Lithographic performance of EUV resists based on polymers having a photoacid generator in the backbone

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» OUTLINE

- OBJECTIVES
- PAGs incorporated in resist main chain:
  - Microstructure
  - Synthesis & Characterizations
  - EUVL exposure and sub 100 nm patterns
  - 193 nm exposure and sub 100 nm patterns – preliminary data

- **OBJECTIVES & TARGETS**
- ***MATERIALS DESIGN & MODIFICATION SPECIFICALLY FOR EUVL***

Polymer Bound PAG

Compatibility- Improving acid uniformity

Enhanced lithographic properties such as photospeed (& LER)

AROMATICITY

Transparency

Etch Resistance

EUV RESIST PARAMETERS

Thin Film : 100 nm

Resolution : 35 nm

Sensitivity : < 10 MJ/cm2

Contrast : > 5

Etch Resistance : PHS

Adhesion

Low outgassing

Low LWR

Resist Material Design

Adhesion Units / Etch Resistance	Acid Labile Units / Etch Resistance	Polymer-Bound PAG
•Adhesion on Substrates	•Deprotection Reaction for polarity change	• Compatibility • Reduction of Outgassing • Improvement of Acid Uniformity
• Hydroxystyrene	• Adamantyl Protecting Group	• Ionic & Covalent PAG

Chemically amplified resists (CAR) with PAG units in the polymer chain

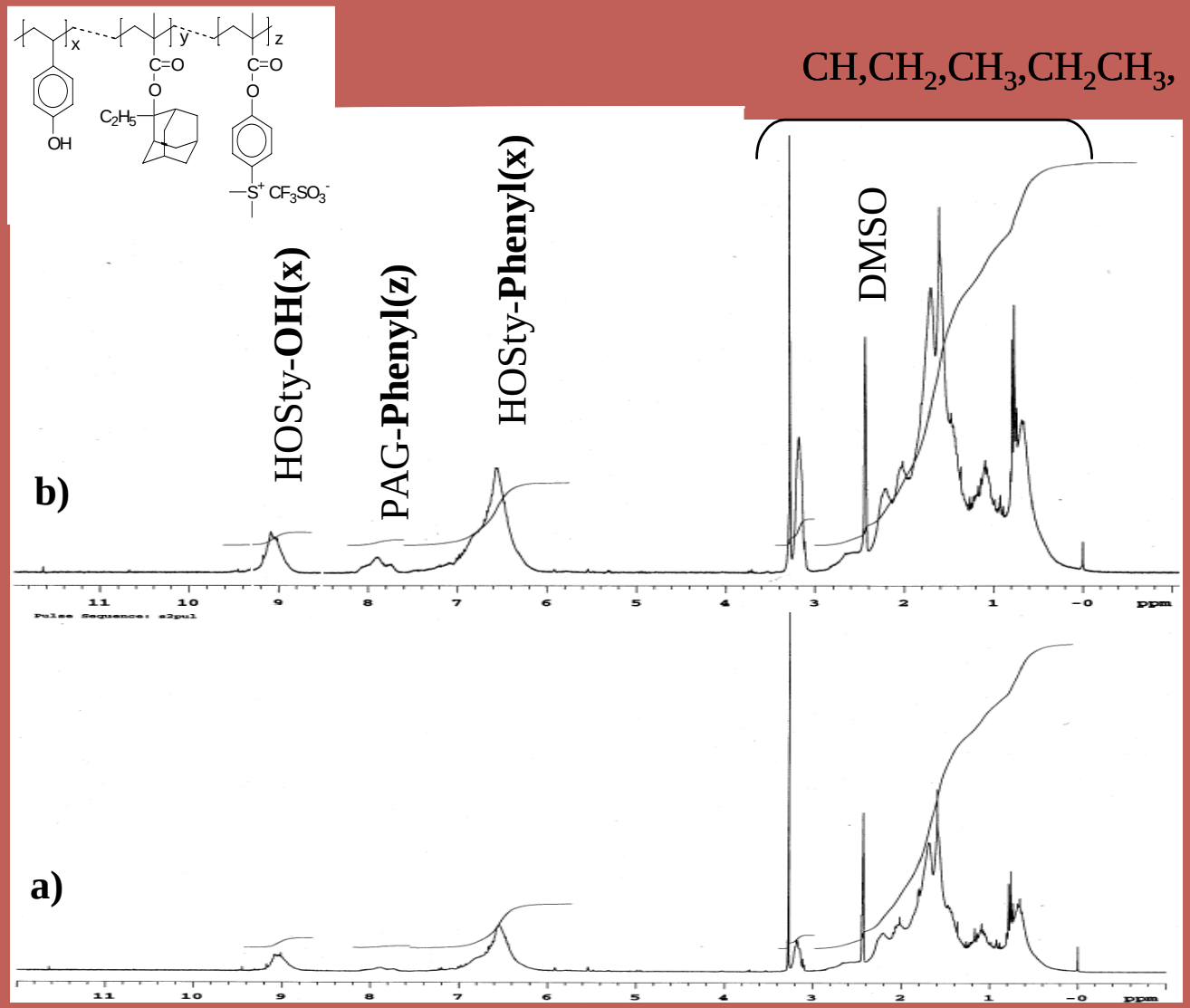
References :

