NON-PFOS PHOTOACID GENERATORS: A POTENTIAL CANDIATE FOR NEXT GENERATION LITHOGRAPHY

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Contents

- Photoacid Generators (PAGs) - Perfluorooctylsulfonate (PFOS) and PFOS PAG
- Non-PFOS PAG – Structural design, synthesis and Characterization
- Non-PFOS PAG versus PFOS PAG – Absorbance, PAG Distribution, Performance and Environmental properties
- Summary and outlook

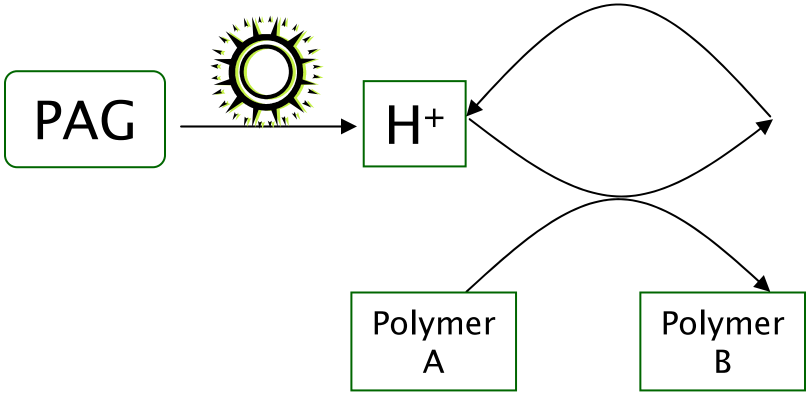
Chemical Amplification and Photoacid Generators

Table 1. Lithography and Sensitivity

Lithography	Energy (eV)	Resist Dose (mJ/cm^2)	Number of quanta for 50 nm pixel
ArF	6.4	20	500 000
EUV	92	2	3400
X-ray	920	40	6800
e-beam	50000	150 (3 μC/cm^2)	470
Ion beam	100000	50 (0.5 μC/cm^2)	78

Timothy A. Brunner *J. Vac. Sci. Technol. B* 21(6), 2632 (2003)

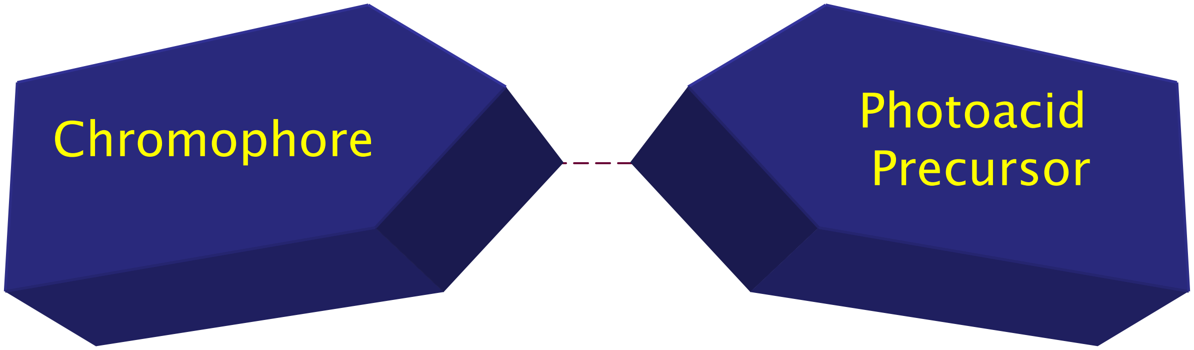
Figure 1. Chemical Amplification



- Higher Catalytic Chain Length – higher Φ
- Low Dose (1 – 5 mJ/cm^2)
- More sensitive than DNQ-Novoac resist
- PAG critical component in CA

H. Ito C. G. Willson CG and J.M. J. Fréchet *Digest of Technical Papers of 1982 Symposium on VLSI Technology 86* (1982); Hiroshi Ito *Adv Polym Sci.,* 172, 37 (2005)

Anatomy of Photoacid Generators



Chromophore

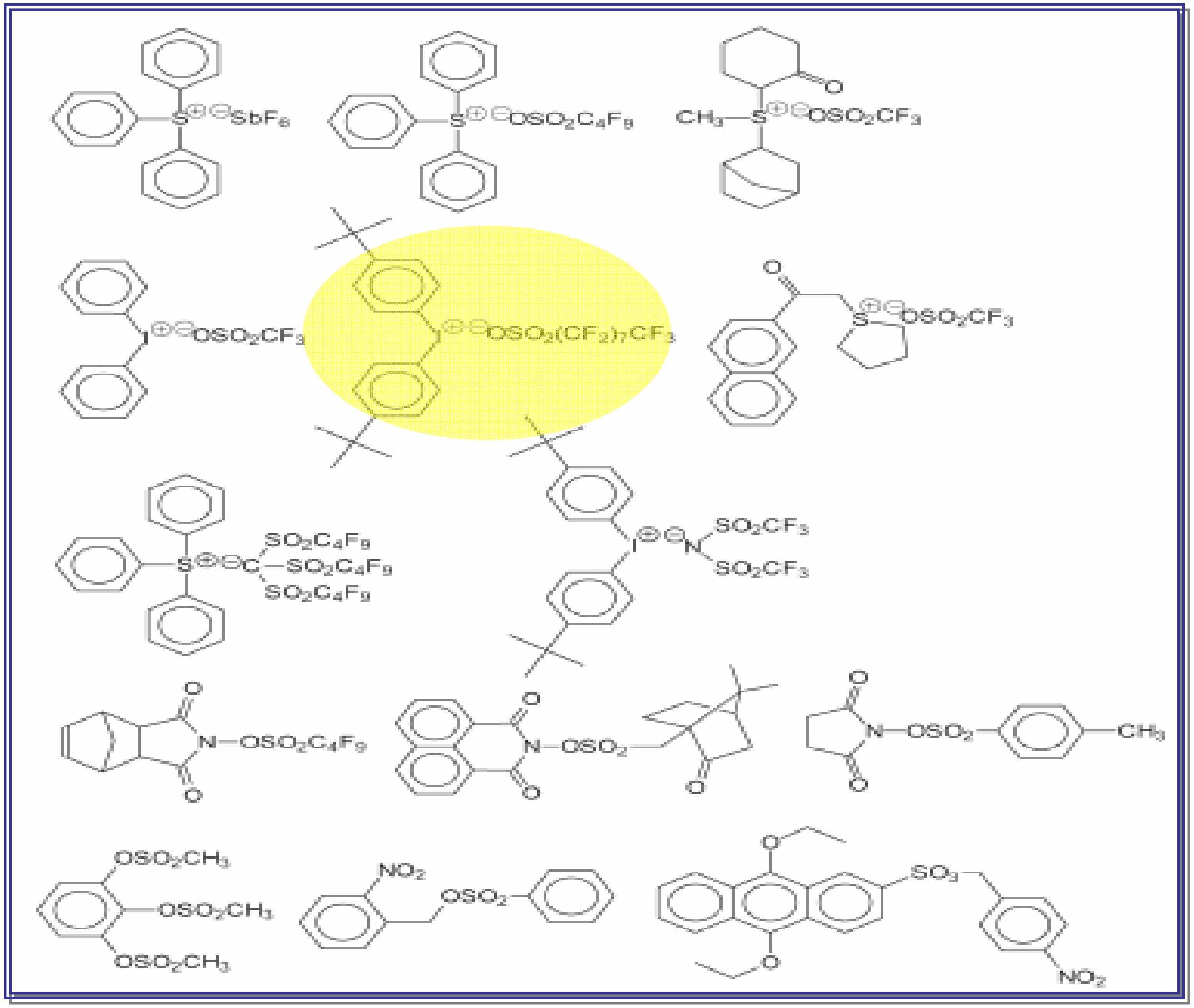
Photoacid Precursor

Molar absorption coefficient	Acid strength, Volatility and Diffusion length
Photosensitization	Nucleophilicity
Thermal/Hydrolytic stability	Anion stability
Dissolution Rates	Rate constants

