EAMA blend F4-IBBS.TPS	40	60		45.8	54.2	7.1 (wt%)	58.5	4500 (2.5)	156.9	113.2
HOST-EAMA-F4-MBS.TPS	25	72.5	2.5	35.0	57.9	7.1	37.3	3600 (1.6)	138.1	**

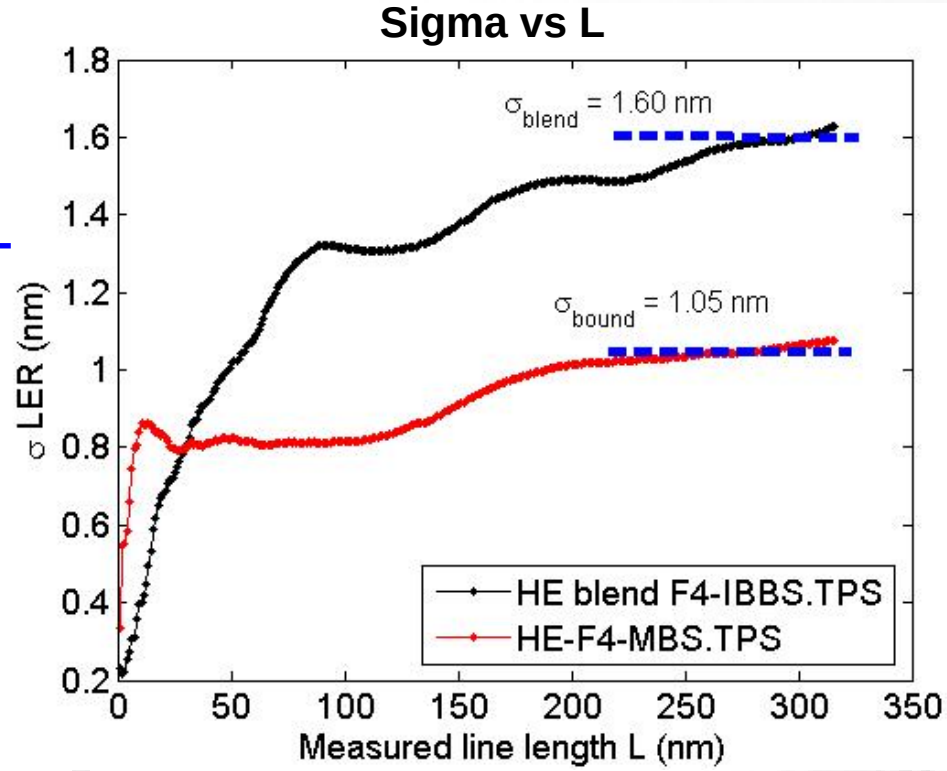
LER for blend and polymer-bound PAG resists

HE-F4-MBS.TPS (124 uC/cm²)

HE + F4-IBBS.TPS (120 uC/cm²)



We believe this improvement is due to:
- **homogenous PAG distribution**
- **reduced photoacid diffusion**



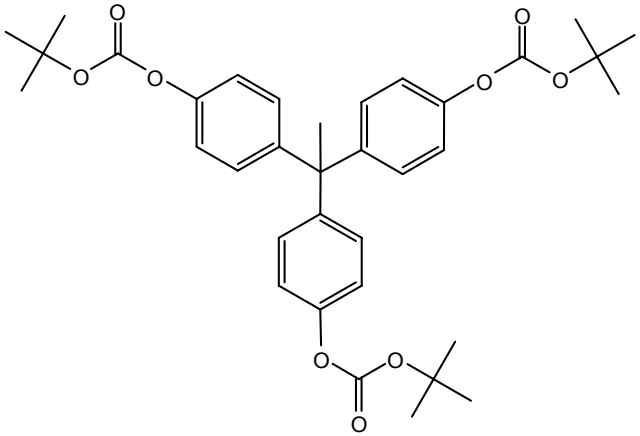
- Polymer-bound PAG sample showed 50% smaller 1σ LER (1.05 nm) than the blend one (1.60 nm). This result corresponds to 1.65 nm difference in the 3σ LER .

Lessons Learned So Far

- Polymer-bound PAG Resists
  - Binding anion to polymer reduces photoacid diffusivity substantially while binding cation has little effect
  - Bound-anion materials show significantly better LWR performance than analogous blended or cation-bound resists
  - High PAG loading possible in these systems maintain photospeed comparable to blended systems
- Molecular Glass Resists
  - Smaller molecular size does appear to have some advantage for improving ultimate LWR performance
  - Exact control over molecular structure eliminates problems with inconsistency in terpolymer polymerization
  - Superior dissolution properties – each molecule in the glass is identical, while in the polymer there is a distribution of molecular weights and chain lengths; polymer chains can be partially-deprotected

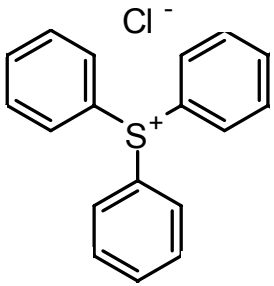
CONCEPT: Combine the best of both solutions by making single component molecular glass resists that contain PAG functionality directly in the molecule.

From Blended Molecular Resists to Single Component Molecular Resists: A Model Compound Proof of Concept