1. H. Wu and K. Gonsalves, Adv. Funct. Mater., 11(4), 271 (2001)
2. H. Wu and K. Gonsalves, Adv. Mater., 13(3), 195 (2001)
3. H. Wu and K. Gonsalves, Adv. Mater., 13(9), 670 (2001)

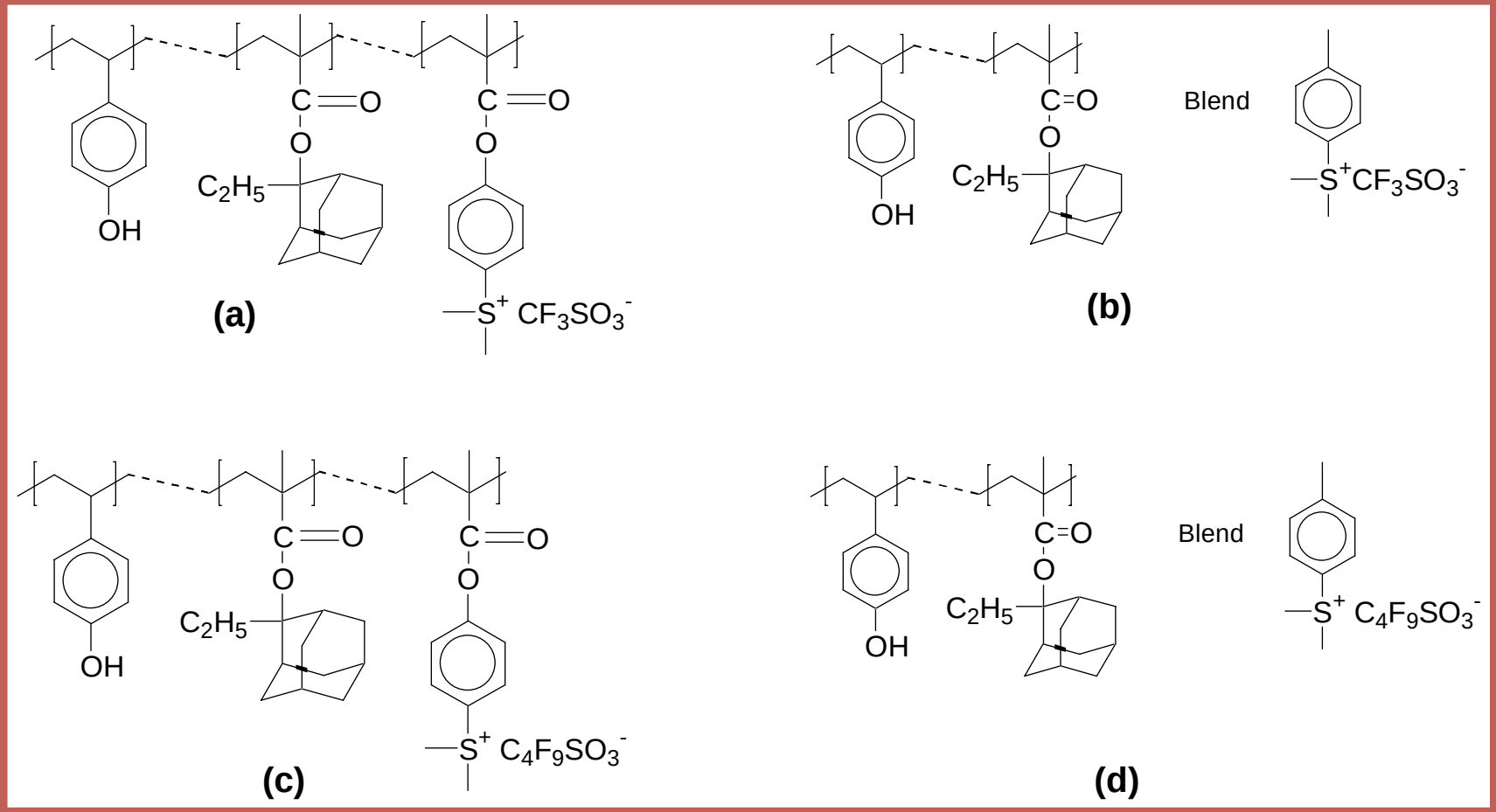
Polymerization Results of poly(4-hydroxystyrene-co-2-ethyl-2-adamantyl methacrylate-co-phenylmethacrylate dimethylsulfonium triflate)