Radiation, Miscibility/Solubility, Plasticizing effect, Synthetic route, **Toxicity** and Manufacturing Costs

James V. Crivello *J. Polym. Sci: Part A: Polym. Chem.* 37, 4241 (1999)
Hiroshi Ito *Adv Polym Sci.*, 172, 37 (2005)

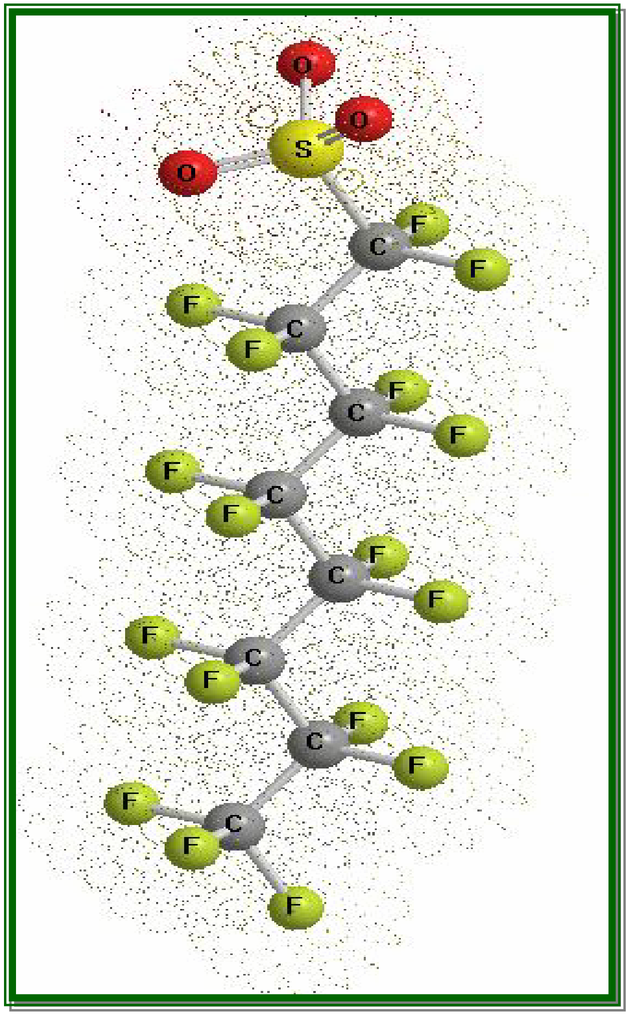
Photoacid Generators



Hiroshi Ito *Adv Polym Sci.*, 172, 37 (2005)

Perfluorooctylsulfonate (PFOS)

- Perfluoroalkylsulfonate ($C_8F_{17}SO_3R$; PFAS) family
- Strong C-F bond – Unusual properties
- Surface treatment, Protective coatings, Performance Chemicals

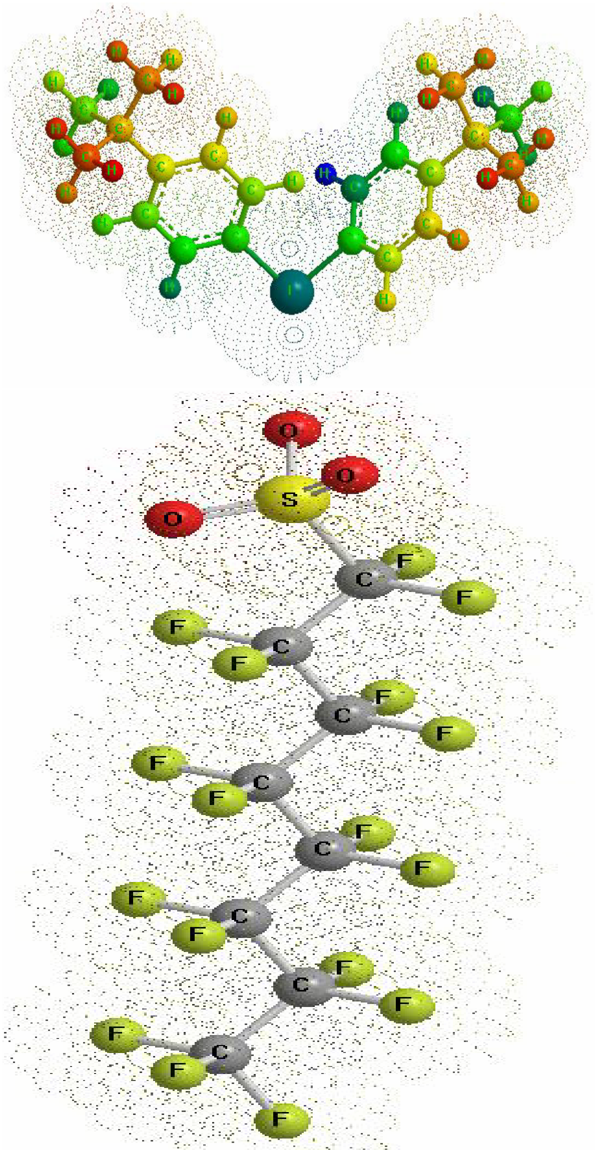


PFOS Case Study, *Intl .Biomonitoring Work Shop*, (2004) Sept. 21

Perfluorooctylsulfonate (PFOS) PAG

- Strong acid (pKa ~ -11) – sensitivity & speed
- Non-polar tail – solubility, miscibility, low contamination, defects, thermal (MP = 170 °C) and hydrolytic stability
- Optical properties – Uniform exposure/image contrast
- Size (272 cm^3) – low acid volatility/diffusion length

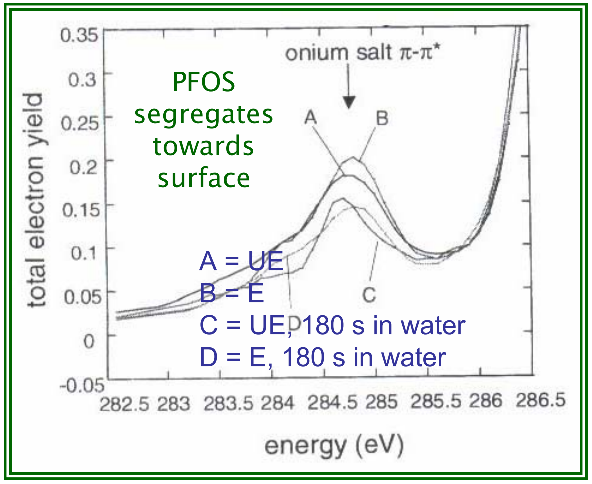
Y. Suzuki et al., *SPIE* (1998); M.J. Bowden et al., *Proceedings - Electrochemical Society* (2002)