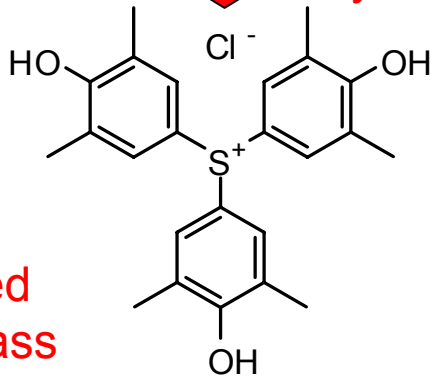
Literature Molecular Glass

Core looks similar in some sense to

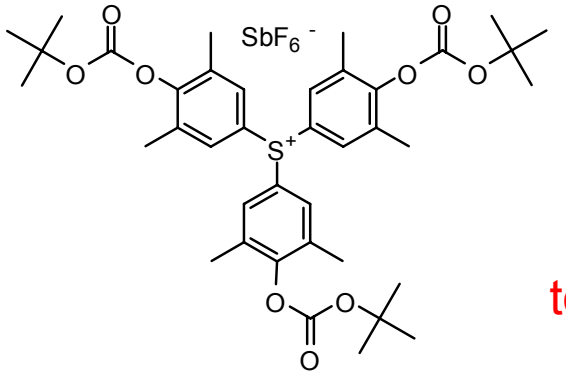


Triphenyl sulfonium PAG

Which can be made very alkaline soluble

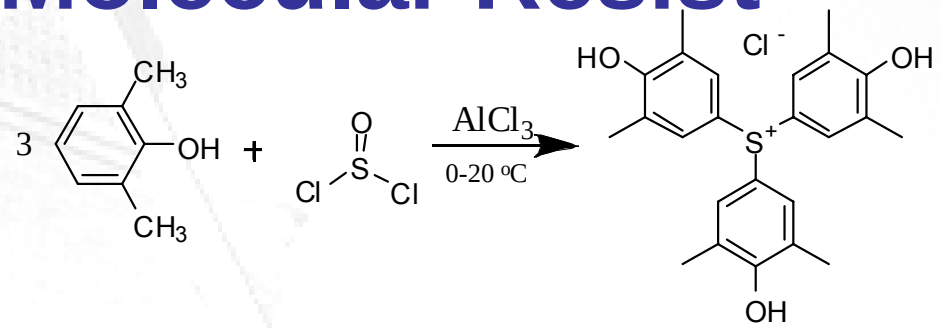


Which can be protected to make a molecular glass resist

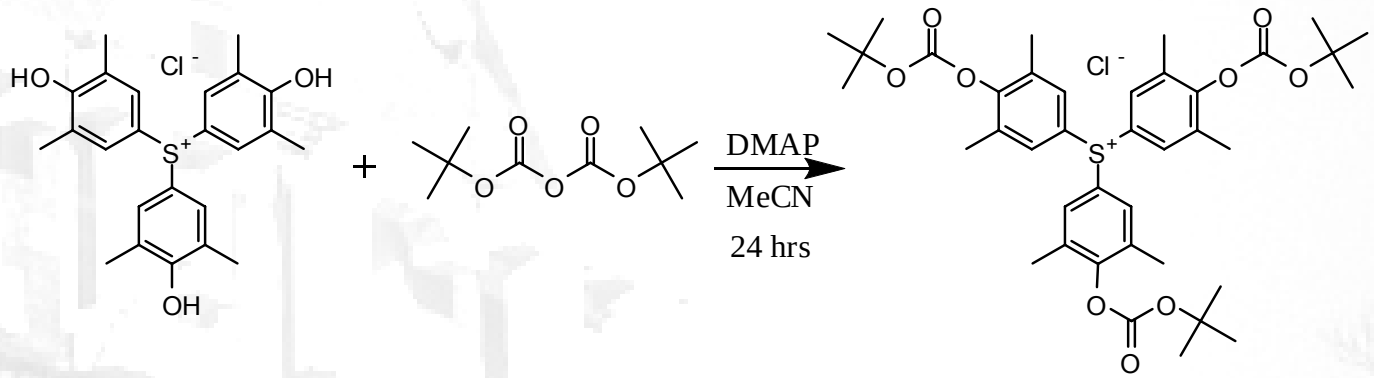


Synthesis of Triarylsulfonium (TAS) Molecular Resist

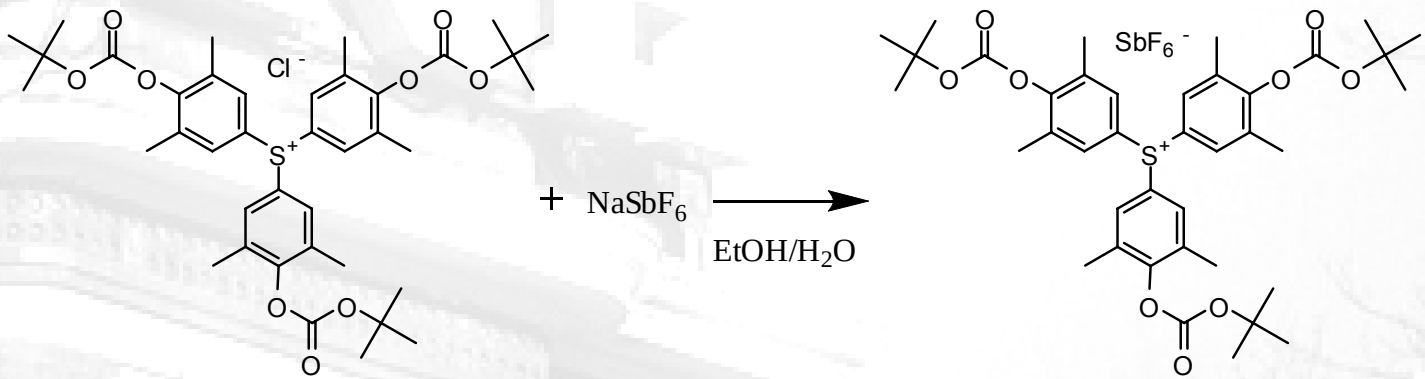
Synthesis



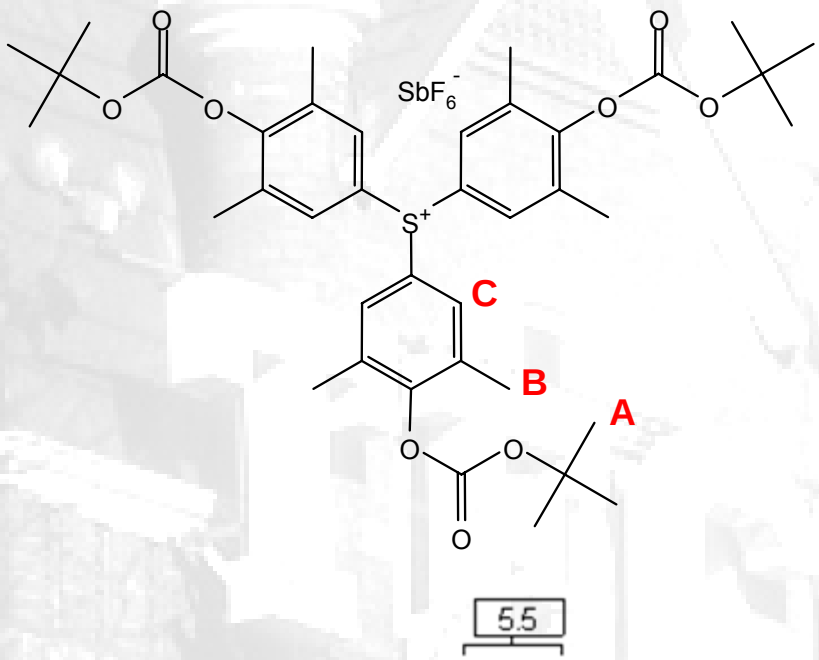