Polymer	Molar Feed Ratio			Copolymer Composition (by ^{1}H NMR)			Yield (%)	Mw (MWD)
	HOST	EAMA	PAG	HOST	EAMA	PAG		
1*	33.4	64.0	2.6	45.2	52.8	2	80	3000(2.0)
2*	31.5	63.2	5.3	46.0	49.0	5	72	2500(1.8)
3*	30.0	60.0	10.0	38	55.0	7.0	83	2800(2.0)
4	30.0	57.0	13.0	42.0	47.5	10.5	78	1900(1.6)

500MHz ^{1}H NMR spectra of Poly(HOST-co-EAMA-co-PAG), using DMSO-d_6. a)2 % PAG loading in the polymer ; b) 5% PAG loading in the polymer

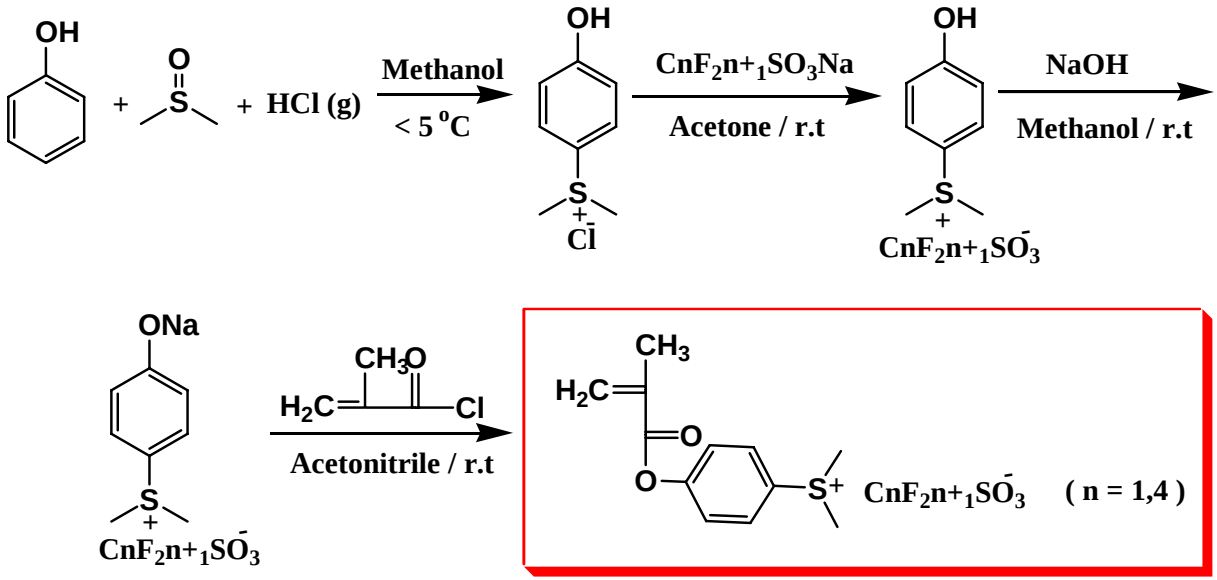


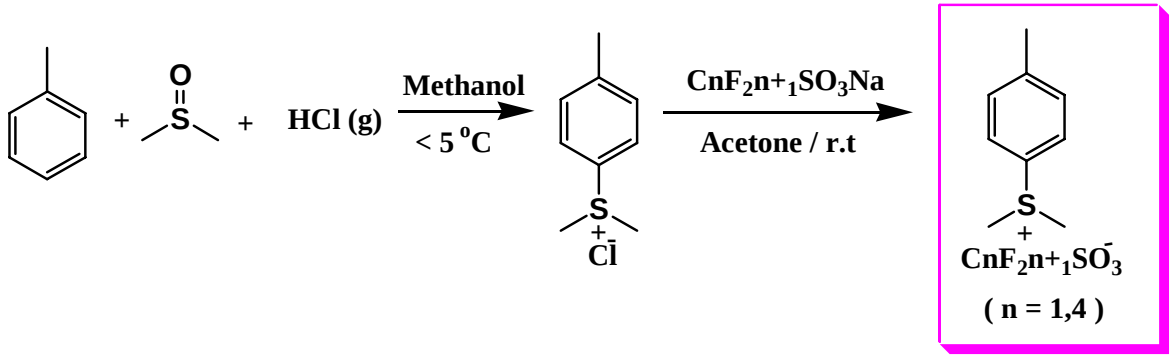
MICROSTRUCTURES OF POLYMERIC RESISTS



a) Poly(HOST/EAMA/PAG1): M_w 2500 ; b) Poly(HOST/EAMA) blend PAG3): M_w 2750 ; c) Poly(HOST/EAMA/PAG2): M_w 3245; d) Poly(HOST/EAMA) blend PAG4) : M_w 3320