(DTBI$^+$ PFOS) PAG

Perfluorooctylsulfonate (PFOS) PAG Issue

1. Segregation & Leaching

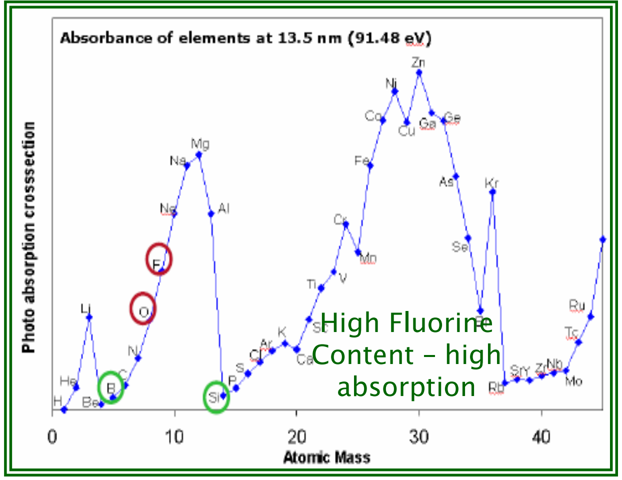


PFOS segregates towards surface

A = UE
B = E
C = UE, 180 s in water
D = E, 180 s in water

J. L. Lenhart et al., Langumir, 2005;
W. Hinsberg et al., SPIE, 2004

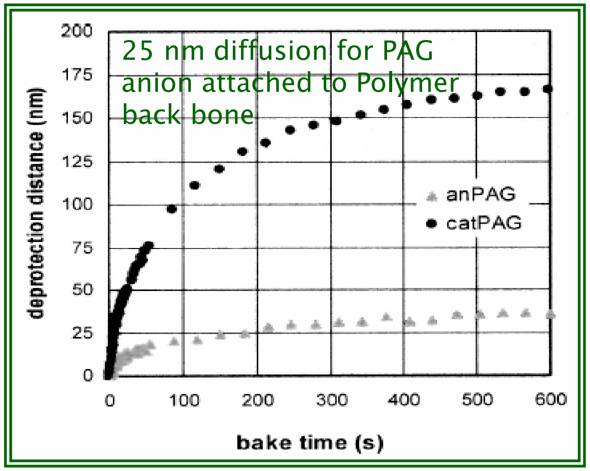
2. Fluorine Absorption @ EUV



High Fluorine Content – high absorption

C. K. Ober et al., 3rd International EUVL Symposium, 2004

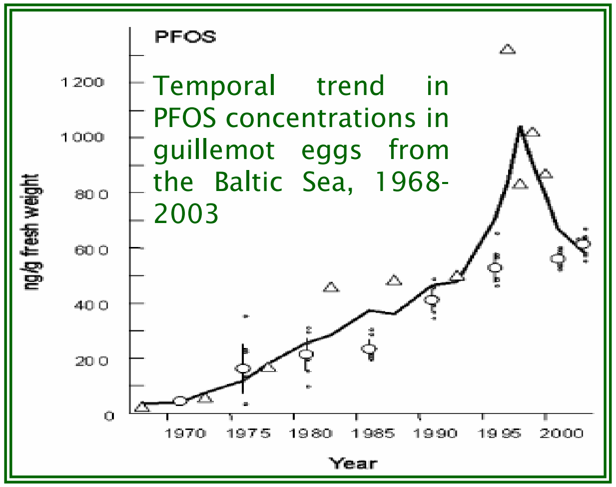
3. Acid Diffusion



25 nm diffusion for PAG anion attached to Polymer back bone

M. D. Stewart et al., *JVSTB* **2002**

4. Bioaccumulation



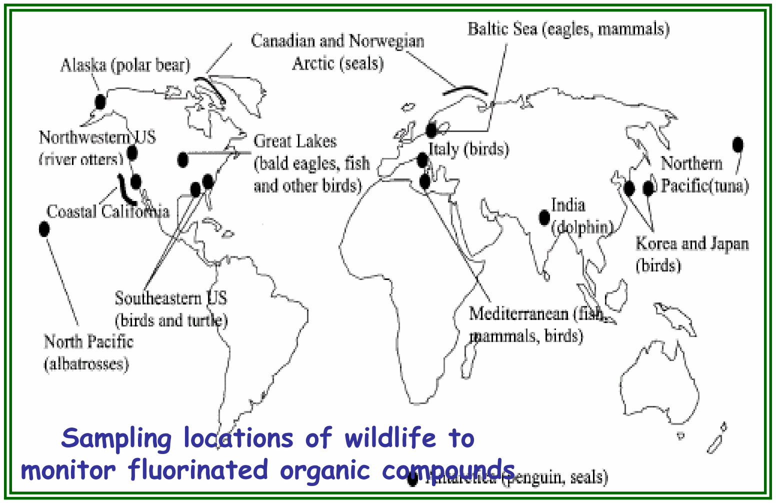
Temporal trend in PFOS concentrations in guillemot eggs from the Baltic Sea, 1968-2003

K. E. Holmstrom et al., *EST* **2005**

A. Hand, *Semiconductor International*, (2003); Jim Jewett, ERC Presentation (2005)

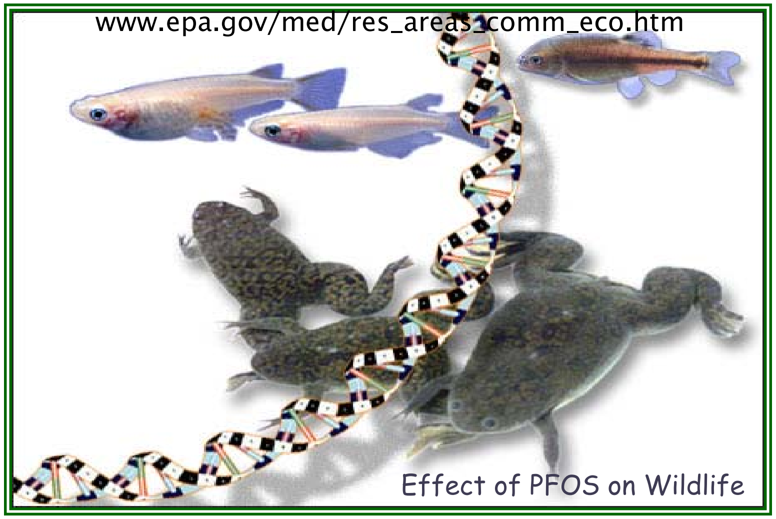
PFOS: Persistent, Bioaccumulation, Toxic (PBT) Concern

- Fluorine – Long Biological Life
- Global Distribution
- Higher P_{ow} coefficient
- Toxic



Sampling locations of wildlife to monitor fluorinated organic compounds

www.epa.gov/med/res_areas_comm_eco.htm



Effect of PFOS on Wildlife

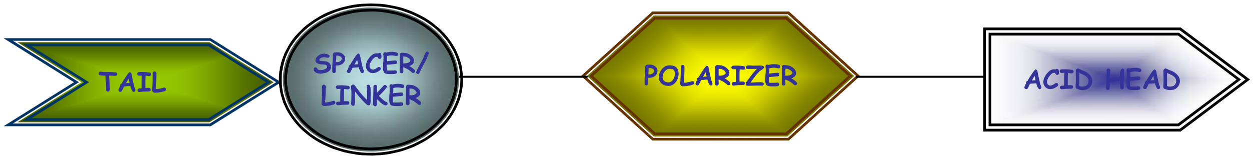
“New non-PFOS PAGs for NGL”

J. P. Giesy et al., *Environ. Sci. Technol.* (2001); K. Kannan et al., *Environ. Sci. Technol.* (2001); PFOS Case Study, *Intl .Biomonitoring Work Shop*, (2004); L. Peters, *Semiconductor International*, (2004).