Protection

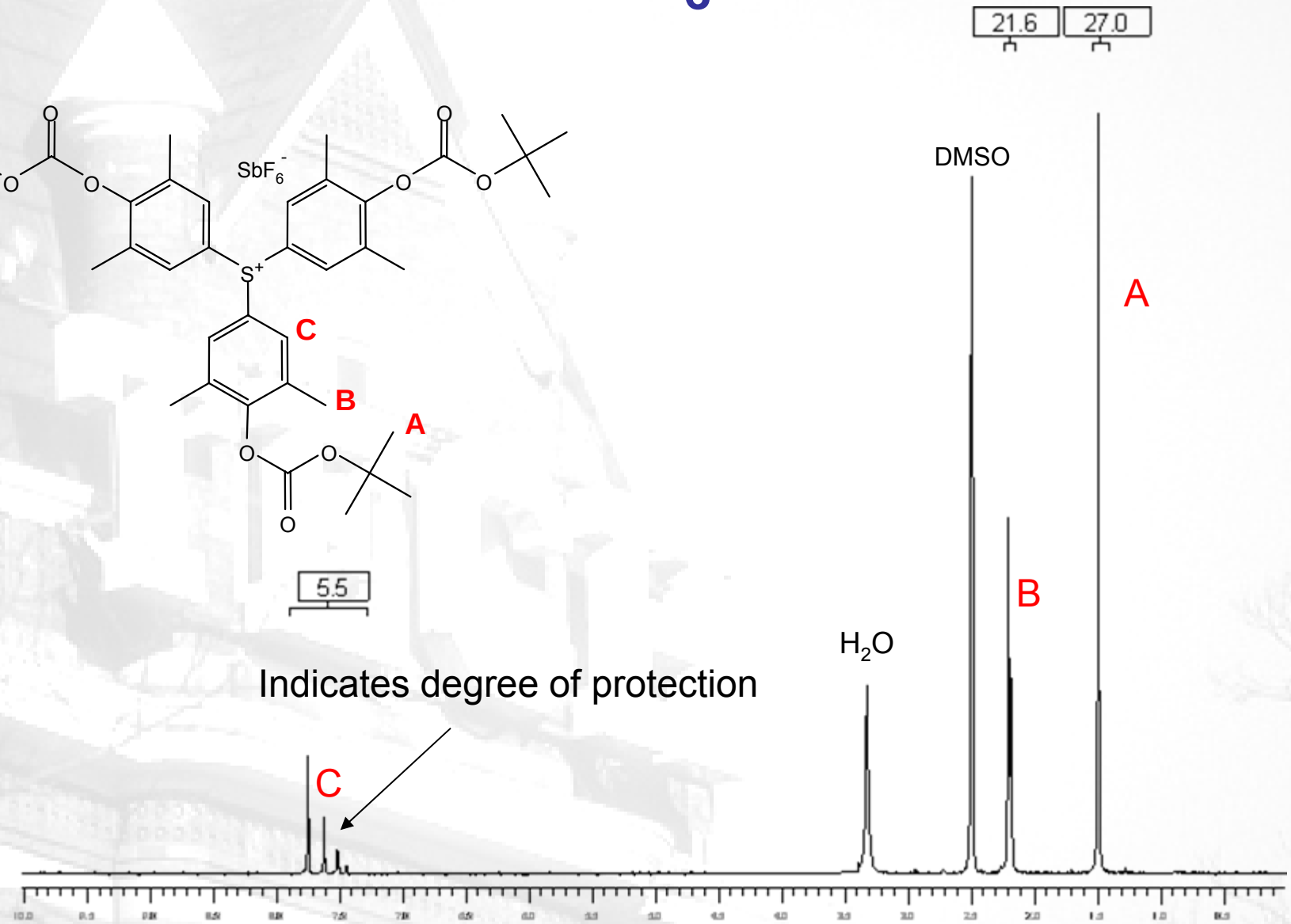


Metathesis



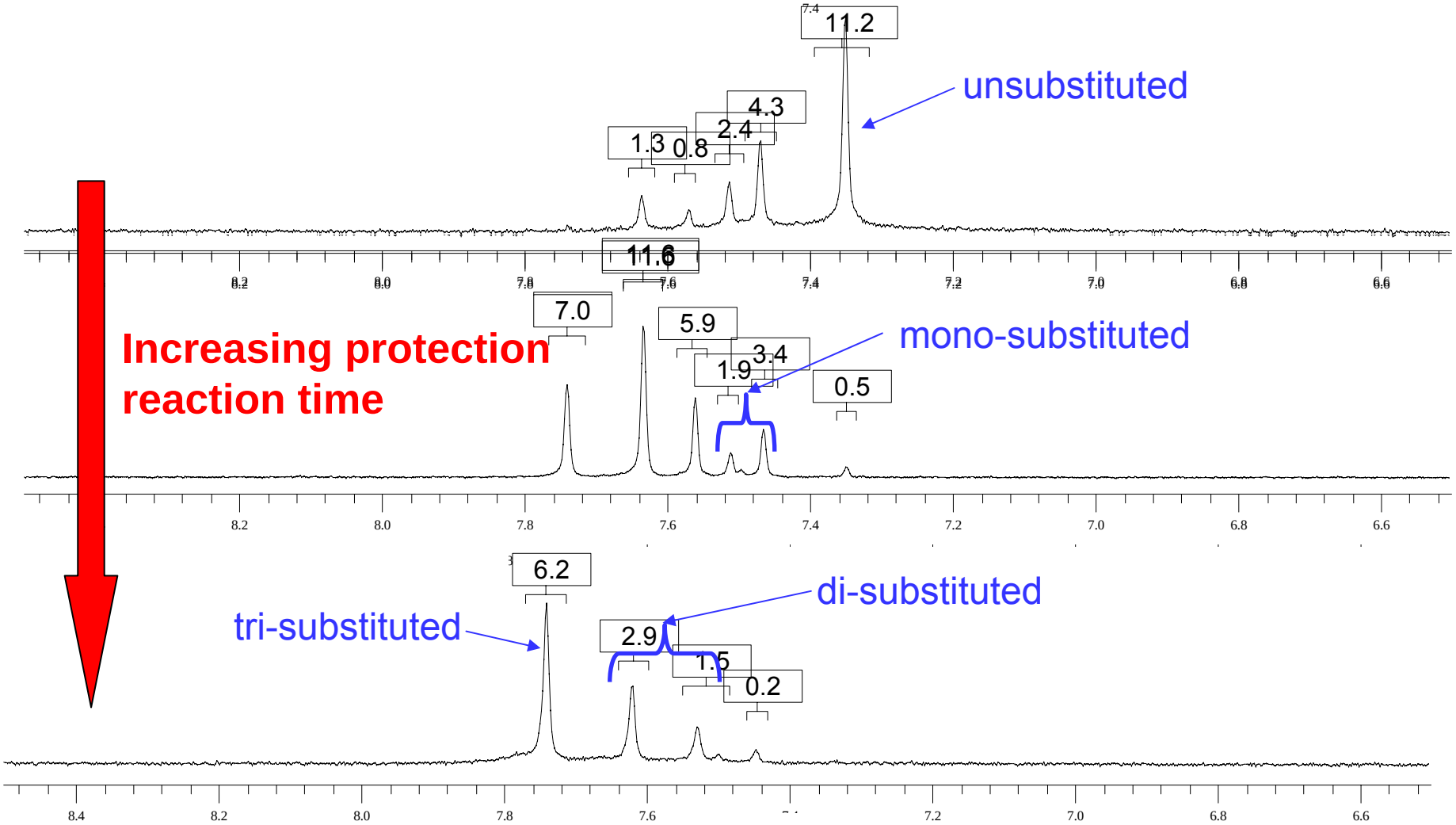
TAS-SbF_6 NMR





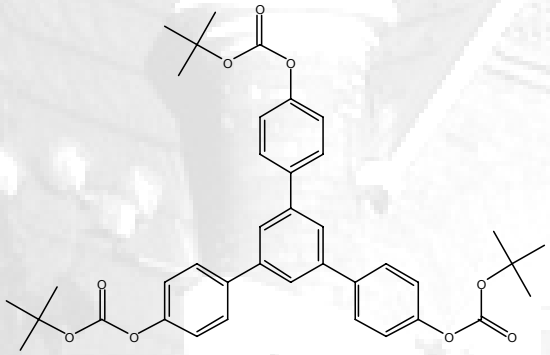
Indicates degree of protection

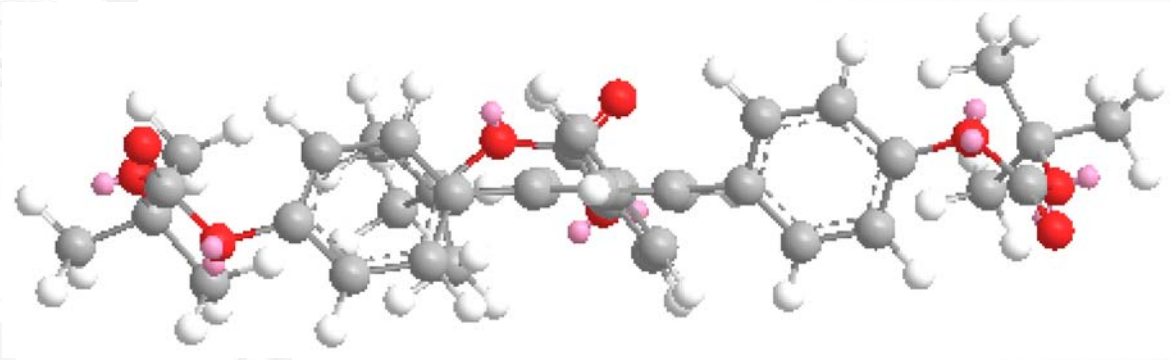
TAS-SbF_6 NMR- Protection Levels

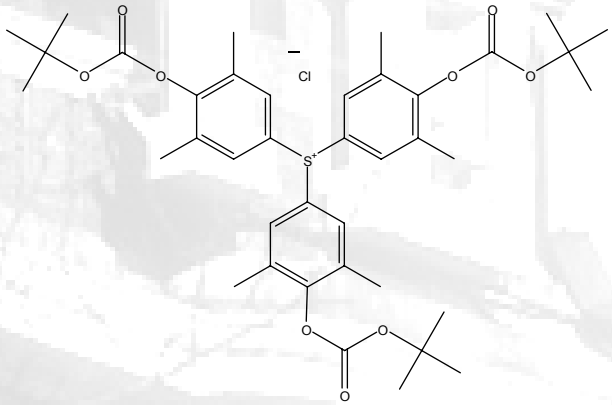


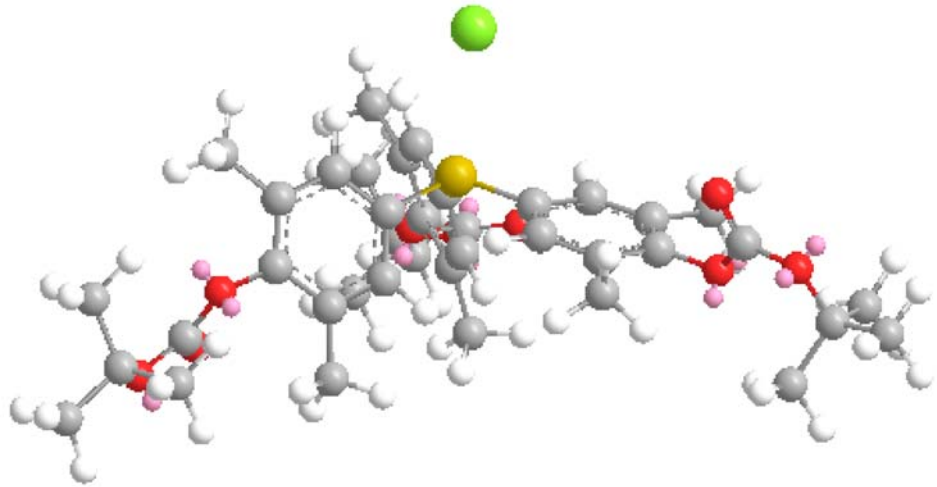
Tests reported here run on the highly substituted (i.e. highly protected) material (57.4% tri-, 40.8% di-, 1.8% mono-protected).