The Synthesis of Known PAG Monomers & PAGs





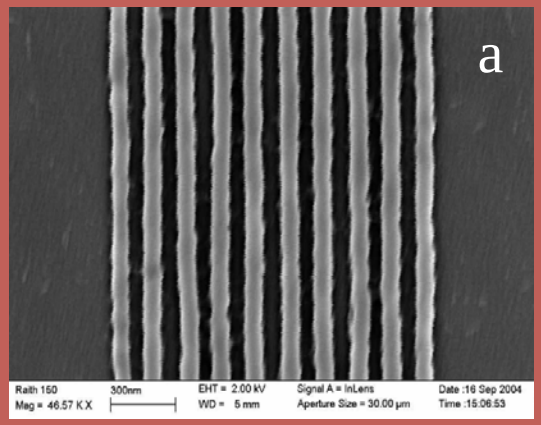
FORMULATIONS

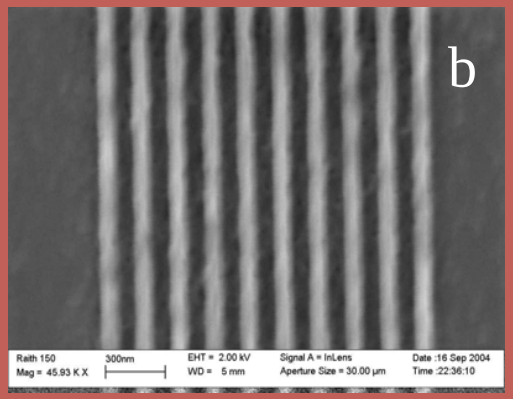
Poly(Hosty-*co*-EAMA-*co*-IPG)

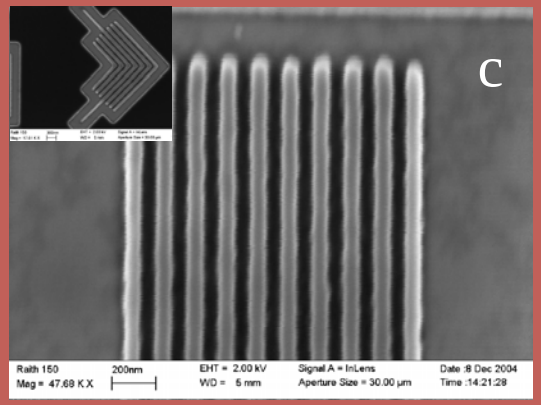
- Tetrabutyl ammonium hydroxide (TBAH) (0.2 wt %); added to control acid diffusion
- Solvent PGME
- Resist thickness 120 nm
- Post apply bake 100C/90 s
- Exposure at LBNL
- PEB 105C/90 s
- Development 2.38 % TMAH 60 s

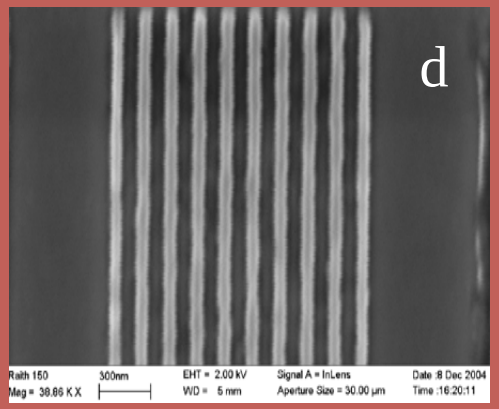
Same process used with polymer blend cationic PAG process.