Next Generation Photoacid Generators

Properties	Parameters
Sensitive Optimum absorption Acid size Acid strength Low/no photoinduced outgassing High thermal/hydrolytic stability Homogenous distribution and diffusion Low/no leaching in Liquid media Friendlier chemical – Non-PFOS	Molecular Structure Elemental composition Molar volume pKa Boiling/Melting Point Hazards to Optics Photochemistry Chemical Linkages Molecular arrangements Interaction between Functional groups Chain Vs nonchain PAG cation-anion interaction Energy calculation Partition coefficient

Structural Consideration for Non-PFOS PAG Anions



Head – Sulfonic, carboxylic, methide and others

Polarizer – Group to maintain strong polarization of the head group

Spacer/Linker – Break Seal

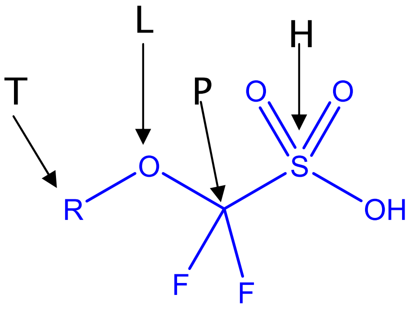
Tail – Group to enhance miscibility, solubility, diffusivity, hydrophobic/hydrophilic

Christopher K. Ober et al., *US Pat. Appl. No. 60/553,238*

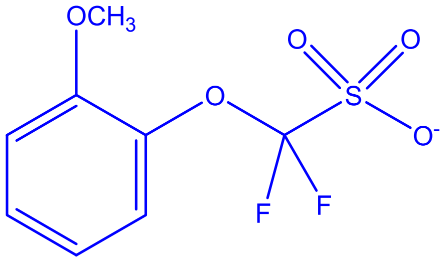
Non-PFOS Anions ?

Non-PFOS anions: $[-CF_2-] < 8$
Persistent: $[-CF_2-]$ 4 and > 4

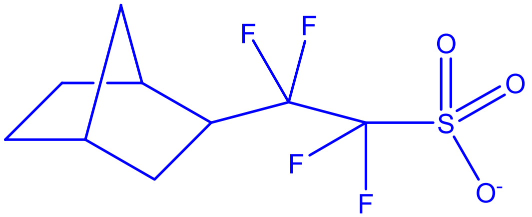
“Conventional Photoacid Design”



US20040087690 (3M)

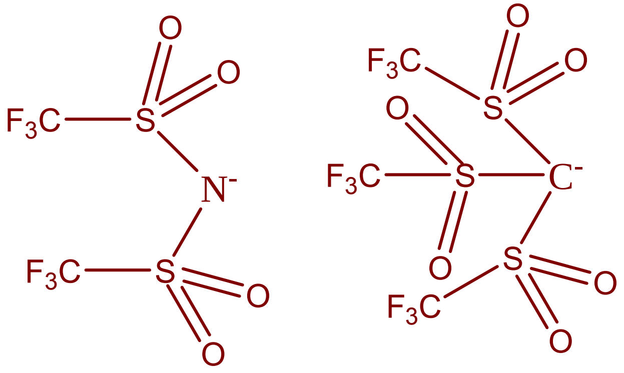


WO 2002082185 (ARCH)



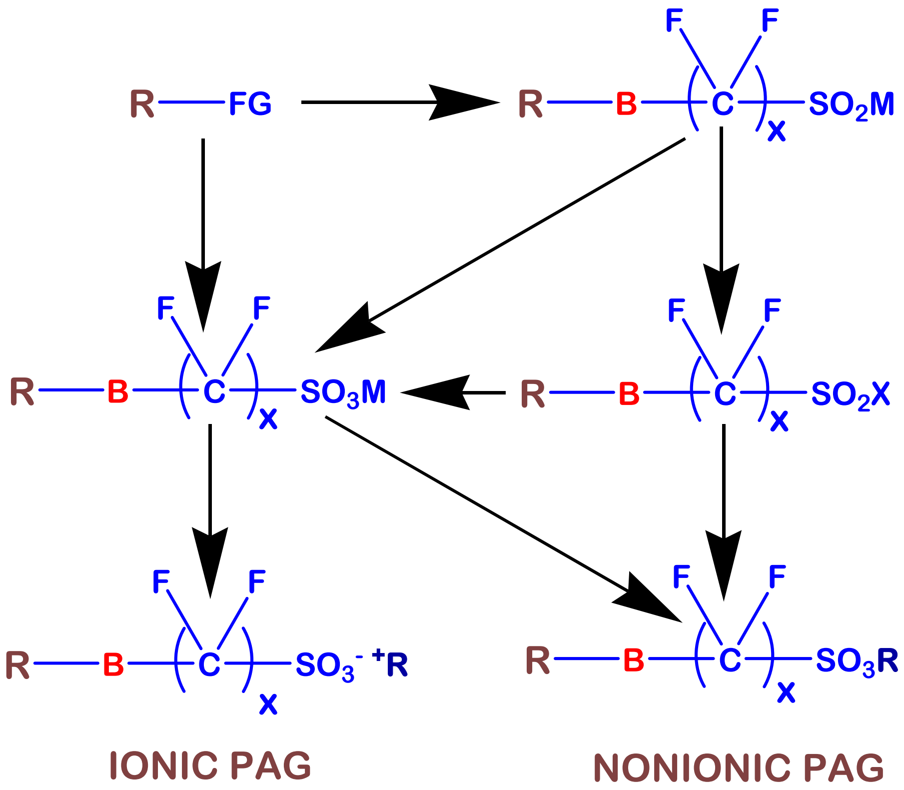
EP1270553 (JSR)

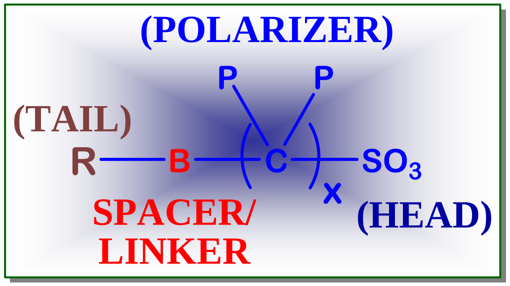
“Unconventional Photoacid Design”



SPIE 2002 (3M)

Synthesis and Structural Identification of Non-PFOS PAG





Analytical Tool	Information
NMR (^{1}H, ^{19}F, ^{13}C)	Purity
ESI-MS and Elemental	Purity/ Structure
TGA and DSC	Thermal Properties
UV-VIS/VUV spectroscopy	Absorption Characteristics, Residual acid, Solubility
ICP/AAS	Metal content
Lithography	Performance

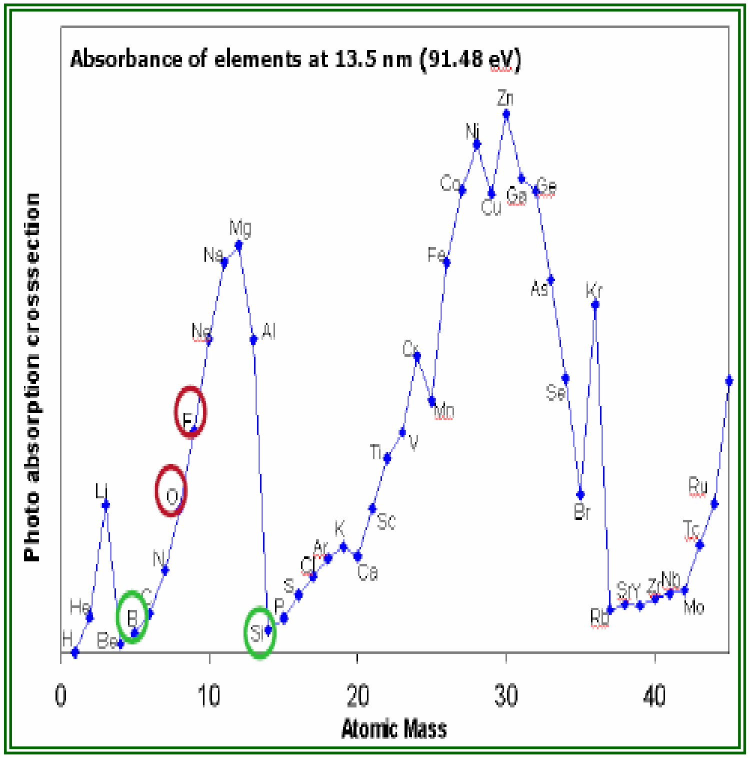
Key steps: Substitution, Hydrogenation, Dehalogenosulfination, Dehalogenosulfonation, Chlorination/Oxidation, Ion-exchange reaction, Esterification/Coupling