Comparison of Glass 3-D Structures





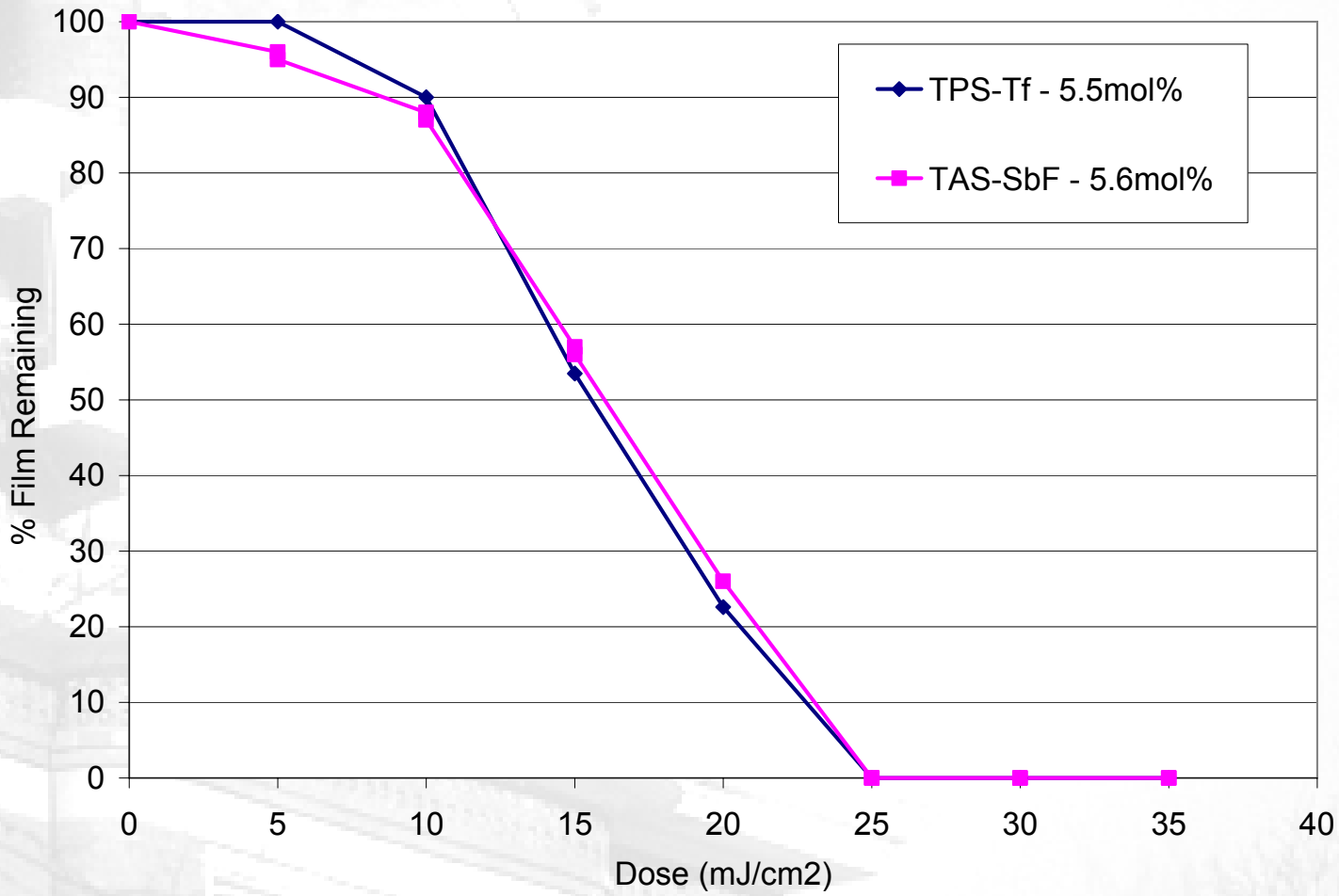




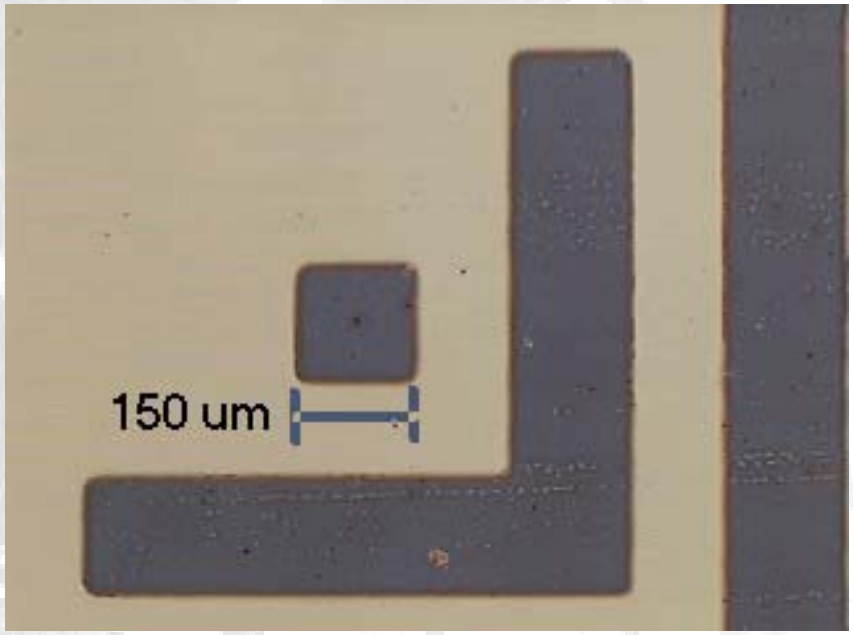
- TAS appears to be less planar than other similar reported molecular glasses
- Anion appears to possibly improve non-planar character
- Structures obtained by MM2 method energy minimization

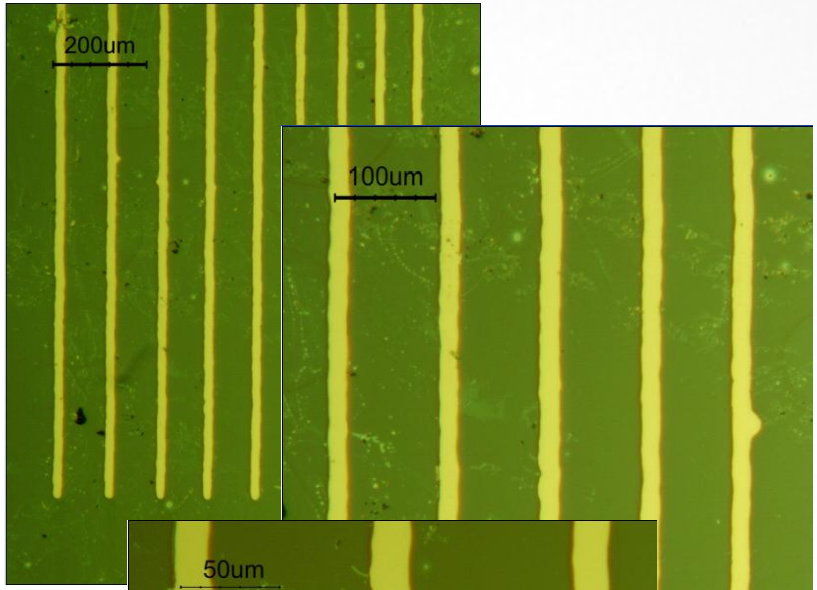
Proof of PAG Activity

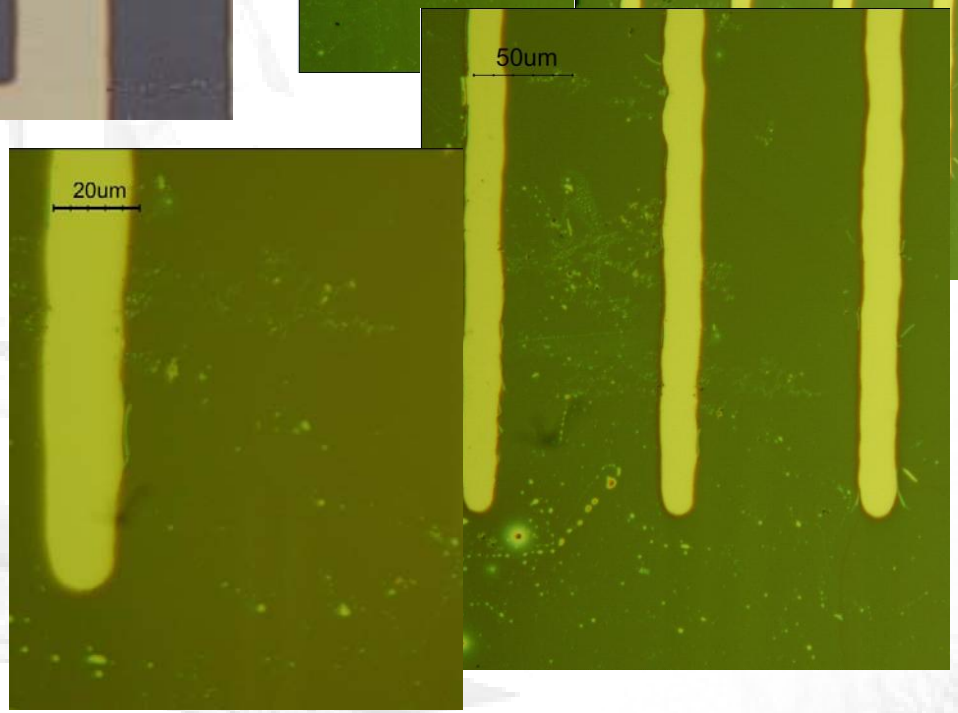
- After synthesizing the TAS, it's imaging performance was compared to commercial triphenylsulfonium triflate by using them both purely as PAGs in a fully protected tris(4-*tert*-butoxycarbonyloxyphenyl)ethane molecular glass resist and comparing the contrast curve using 248 nm UV light. The two PAGs perform similarly.