EUV Images: PAG *bound* Vs *Blend* <u>Nonaflate</u> PAG



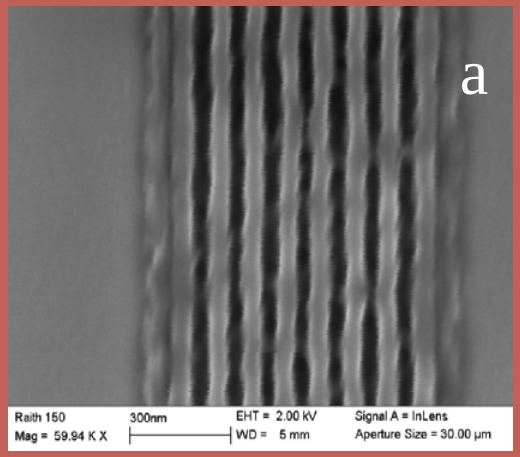


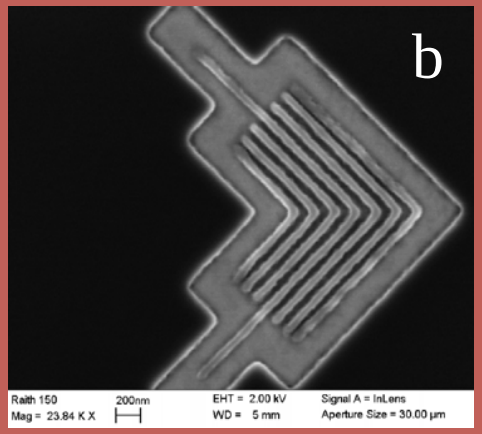




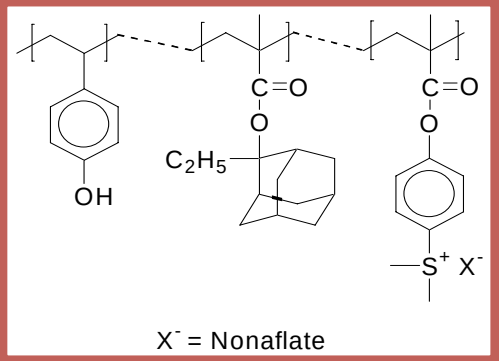
Top-down Scanning electron micrograph images of 70nm (L/S) (1:1) pattern profile of a) Poly(HOST-co-EAMA-co-PAG1); b) poly(HOST-co-EAMA)blend PAG3; c) Poly(HOST-co-EAMA-co-PAG2) and d) poly(HOST-co-EAMA)blend PAG4. Images obtained under identical formulation conditions. 5% PAG incorporated in the main chain of polymer and blended in the polymer matrix.

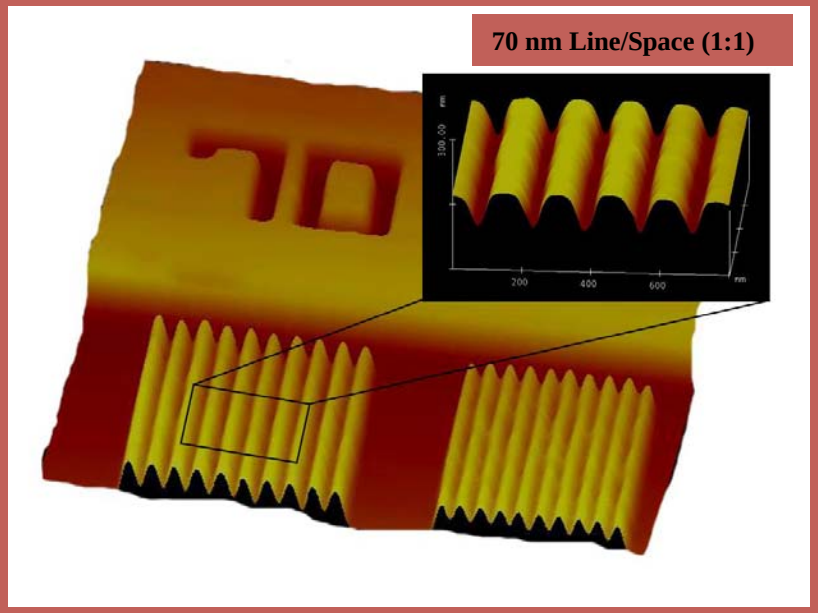
a) **45 nm Line (90 nm pitch) pattern profile of Poly (HOST-co-EAMA-co-PAG2): 5% PAG containing nonaflate counter anion in the main chain; b) Corresponding elbow pattern**





AFM Analysis





- **Tapping Mode**

  Surface Roughness (RMS) :0.45 nm

- **Polymer *Bound* (Nf) PAG showed *Less Surface Roughness* than the *Blend* PAG samples**

Photospeed and Line edge roughness measurements of polymer bound and blend PAG resists

LER Measurements done using SUMMIT Software *

Sample	LER(nm)	Photospeed(mJ/cm^2)
poly(HOST-co-EAMA-co-PAG1)	5.7	8.7
poly(HOST-co-EAMA) blend PAG3	6.9	10.8
poly(HOST-co-EAMA-co-PAG2)	4.6	6.5
poly(HOST-co-EAMA)blend PAG4	6.7	8.0

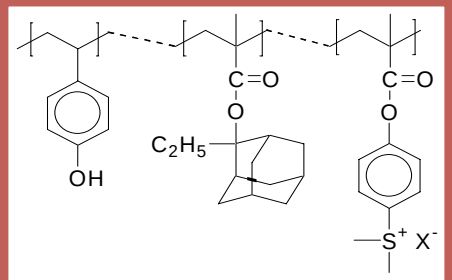
- **Polymer *Bound* PAG resist showed less LER and high photospeed than *Blend* PAG resists**

- **Energy Transfer from Polymer to PAG through covalent bond is efficient**

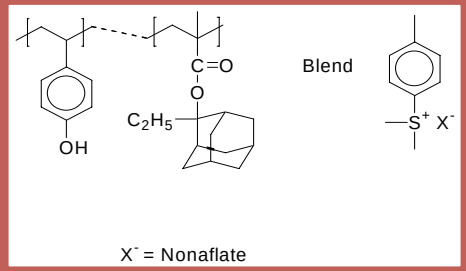
- **L.E.Ocola, Mater.Res.Soc.Symp.Proc. 705,(2002) 23**