C.K. Ober et al., *unpublished Results*

Absorption at EUV

Absorption = -log (T)/d (μm^{-1})
T- % Transmittance and d – thickness of the resist (μm)

- F, O, I absorbs strongly
- C, H, S are transparent
- Low absorption of PAG – Reduces sensitivity
- High absorption – poor resist profiles
- Optimum absorption - PAG anion with minimum amount of F, O (non-PFOS) and Chromophore with S, C, H



C. K. Ober et al., 3rd International EUVL Symposium, 2004

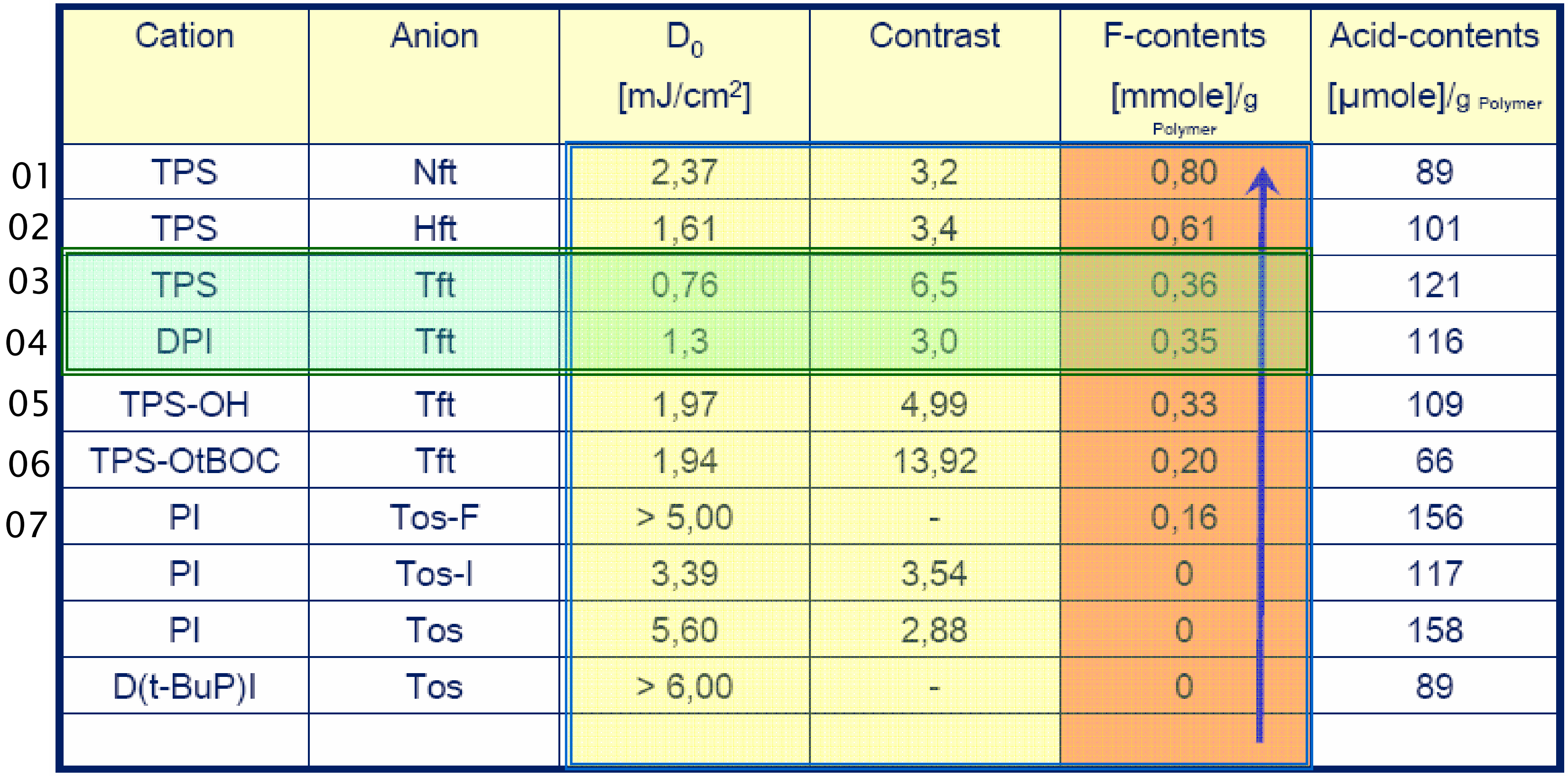
Fluorine Absorption at EUV

PAG CODE	PAG/POLYMER ABSORBTION (μm^{-1})	PAG ABSORBTION (μm^{-1})	% FLUORINE
Poly(hydroxystyrene) [PHS]	1.7325	-	-
PHS + PFOS	2.2943	0.5618 (24 %)	17.52
PHS + PFBS	2.0580	0.3255 (16 %)	10.40
PHS + TF	1.8393	0.1068 (6 %)	3.82
PHS + non-PFOS CUPAG9	1.8748	0.1423 (8 %)	4.70

[Poly (hydroxy styrene) = 6 %; PAG = 10 % (wrt to polymer): Cation – Triphenylsulfonium; % Transmittance - estimated using http://www-cxro.lbl.gov/optical_constants/filter2.html; Polymer density (1.19 g/cm^3); Thickness = 125 nm; A = -log (T)/d (μm^{-1})]

- Higher Absorption of PFOS – limits the formulation flexibility
- Non-PFOS PAGs – Formulation flexibility

Effect of Fluorine Content on Sensitivity and Contrast at EUV



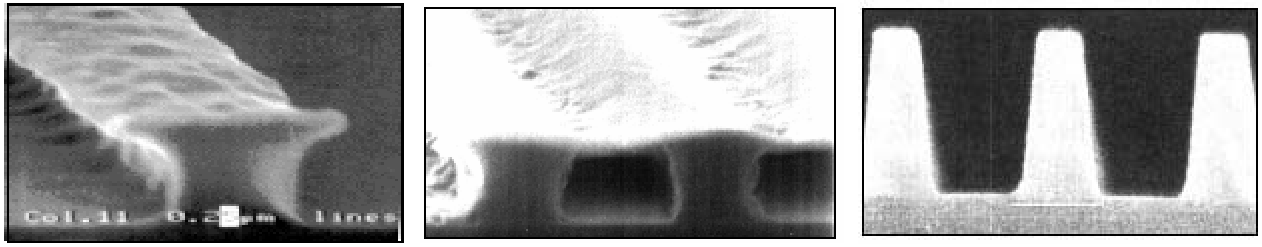
	Cation	Anion	D_0 [mJ/cm^2]	Contrast	F-contents [mmole]/g Polymer	Acid-contents [µmole]/g Polymer
01	TPS	Nft	2,37	3,2	0,80	89
02	TPS	Hft	1,61	3,4	0,61	101
03	TPS	Tft	0,76	6,5	0,36	121
04	DPI	Tft	1,3	3,0	0,35	116
05	TPS-OH	Tft	1,97	4,99	0,33	109
06	TPS-OtBOC	Tft	1,94	13,92	0,20	66
07	PI	Tos-F	> 5,00	-	0,16	156
	PI	Tos-I	3,39	3,54	0	117
	PI	Tos	5,60	2,88	0	158
	D(t-BuP)I	Tos	> 6,00	-	0	89