DUV Patterning of TAS-SbF_6 Film

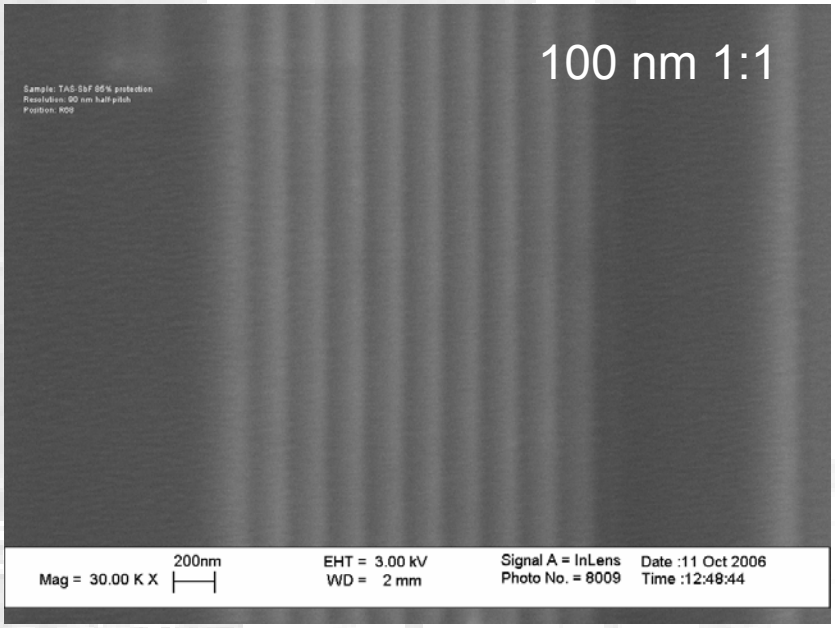


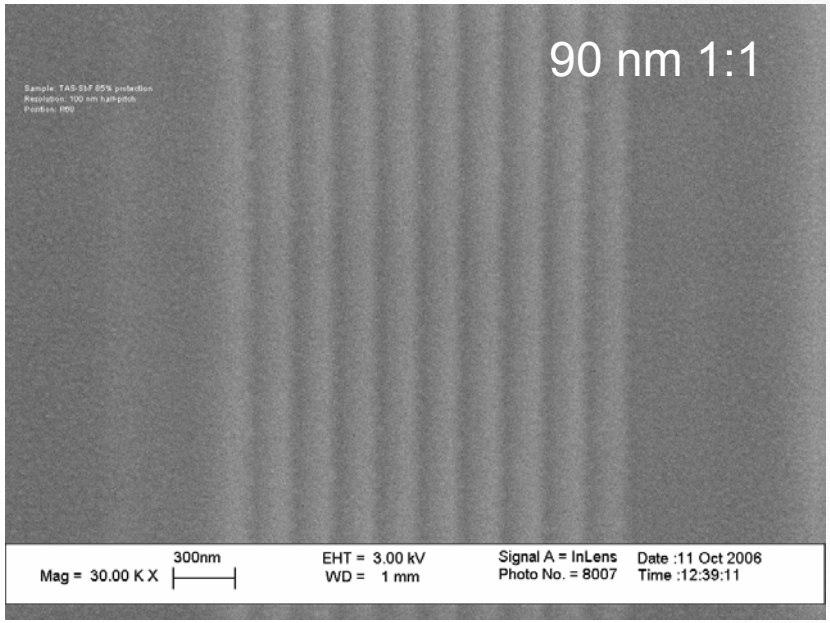


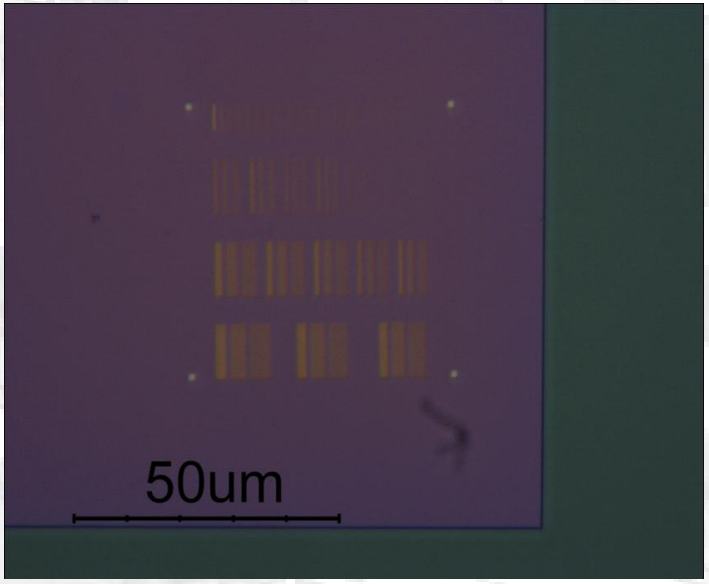


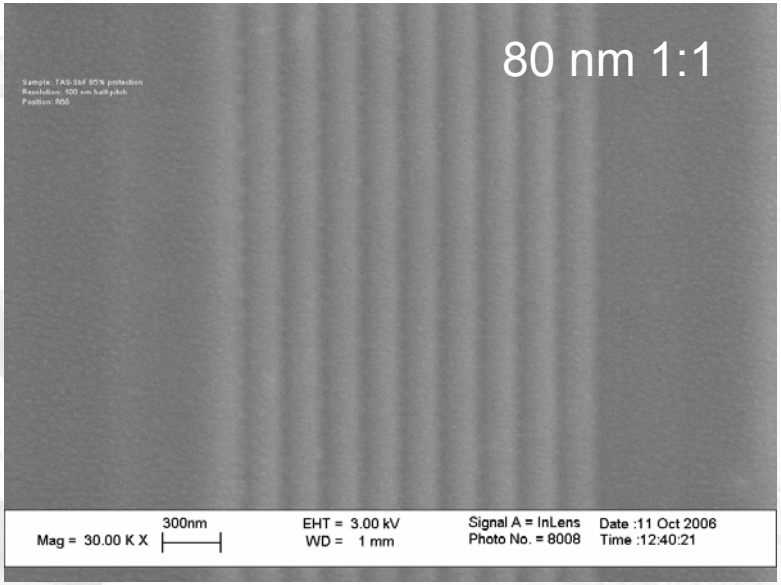
Contact printed first at DUV to verify ability to image and check PEB conditions (100 C for 60 s).