* http://euvl.com/summit/

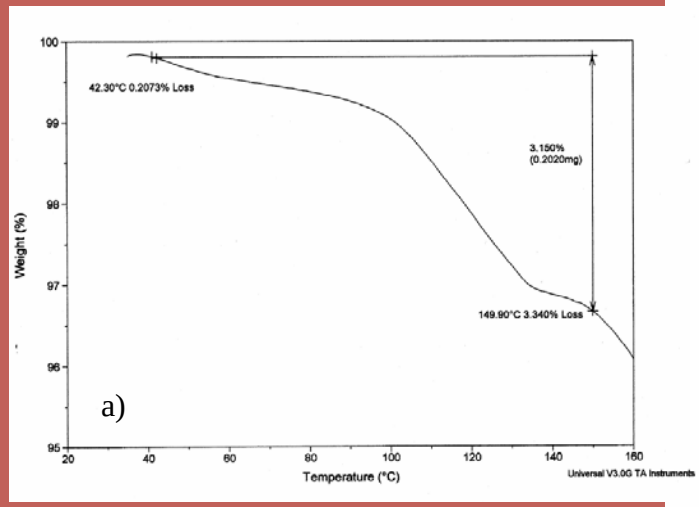
Thermogravimetric Analysis curves of a) Poly (HOST-co-EAMA-co-PAG2) and b) poly(HOST-co-EAMA) blend PAG4. The weight loss (%) calculated under identical experimental condition and temperature range of 40ºC and 150ºC.

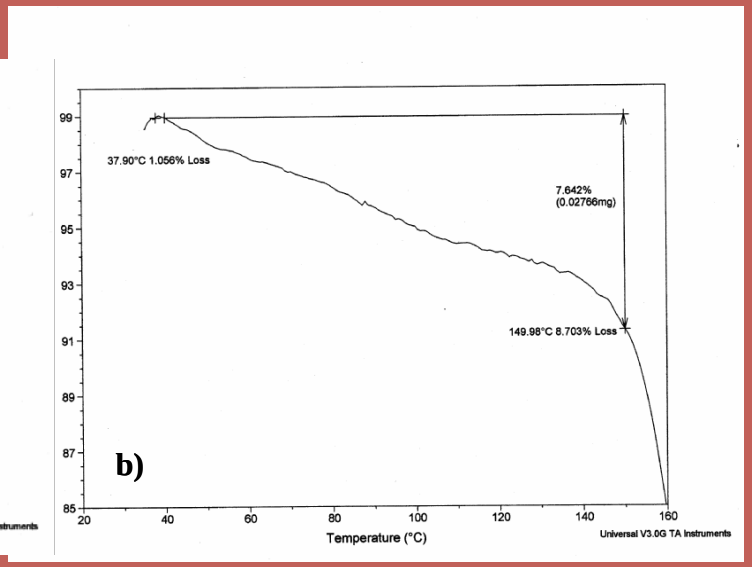


X^- = Nonaflate



X^- = Nonaflate

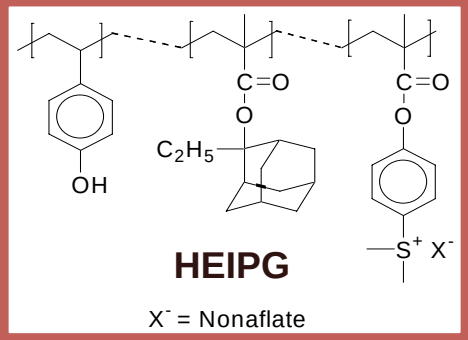


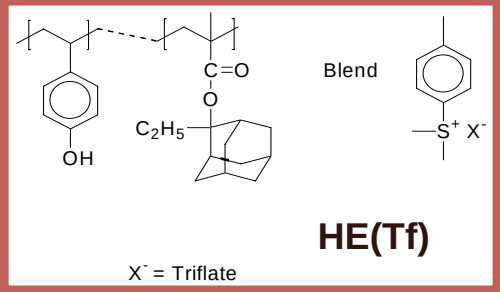


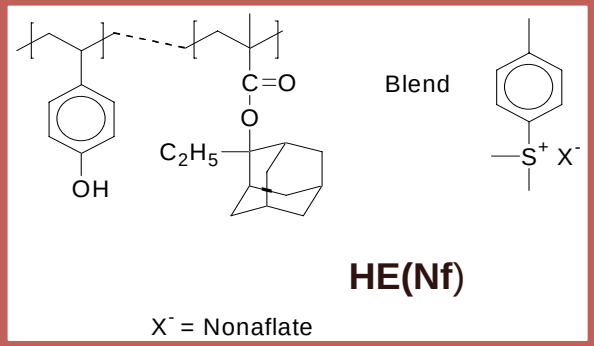
➢ **Weight loss of Polymer *Bound* PAG resist is less than *Blend* PAG sample**

Outgassing Data

OUTGASSING DATA		Canister				Desorption	
Products	HE1PG	HE(Nf)	HE(Tf)		HE1PG	HE(Nf)	HE(Tf)
Carbon dioxide	92.61	84.4	83.8				
Norflurane		1.46	1.16				
Methanol		0.5					
Ethanol	2.07	0.58					
Acetone	1.66	1.57					
Benzene		4.5	5.24			38.86	35.08