- Low fluorine content – better sensitivity and contrast (column 3 – 5) & (row 01, 02 & 03)
- Dissolution Inhibition – better contrast (row 05 & 06)
- Sulfonium PAG are better than iodonium (row 03 & 04)
- Non-PFOS PAGs with chromphore having Sulfur

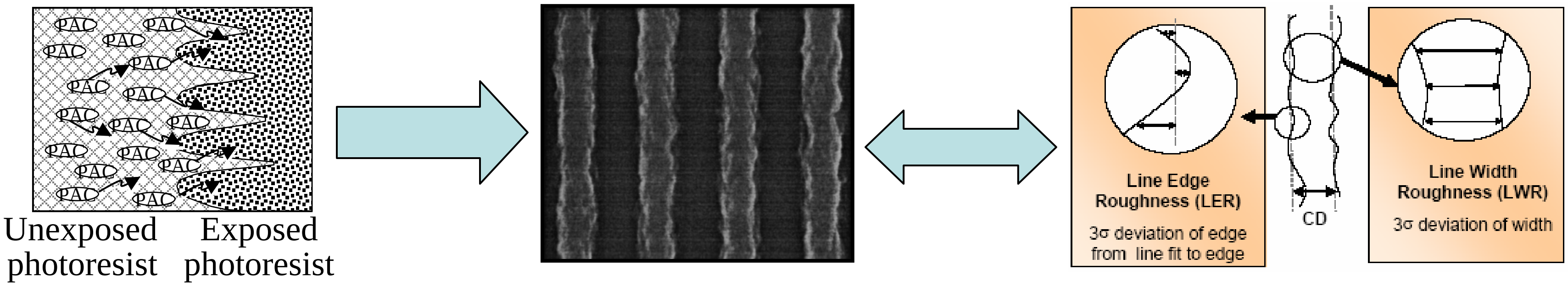
Wolf-Dieter Domke, Stefan Hirscher, Oliver Kirch, Karl Kragler, Klaus Lowack, Resist Characterization for EUVLithography *2. Int. EUVL-Symposium*, **2003**

PAG Distribution and their Effect on Resist Performance

1. PAG Segregation - T- Topping, Skin, Footing – *Leaching in 193 nm immersion*



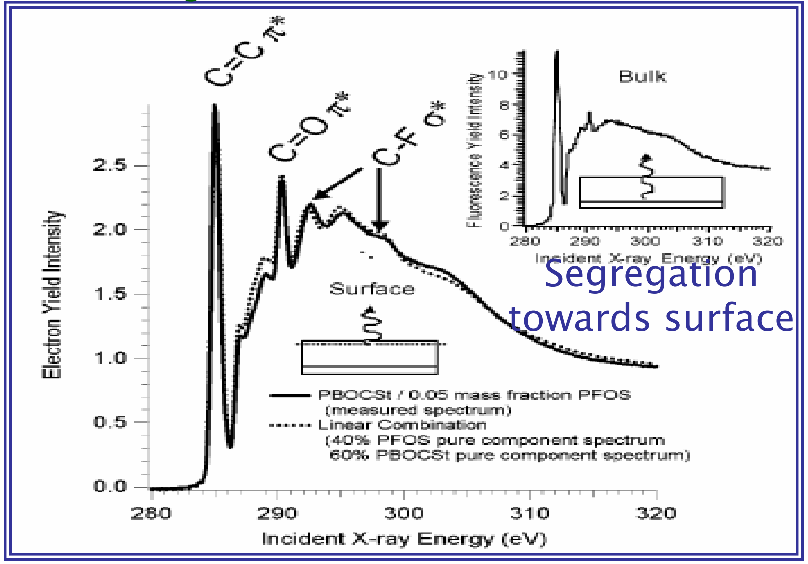
2. Line Edge or Width Roughness - Excess Acid Diffusion and non-uniform PAG distribution



3. Depth profiling techniques - **Rutherford Back Scattering (RBS), Near Edge X-ray Absorption Fine Structure (NEXAFS)** and X-Ray Photo-electron Spectroscopy (XPS) - Surface and Bulk Distribution of PAGs

PFOS Vs Non-PFOS PAG Distribution by NEXAFS

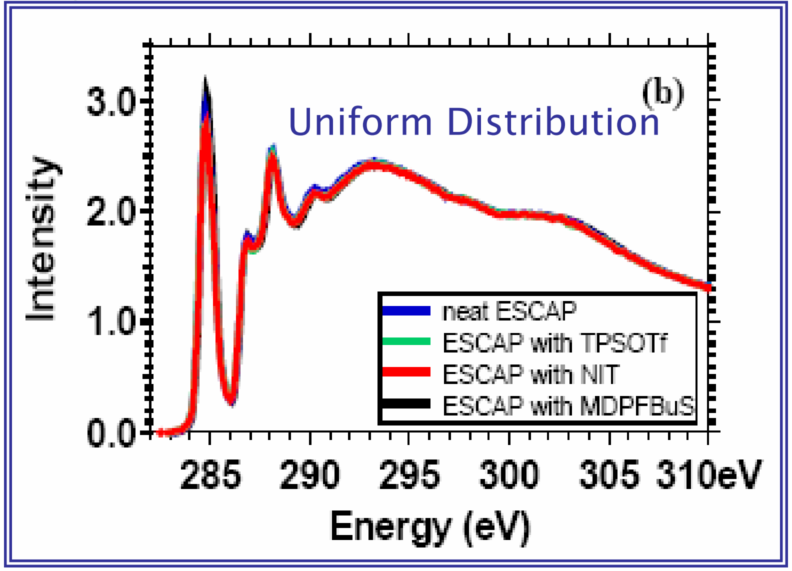
Figure 2. PFOS PAG in PtBOCs matrix



Segregation towards surface

J. L. Lenhart et al., *Langumir*, (2005)

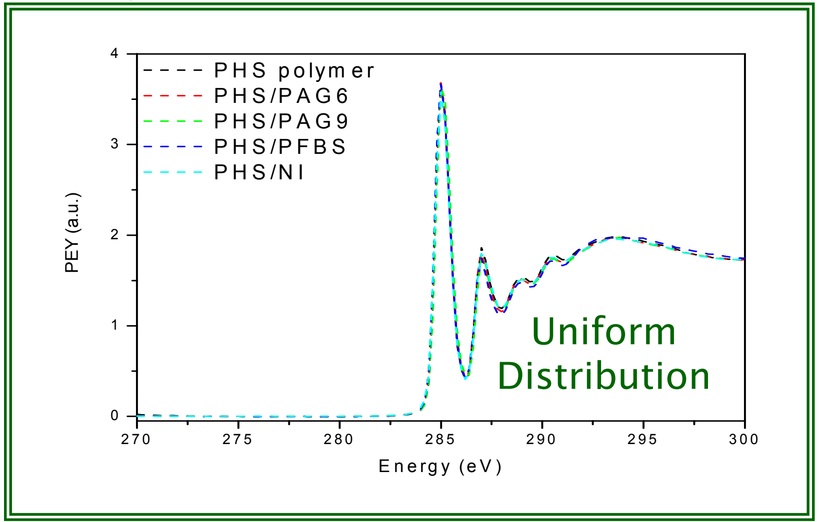
Figure 3. TF,PFBS PAG in ESCAP type resist