E-beam Patterning of TAS-SbF_6 Films









Etch Performance of TAS-SbF_6

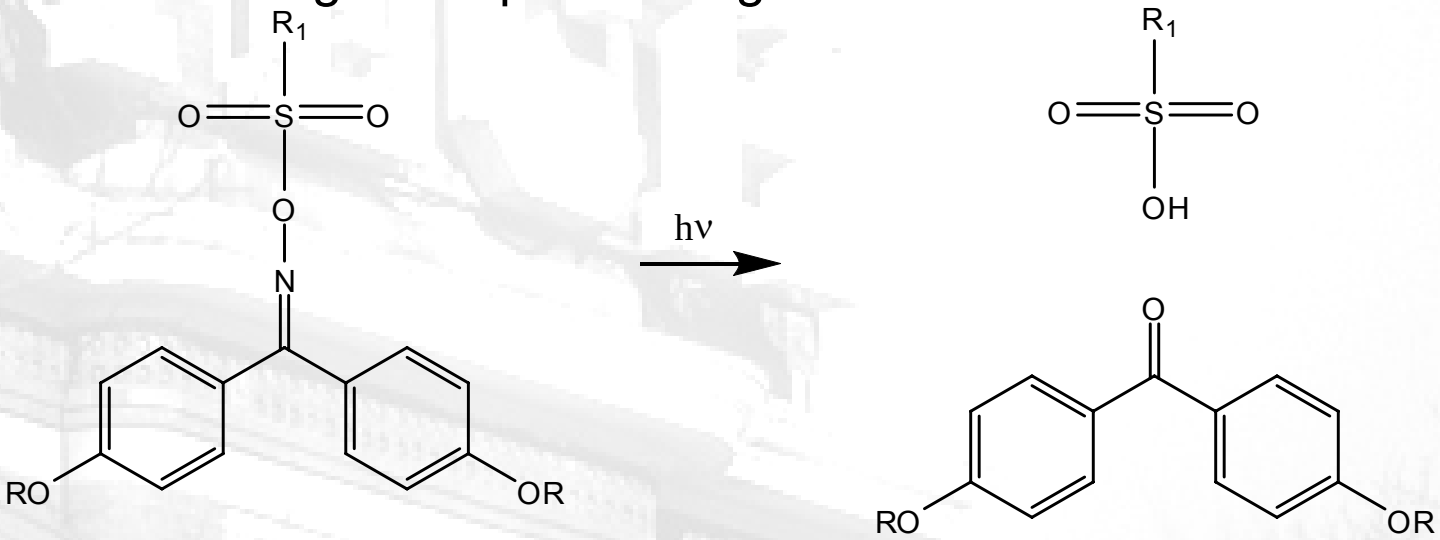
- Silicon oxide RIE halogenated etch (PlasmaTherm)

	Etch Rate (nm/s)	Normalized Etch Rate
Novolac Resist (Shipley 1813)	3.0	1
PHOST	4.1	1.37
TAS-SbF_6 molecular glass	3.2	1.07

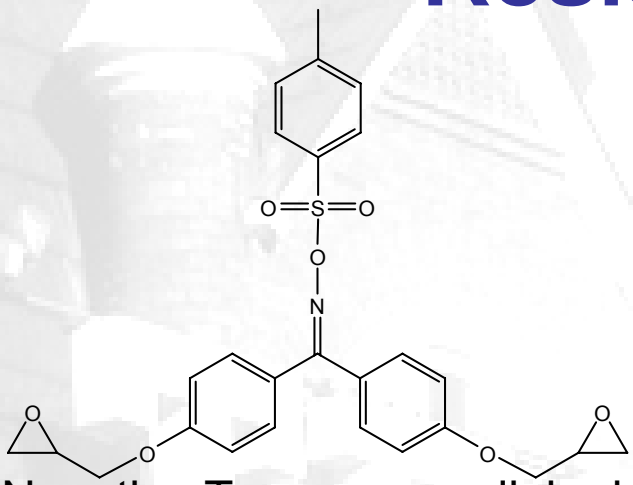
Generation 2 Single Component Molecular Glass Resists:

Non-ionic PAG Functionalized Glasses

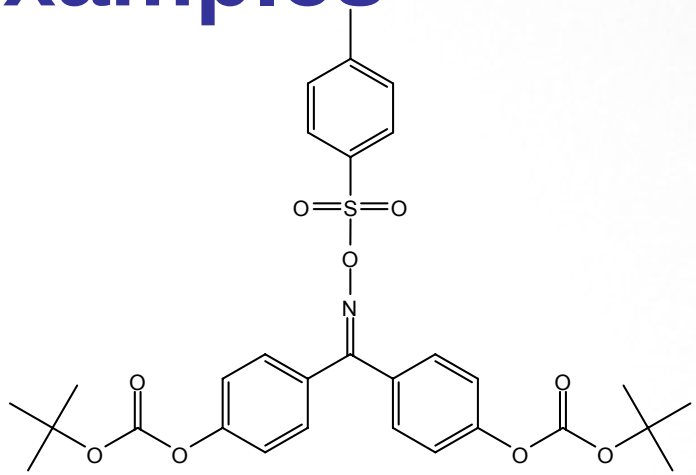
- Onium salt based PAG compounds have limited solubility in solvents and triphenyl sulfonium core can fragment to produce benzene and other products that can outgas.
- Non-ionic PAG functional groups are being explored to increase solubility of compounds and lower outgassing.
- Oxime sulfonate based PAGs provide good flexibility for molecular design. Since core remains essentially intact after exposure, also opens easy routes to single component negative tone resists.



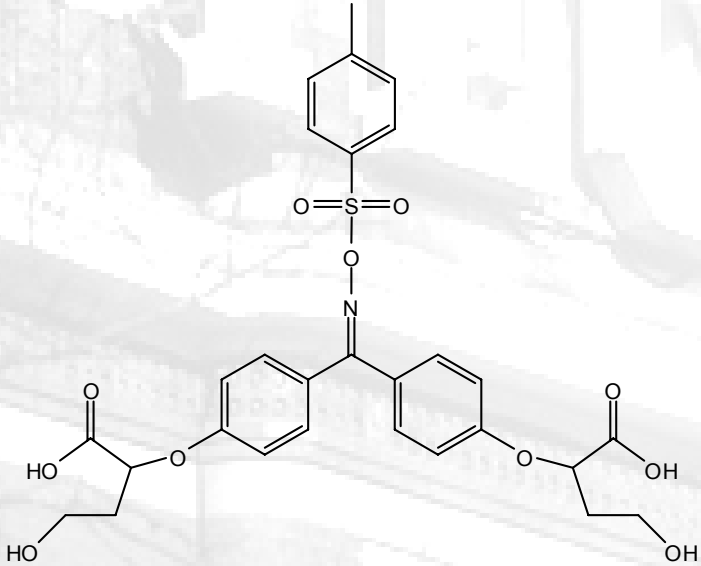
Next Generation Non-Ionic Molecular Resist Examples

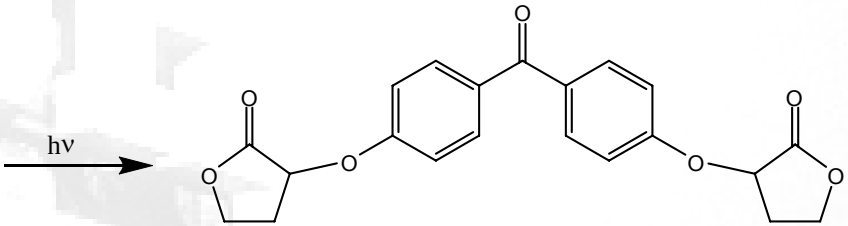


Negative Tone – cross-linked



Postive Tone - deprotection

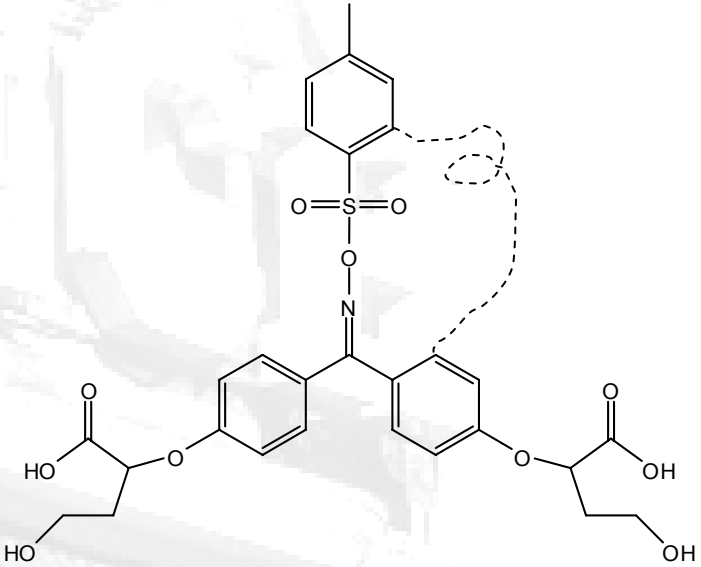




Negative-tone based on acid-catalyzed lactone ring closing

Tethering of Photoacid Anion to Molecular Glass Core

- Exploring chemistries to make tethered photoacid glasses.
- Exploring impact of tethering photoacid on resist sensitivity.
- Exploring impact of tehthering photoacid on catalytic chain length.



A Near Zero Mass Loss Single Component Molecular Glass Resist.