- Outgassing data of polymer bound PAG and Blend PAG resists: Norflurane observed in blends only, as well as benzene

Photoacid Diffusion Coefficients via IDEs

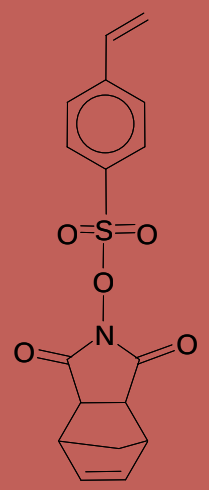
Preliminary Initial Data

in collaboration with
Prof.Clifford L. Henderson
School of Chemical & Biomolecular Engineering
Georgia Institute of Technology

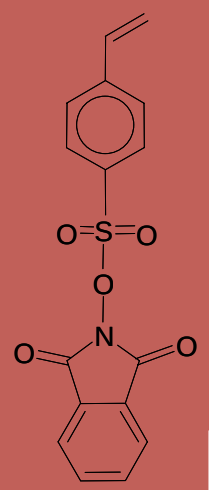
Resist Type	D (cm^2/s)
Blend	7×10^{-13}
Bound PAG	3×10^{-13}

Norbornene and Phthalimide based Covalent PAGs

I

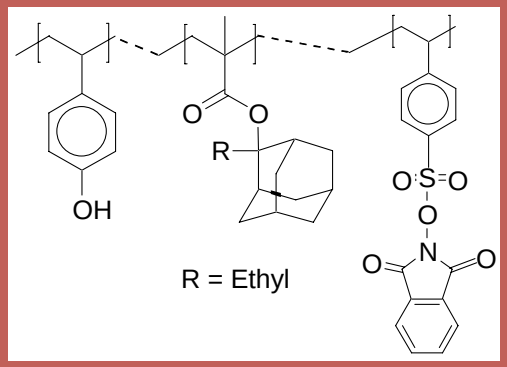


II



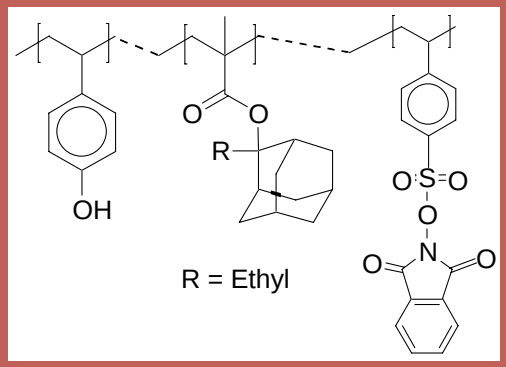
Polymeric PAG's:

IN-styrenesulfonyloxy-5-norbornene-2,3 dicarboxyimide (SSNI)
IIN-styrenesulfonyloxy phthalimide (SSPI)



Poly(HOST-co-EAMA-SSPI) 1

Polymer	Feed Ratio (mole %)			Mole Ratio in the polymer (mol) %)		
	HOST	EAMA	SSPI	HOSty	EMA	SSPI
1	46.3	48.2	5.5	56.9	35.1	**8**

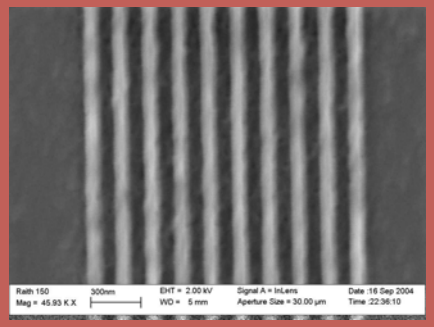


Poly(HOST-co-EAMA-SSNI) 2

Poly mer	Feed Ratio (mole %)			Mole Ratio in the polymer (mol %)		
	HOST	EMA	SSNI	HOST	EMA	SSNI
2	46.5	48.2	5.3	55.5	38	**6.5**

Lithographic evaluation:

A preliminary attempt has been made to image the covalent PAG bound polymer resist, poly(HOST-co-EAMA-co-SSPI). The bases used were tetrabutyl ammonium hydroxide (TBAH) and trioctyl amine. The resist formulated with TBAH, did not image. We are able to obtain the image for the resist formulated with base, trioctylamine.



Scanning electron micrograph of EUVL pattern profile of Poly(HOST-co-EAMA-co-SSPI) : 8% PAG loading in the main chain. 100 nm line (200 pitch) pattern was obtained using trioctylamine as base. Exposure done at Lawrence Berkeley National Laboratory.

This resist show 100nm line (200 pitch) pattern at photospeed of 13.6 mJ/cm^2. The acid moiety is attached to the main chain after exposure, not free. Therefore a high dose was required to print the features.

PROJECT SUMMARY

- • *Polymer bound* PAG resists, poly (HOST-co-EAMA-co-PAG) have been synthesized and evaluated as EUV resist materials with enhanced lithographic properties such as photospeed and LER.