Uniform Distribution

J. L. Lenhart et al., *AIP Conference Proceedings* (2003)

Figure 4. Non-PFOS CUPAG in PHS matrix



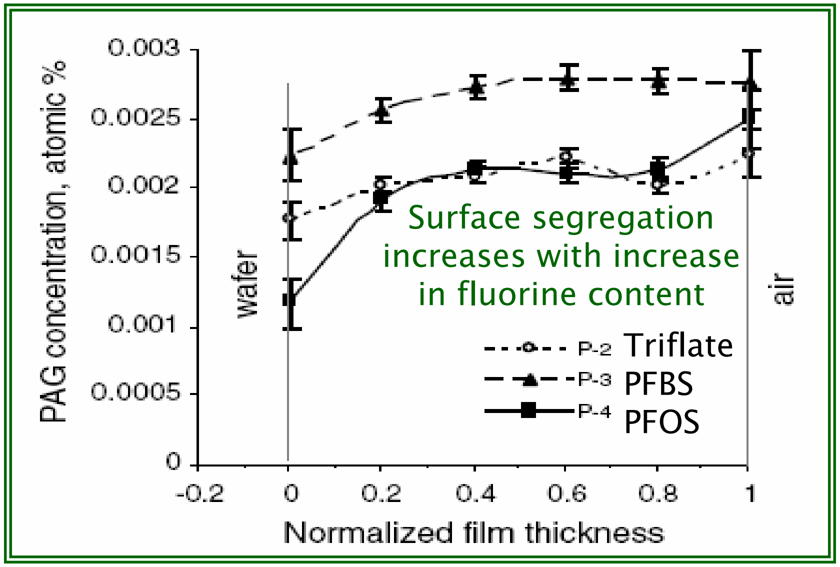
Uniform Distribution

C.K. Ober et al., *unpublished Results*

“Homogeneous Distribution for PAG with lower amount of fluorine (or non-PFOS) – better performance”

PAG Distribution Versus PAG Leaching : RBS, NEXAFS and XPS Analysis

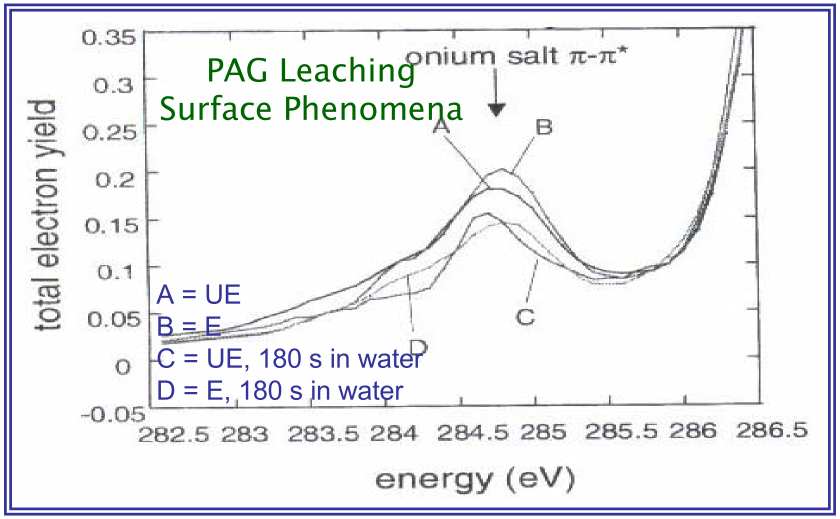
Figure 5. RBS Depth Profile of polar PAGs in a IBMA-MMA-MAA-t-BMA matrix



Surface segregation increases with increase in fluorine content

C.K. Ober et al., *JPST* (1999)

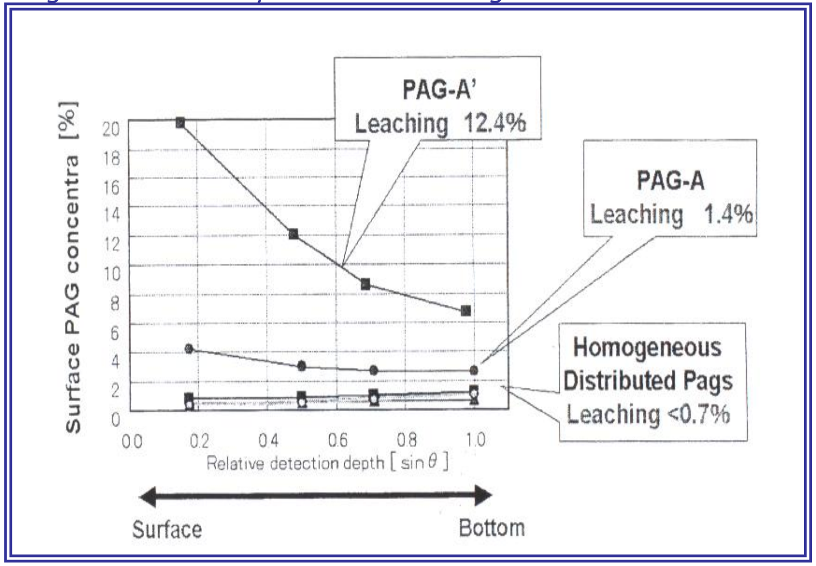
Figure 6. NEXAFS analysis of PFOS PAG Leaching in IBMA-MMA-MAA-t-BMA matrix



PAG Leaching
Surface Phenomena

W. Hinsberg et al., *SPIE* (2004)

Figure 7. XPS analysis - PAG Leaching versus Distribution



PAG-A'
Leaching 12.4%

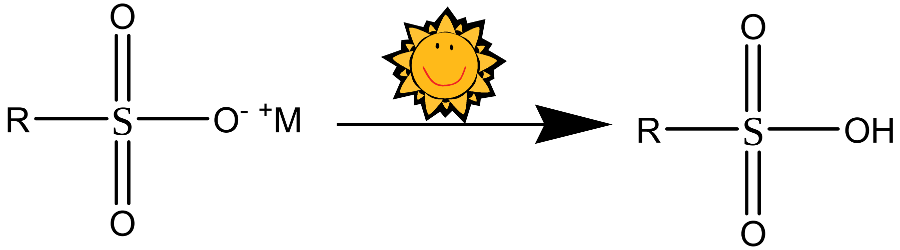
PAG-A
Leaching 1.4%

Homogeneous
Distributed Pags
Leaching <0.7%

S. Kanna et al., *SPIE* (2005)

"Non-PFOS PAG with suitable hydrophobic/hydrophilic character"

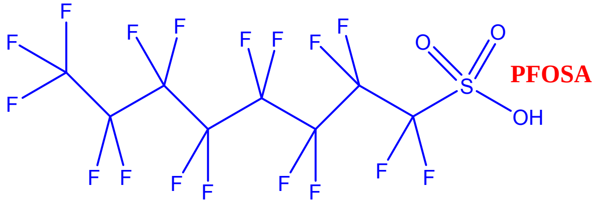
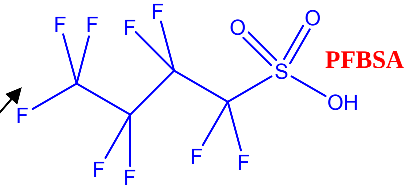
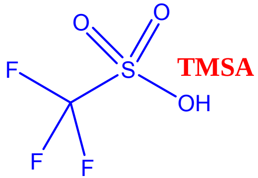
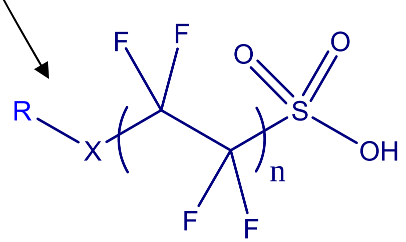
Impact of Photogeneratedacid (PGA) Structure on Resist Performance



Acid Properties		Impact on Resist performance
Acid Strength	pKa	Deblocking efficiency, Photospeed, Sizing energy, PEB Sensitivity, delay stability
Acid Size	Molar volume	Diffusion, Resolution, loss/evaporation, delay stability
Acid Volatility	Boiling/Melting point	loss/evaporation, delay stability

