

# Anionic PAG bound photoresists for EUV

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## 1. Objectives & Targets

### Material Design & Modification Specifically for EUV

#### Aromaticity

Transparency, Etch Resistance

#### Chemically Amplified Resists

Resolution, Sensitivity, Contrast

#### Polymer-Bound PAG

Compatibility, Improving Acid Uniformity



## 2. Advanced Photoresist Microstructures for EUV

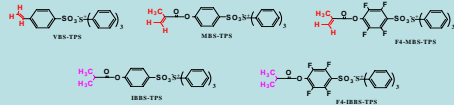
**HOST**  
-Adhesion to Substrate  
-Etch Resistant  
-Transparency

**EAMA**  
-Deprotection Reaction for Polarity Change  
-Etch Resistant

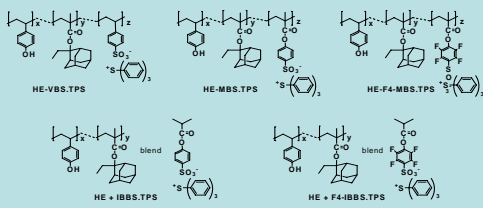
**PAG: R = H, O<sub>2</sub>**  
-Low line Edge roughness  
-Low Outgassing  
-High acid Uniformity  
-High Photospeed  
-High Thermal stability

## 3. Structures of Anionic PAGs & Photoresists

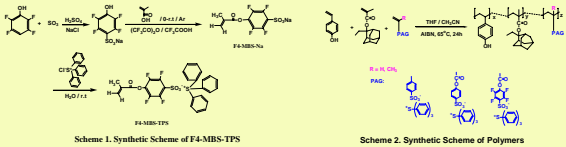
### Anionic PAGs



### Photoresists



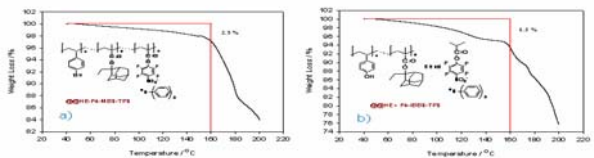
## 4. Synthesis and Characterization of PAGs & Photoresists



### Polymerization Results of Photoresists

Polymer	Mole Feed Ratio			Polymer Composition			Yield / %	Mw / PDI	Stability / °C	T <sub>g</sub> / °C
	HOST	EAMA	PAG	HOST	EAMA	PAG				
HE	40	60		47.2	52.8		60.2	4000 / 1.8	162	113
HE-VBS-TPS	30	65	5	41.7	48.6	9.7	44.3	3700 / 1.7	156	***
HE-MBS-TPS	25	73.5	1.5	37.7	55.8	6.5	35.4	3000 / 1.8	153	***
HE-F4-MBS-TPS	25	72.5	2.5	35.8	57.9	7.1	37.3	3600 / 1.6	145	***
HE-F4-MBS-TPS	25	72.5	2.5	40.2	51.6	8.2	36.8	3100 / 1.9	184	***
HE + IBBS-TPS							6.5**		138	
HE + F4-IBBS-TPS							7.1**		131	
HE + F4-IBBS-TPS							8.2**		130	

\*The Molecular weight was determined by GPC with THF or DMF as mobile phase and polystyrene as narrow standards.  
\*\*w.t%, in order to compare the thermostability and acid generating efficiency of PAG bound polymer with PAG free polymer.  
\*\*\* Could not be determined by DSC, probably due to rigidity of these polymers, resulting from the bulky triphenylsulfonium moiety of the PAG in the polymer chain.  
⊗ These two samples were used for EUV as an exposure.  
⊗⊗ These two samples were used for outgassing and EUV exposure.



PAG bound resist is more thermally stable than the PAG blend resist

## 5. Lithographic properties

### EUV Lithography\*

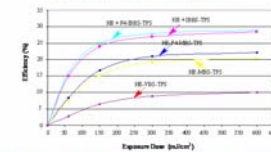
**Formulation**  
Polymers: HE-F4-MBS-TPS, HE-F4-IBBS-TPS  
Solvent: Cyclohexanone  
Resist Thickness: 120 nm  
PAB & PEB: 110°C/30s  
Exposure: Lawrence Berkeley National Lab., 0.3 NA MET based microexposure station  
Development: 2.38 w/vs TMAH developer, 15-s

### E-beam Lithography\*\*

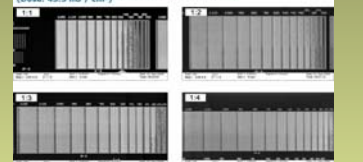
**Formulation**  
Polymers: HE-F4-MBS-TPS, HE-F4-IBBS-TPS  
Solvent: Cyclohexanone  
Resist Thickness: 110-150 nm  
PAB & PEB: 110°C/30 s  
Development: 2.38 w/vs TMAH developer, 15-20 s