Conclusions

- First examples of single component molecular glass resists synthesized & demonstrated.
- Onium salt system demonstrates basic feasibility and shows good contrast, high sensitivity, high resolution, and good etch performance.
- Non-ionic PAG functionalized materials designed and currently being synthesized.
- Both positive and negative tone systems being studied to understand advantages, disadvantages, and capabilities.
- LWR and ultimate resolution studies underway.

- Back up

Future Resist Performance Requirements

2005 International Technology Roadmap for Semiconductors (ITRS)

Year of Production	*2005*	*2006*	*2007*	*2008*	*2009*	*2010*	*2011*	*2012*	*2013*
DRAM ½ pitch (nm) (contacted)	*80*	*70*	*65*	*57*	*50*	*45*	*40*	*36*	*32*
Flash ½ pitch (nm) (un-contacted poly)	*76*	*64*	*57*	*51*	*45*	*40*	*36*	*32*	*28*
MPU/ASIC Metal 1 (M1) ½ Pitch (nm)(contacted)	*90*	*78*	*68*	*59*	*52*	*45*	*40*	*36*	*32*
MPU physical gate length (nm) [after etch]	*32*	*28*	*25*	*23*	*20*	*18*	*16*	*14*	*13*
MPU gate in resist length (nm)	53	47	42	38	33	30	27	24	21
*Resist meets requirements for gate resolution and gate CD control (nm, 3 sigma) **†*	3.3	2.9	2.6	2.3	2.1	1.9	1.7	1.5	1.3
*Resist thickness (nm, single layer) ****	150–265	125–225	110–200	100–180	90–160	80–145	70–130	60–115	55–100
PEB temperature sensitivity (nm/C)	2	1.75	1.75	1.5	1.5	1.5	1.5	1.5	1
*Low frequency line width roughness: (nm, 3 sigma) <8% of CD ******	4.2	3.8	3.4	3.0	2.7	2.4	2.1	1.9	1.7

Exposure Technology	*Sensitivity*
248 nm	10–50 mJ/ cm^2
193 nm	20–50 mJ/ cm^2
Extreme Ultraviolet at 13.5 nm	5–15 mJ/ cm^2
*High Voltage Electron Beam (50–100 kV) *****	5–10 μC/ cm^2
*Low Voltage Electron Beam (1–2 kV) *****	0.2–1.0 μC/ cm^2

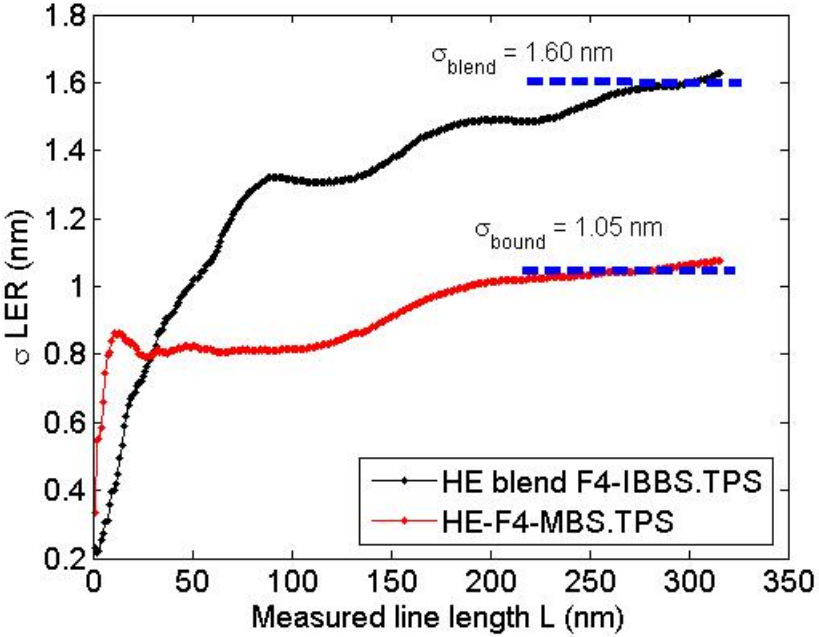
Manufacturable solutions exist, and are being optimized
Manufacturable solutions are known
Interim solutions are known
Manufacturable solutions are NOT known

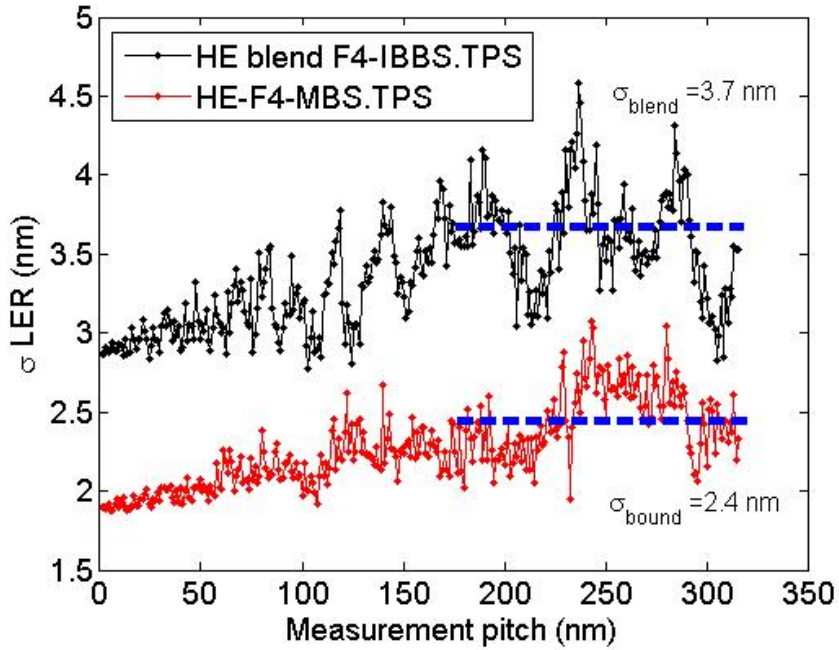
ITRS Lithography 2005

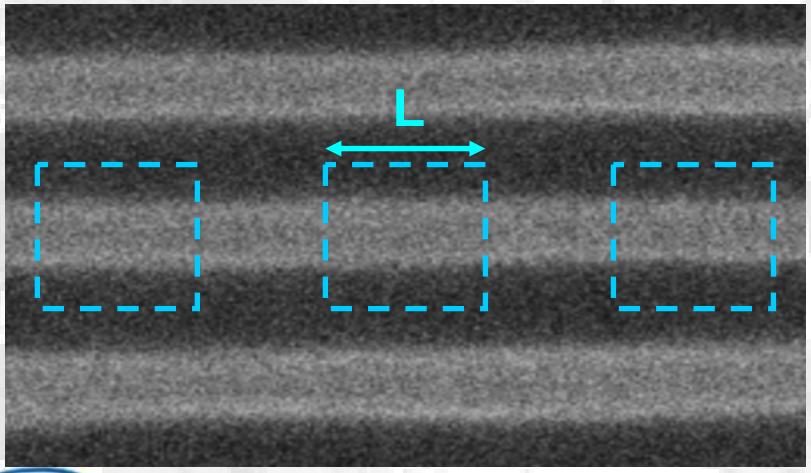
Requirements for NGL resist materials (including EUV) are:

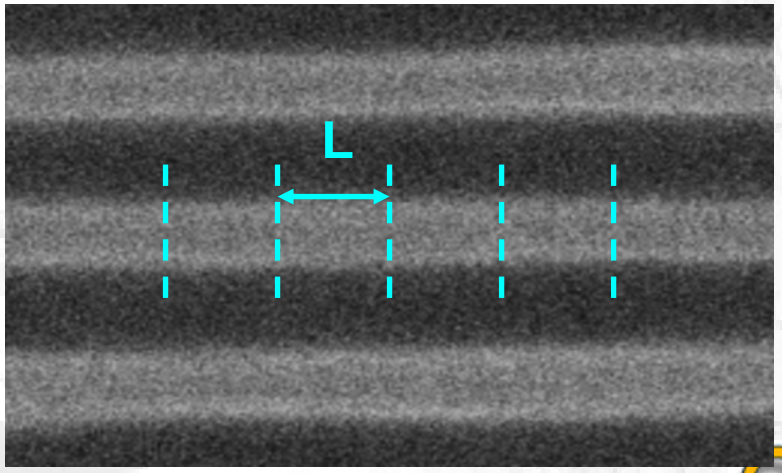
- High sensitivity (absorbance, quantum efficiency, catalytic chain length).
- High resolution (acid diffusion).
- Low line width variation (acid diffusion, homogeneity of material).