- • The polymer bound PAG resists exhibited faster photospeed and lower LER than the corresponding *blend* PAG resists, poly (HOST-co-EAMA).

- • These results imply that this novel resist has advantages over conventional resists and should be further explored for application in EUV lithography.

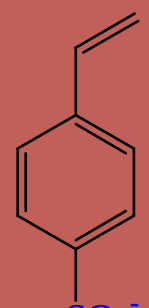
• Furthermore, use of different counter anions such as triflate and nonaflate influenced the lithographic performance. Sub-100nm features were obtained with enhanced lithographic performance using EUV exposure.

Keywords: Photoacid generator (PAG); hydroxystyrene (HOST); ethyl adamantyl methacrylate (EAMA).

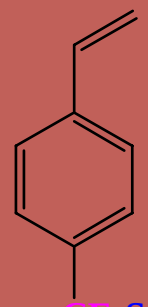
ACHIEVEMENTS

- Synthesis of photoacid generators (PAG)- both *cationic* and *covalen*t analogs.
- Incorporation of PAGs into polymeric microstructures having aromatic and acid labile adamantyl groups.
- Detailed characterizations of the resists by NMR, IR, GPC.
- EUVL exposure at U. Wisconsin at Madison, and LBL : sub-100 nm images obtained
- Assessments of photospeed and LER : 6.5 mJ/cm^2 and LER 4.6 nm for poly(HOST-co-EAMA-co-PAG2)
- Some very initial determination of acid diffusion : blend vs bound PAG (*results not conclusive*)

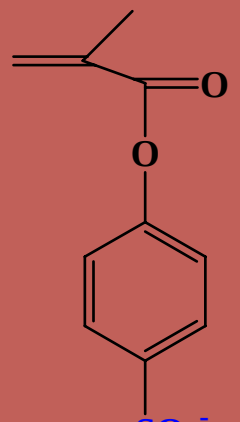
ANIONIC PAGS (Future works)



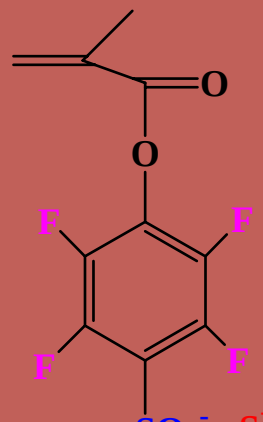
SO_3^- ($S^+ Ø_3$, $S^+ Me_2Ø_3$, $I^+ Ø_2$)



$CF_2SO_3^-$ ($S^+ Ø_3$, $S^+ Me_2Ø_3$, $I^+ Ø_2$)



SO_3^- ($S^+ Ø_3$, $S^+ Me_2Ø_3$, $I^+ Ø_2$)



SO_3^- ($S^+ Ø_3$, $S^+ Me_2Ø_3$, $I^+ Ø_2$)

PUBLICATIONS & PRESENTATIONS

1.“Design and Performance of EUV Resist Containing Photoacid Generator for Sub-100nm Lithography”, with M. Thiyagarajan, K. Dean and E. C. H. Sykes; **J. Nanoscience and Nanotechnology (2005)** *in press*.

2.”Materials Design and Evaluation of Nanocomposite Resists for NGL” **Proc. SPIE 2005** ; with M Thiyagarajan, K. Dean, P. Santiago, L. Rendon, A. Jeyakumar and C. Henderson.

3.“Newly Developed Polymer Bound PAG for Sub 100 nm Pattern by EUV Lithography”; **Proc. SPIE 2005**; with M. Thiyagarajan and K. Dean.

4."New Resists for Nanometer Scale Patterning by Extreme UV Lithography" **Journal of Microlithography, Microfabrication, and Microsystems SPIE (JM³)**; **4(2), April-June 2005** with M. Thiyagarajan and K. Dean.

5.“High Performance Resist for EUV Lithography”, with M. Thiyagarajan, J. H. Choi, P. Zimmerman, F. Cerrina, P. Nealey, V. Golovkina, J. Wallace and N. Batina; **Microelectronic Engr. 2005** Vol 77/1 pp 27-35.

Presentations

1.“Materials Design and Evaluation of Nanocomposite Resists for NGL” SPIE San Jose CA Feb./March **2005** ; with M Thiyagarajan, K. Dean, P. Santiago, L. Rendon, A. Jeyakumar and C. Henderson.

2.“Newly Developed Polymer Bound PAG for Sub 100 nm Pattern by EUV Lithography”; SPIE San Jose CA Feb/March **2005**; with M. Thiyagarajan and K. Dean.

Manuscript submitted

3.“Improved lithographic performance for EUV resists based on polymers having a photoacid generator in the backbone” with M. Thiyagarajan and K. Dean (*submitted JVST B, March **2005** under review*)

- Acknowledgments
- SEMATECH
- Dr Kim Dean Sematech
- LBNL for EUV exposure; Dr Patrick Naulleau