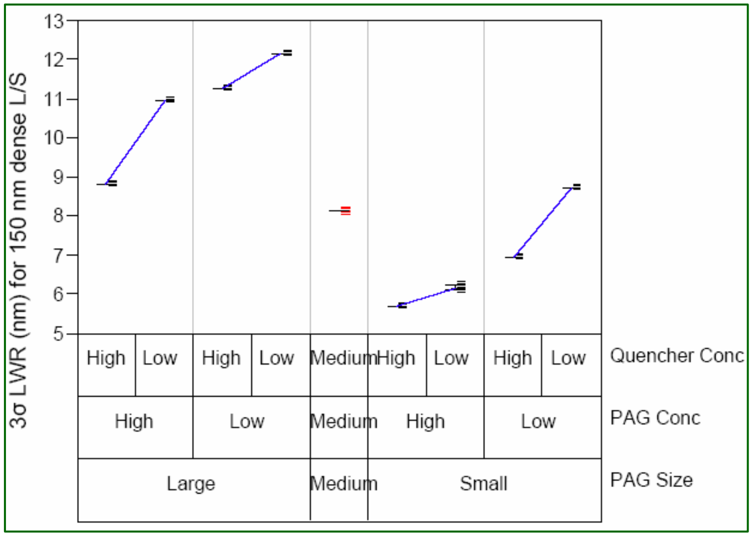
R. D. Allen et al., *SPIE*, **1997**, 3049, 44; J. F. Cameron et al., *SPIE*, **1999**, 3678, 785
Ebo Croffie et al., *JVSTB*, **2000**, 18(6), 3340

Photoacid: Strength, Size and Volatility

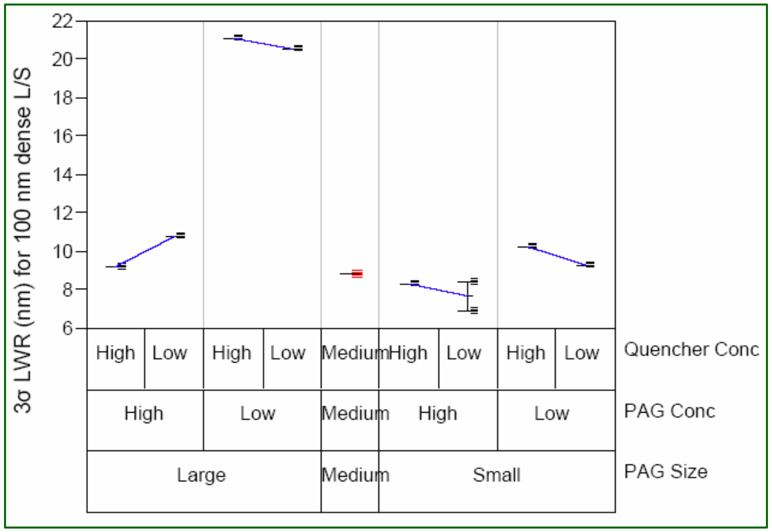
PGA Structure	pKa (Taft)	Size (cm^3)	MP/BP (°C)
 PFOSA	-4.77 (~11)*	272	197
 PFBSA	-4.99 (NA)*	162	183
 TMSA	-5.21 (>-12)*	79	172 (160)
	-3.80 to -4.87	110 to 190	180 to 285

* - Measured; **pKa** - D. D. Perrin, B. Dempsey, E. P. Serjeant, *pKa Prediction for organic acids and bases*, Chapman and Hall, London, 1981; **Size** - ACD lab; **MP/BP** - Marrero-Gani – Group Contribution Method

Effect of PAG size, Concentration on LWR at EUV

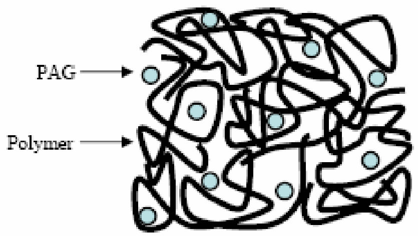


3σ LWR (nm) for 150 nm L/S

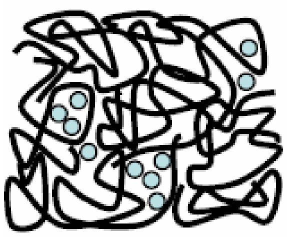


3σ LWR (nm) for 100 nm L/S

- Smaller PAG - better LWR - appropriate diffusion length
- Larger PAG - poor LWR - PAG Clustering
- PAG concentration - reduced LWR - uniform deprotection



Uniform PAG distribution



PAG clustering

Heidi Cao et al., *SPIE* (2004)

Effect of PAG Anion in Resist Performance at EUV

Table 4. Photospeed Consideration for EUV

PAG (Wt%/ PGA)	DUV Dose (mJ/cm^2)	EUV Dose (mJ/cm^2)	EUV R (nm)	3 σ LER at EUV Avg (nm)
6/CS	46	5.4	80	11
6/PFBS	48	3.8	80-90	9.7
6/PFOS	46	6	80-90	10
6/PFBzS	19	3.6	80-90	9.2

No. of F atoms	Acid Size (cm^3)	PAG (Wt%/ PGA)
0	174	6/CS
9	162	6/PFBS
17	272	6/PFOS
5	133	6/PFBzS

P. M. Dentinger et al., *JVSTB* (2002)

"Smaller PAG Anion, with minimum amount of fluorine"

Table 5. Threshold Acid Concentration (μmol/cm³)

Wavelength	ND-Triflate	TPS - Triflate	DTBI-PFOS	DTBI-Triflate
248 nm	7.8	6.5	23.8	12.3
30 keV e-beam	7.1	14.6	15.0	58.3
13.4 nm EUV	5.0	13.2	10.4	21.5
1.0 nm x-ray	7.0	22.3	16.0	26.3

"Higher Number of fluorine influences the acid generation at higher energy"

C. R. Szmanda et al., *JVSTB* (1999)

Cornell Non-PFOS PAG Performance at EUV

Resist	PGA	EUV Dose (mJ/cm^2)	EUV R (nm)	3 σ LER at EUV Avg (nm)
Polymer	non-PFOS PGA	2 - 7	40 - 80	7.3 - 11.1[#]
Molecular Glass Resist	5/PFBS	31[*]	30 - 35	4.3[*]
Molecular Glass Resist	5/non-PFOS PGA	21[*]	25 - 30	5.0[*]

- LER @ 100 nm; * Energy to Size & LER @ 60 nm

C.K. Ober et al., *unpublished Results*

Environmental Properties of non-PFOS Photoacids

- Non-PFOS anions - low fluorine content *(BCF Chain length dependent - 3M)*
- Functional groups
- Bioaccumulation - Partition coefficient (P or K) and Bioconcentration Factor (BCF)
- *Estimation structural/ electronic properties or biological properties (EPA Suite)*
- EHSR Profile - Toxicity (eco and mammalian) and Bioconcentration factor

Acid	log K_{ow}	BCF = [fish]/[water]	Biodegradation Timeframe (Primary & Ultimate)	
TMSA	-0.4870	3.162	Days-Weeks	Weeks-Months
PFBSA	2.4113	3.162	Weeks	Recalcitrant
PFOSA	6.2757	56.23	Months	Recalcitrant
PTSA	-0.6177	3.162	Days-Weeks	Weeks
CSA	-0.1697	3.162	Days-Weeks	Weeks-Months
PGA2	*0.7924*	3.162	Days-Weeks	Weeks-Months
PGA4	*1.7746*	3.162	Days-Weeks	Weeks-Months
PGA6	*2.3298*	3.162	Days-Weeks	Weeks-Months
PGA8	*3.2198*	3.162	Weeks	Months

Summary and Outlook

- PAGs, PFOS and PFOS PAGs

- Structural design, synthesis, identification and properties

- Absorbance, Segregation, Performance, Bioaccumulation - Non-PFOS PAG

- Non-PFOS PAG anion low/no bioaccumulation

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