Sample		Resist	HE-F4-MBS-TPS	A3209	resist	exposure F-117
R.T. (nm)	prob. area	Area	coverage	Area (μm <sup>2</sup> )	Area (μm <sup>2</sup> )	exposure time for single cycle (min)
2475	40004	Resist	78	7.87E-10	7.87E-10	9.17E-12
8287	3028	Cyclohexanone	112.77	7.87E-10	7.87E-10	5.12E-10
10288	4648	Enhance 611	85.642	7.87E-10	7.87E-10	9.87E-10
15460	34732	Enhance C11 lower	142.91389	7.87E-10	7.87E-10	1.71E-12
18466	9835	Enhance Advantec/Impreg	139.246	6.44E-10	6.44E-10	2.09E-11
						<b>Total</b>
						<b>1.67E-13</b>

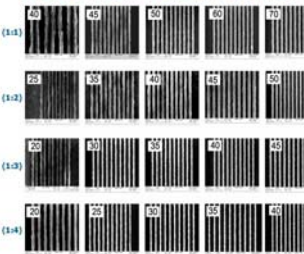
### Acid Generation Efficiency at 254 nm



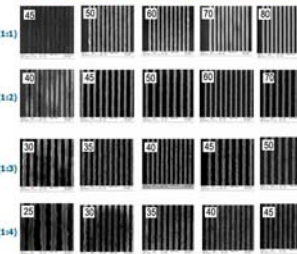
### SEM of PAG bound Polymer (20-120nm) Line/Space



### SEM of PAG bound Polymer Line/Space (Dose: 43.5 mJ / cm²)



### SEM of PAG blend Polymer Line/Space (Dose: 24.7 mJ / cm²)



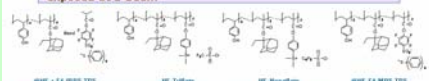
### SEM of PAG bound Polymer Elbow Pattern (Dose: 43.5 mJ / cm²)



### SEM of PAG blend Polymer Elbow Pattern (Dose: 24.7 mJ / cm²)



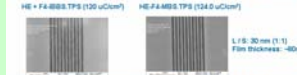
### LER comparison of different PAGs bound or blend polymers exposed at E-beam



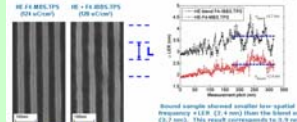
EUV nm Resist	HE ratio (mol%)	PAG loading (mol%)	Film thickness (nm)	Half pitch resolution (nm)	Photospeed (nm/s)	3σ LWR (nm)
HE + F4-IBBS-TPS (120 nm)	45.8 / 54.2	7.1 (w/vs)	91.2	30	26	10.7 / 15.6
HE + F4-MBS-TPS (120 nm)	45.0 / 49.0	6.0	76.1	40	25	9.5 / 13.6
HE + IBBS-TPS (120 nm)	N/A	N/A	103.7	50	31	6.4 / 12.0
HE + F4-IBBS-TPS (120 nm)	35.0 / 65.0	7.1	84.8	30	33	7.8 / 11.4

LER: 1) Anionic PAG bound polymer > Cationic PAG bound polymer > Anionic PAG blend resists, 2) LER of EUVL is within the same range as EBL, in both cases no loss was added.

### SEM of PAG bound or blend Polymers exposed at E-beam



### Spatial-frequency dependent LER of PAG bound and blend samples



Conclusion: PAG bound sample showed smaller low spatial frequency LER (1.0 nm) than the blend one (3.7 nm). This result corresponds to 0.9 nm difference of PAB.PEB.

### Acknowledgments

- Intel Corp.: Financial support, Outgassing & EUV
- Dr. H. Cao
- Lawrence Berkeley Lab., EUV exposure
- University of Wisconsin @ Madison, CNTech & SRC (Outgassing test)
- Georgia Institute of Technology: E beam @ LER
- AZ Electronic Materials Ltd: Supporting monomers

### Summary

- Designed and characterized novel anionic PAGs and corresponding EUV resists (anionic PAGs bound polymers and PAG blend polymers)
- Lithographic properties:
  - HE-F4-MBS-TPS > The PAG bound polymers:
    - a) Thermostability, b) Controlling acid generation,
    - c) Resolution, d) LER
  - HE-F4-IBBS-TPS > The PAG blend polymers:
    - a) Photospeed

### Future Plans

- To improve the LER by adding base for series of polymers exposed at EUV
- Effect of Solvents (Ethyl Lactate, PCME) Study Ongoing at LBL
- Cross section of EUVL patterns by SEM & AFM using high aspect ratio nanolith
- To develop new PAGs with respect to higher photospeed