Spatial-frequency dependent LER for EUV blend and polymer-bound PAG samples



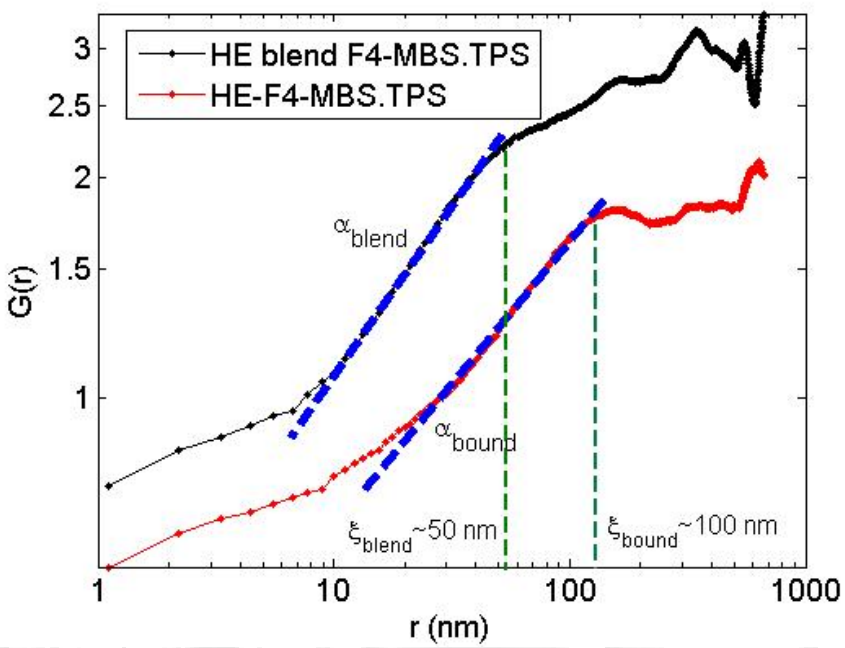




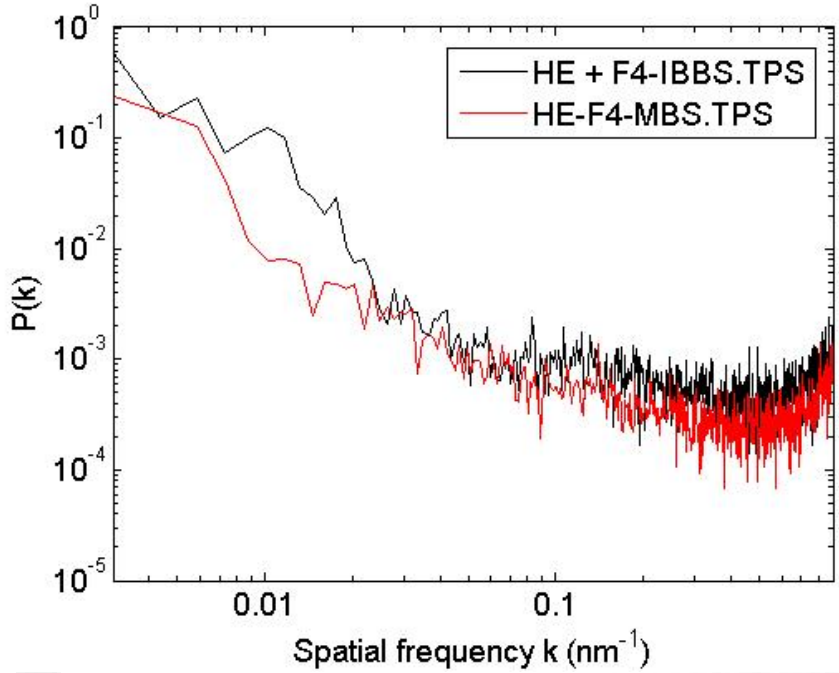


Spatial-frequency dependent LER for EUV blend and polymer-bound PAG samples

Height-height correlation



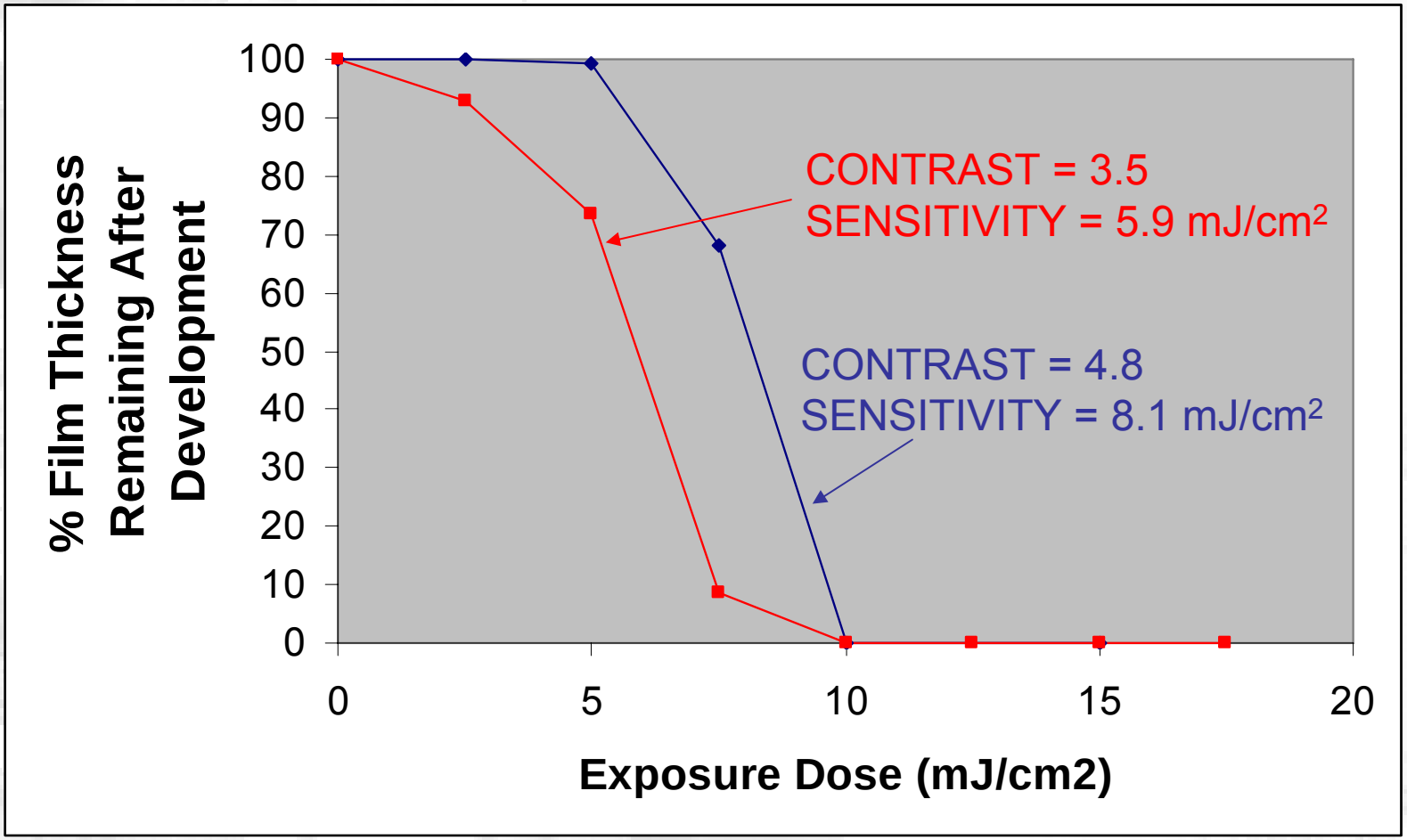
Power spectra (DFT)



- Blend sample showed smoother high-frequency LER (smaller roughness exponent) and shorter correlation length (shorter line length over which the LER becomes independent of measured line length).
- Low spatial-frequency components are most significant for LER in both samples.

DUV Contrast Curve of Pure TAS Films

- Sensitivity and contrast of a pure 100 nm thick TAS film was tested using 248 nm UV light, with a PEB of 100°C for 60 seconds



Basis for Design of a Model Single Component Molecular Glass Resist

- Many molecular glasses are made of star-shaped molecules with a phenyl rings extending from a common core. This looks very similar to triphenylsulfonium. Thus is was thought a functionalized triphenylsulfonium core would probably be able to form amorphous films and function directly as a resist.

- It was also desired to incorporate an acid-catalyzed solubility switch into the compound. This would be suitably achieved using phenolic hydroxyl groups protected using t-Boc or other similar groups.

- The t-Boc unit was also thought to be able to prevent crystalline packing, forcing the molecule to be amorphous.