Task Number: 425.029

Task Title: Sugar-Based Photoacid Generators ("Sweet" PAGs): Environmentally Friendly Materials for Next Generation Photolithography

Deliverable: Report on next generation PAGs and their lithographic performance and environmental compatibility

I. Summary/Abstract

This report describe the development of new triphenylsulfonium photoacid generators (TPS PAGs) with fluorinated sulfonate anions containing norbornyl, γ-butyrolactone, or glucose groups, and their successful application to pattern sub-100 nm features using 193 nm and EUV lithography. Their TPS PAGs were efficiently synthesized in high purity and high yield. These new PAGs are very attractive materials for photoresist applications and they are particularly useful to solve the environmental concerns caused by perfluorooctanesulfonate (PFOS) and the challenges raised by 193 nm and EUV lithography. The chemical and microbial degradation potential of novel PAGs was evaluated. Glucose or other natural units in the PAG structure assist in bio-degradation processes, which result in decreasing accumulation of waste PAG in the ecosystem. This approach is expected to resolve current issues related to the lithographic performance and environmental impact of these key materials.

II. Technical Results and Data

Photoacid generators (PAGs) are photosensitive compounds capable of releasing protons (H^+) under UV exposure conditions. Because the generation of strong acid is fast and well controlled, PAGs have been extensively used in the field of photolithography for microelectronic device fabrication, coatings and adhesives.[1-3] Among the many types of PAGs, ionic materials based on the perfluorooctane sulfonate (PFOS) anion have been widely used because of their unique properties, including exceptional strength of the photo-released acid and good solubility in common processing solvents. However, recently the use of PFOS-based PAGs has come under regulation, as environmental investigations revealed toxic properties and bioaccumulation problems with PFOS. In addition to environmental concerns, PFOS-based PAGs have the additional disadvantage of PAG segregation from the photoresist induced by their highly fluorinated nature. It is thus desirable to develop alternative PAGs which satisfy both environmental and materials performance issues.

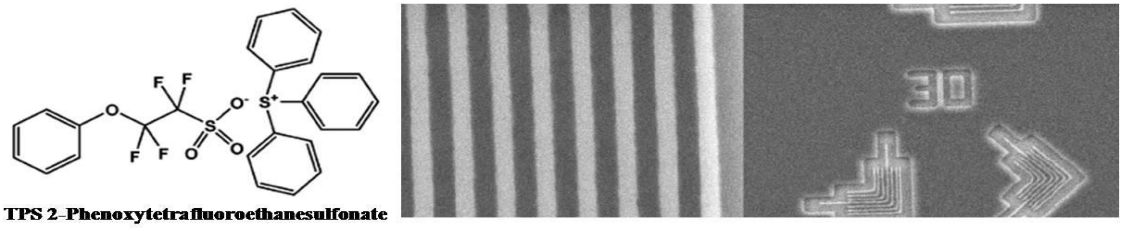

Figure 1. Chemical structure of PAG based on 2-phenoxy tetrafluoro-ethanesulfonate and SEM micrographs obtained with P(GBLMA-*co*-MAdMA) film containing PAG (*E*s = 7.5 mJ/cm^2; LER (100 nm 1:1 L/S) = 7.7±0.8 nm) exposed to EUV radiation and developed using 0.26 N TMAH.

Design and Synthesis of the new PAGs

We have investigated ionic PAGs based on non-PFOS backbones, for example, 2-phenoxy tetrafluoroethanesulfonate anion (Figure 1).[4] It showed excellent performance under EUV exposure conditions. However, because of the material's strong UV absorption under ~193 nm radiation, it is not

regarded as suitable for next generation immersion lithography employing an ArF eximer laser (λ=193 nm) light source. Therefore, our efforts were directed to replacing the phenyl group with a UV-transparent alicyclic moiety such as norbornyl, γ-butyrolactone, or glucose units.[5] In particular, a glucose unit has been chosen expecting that the naturally occurring material would improve both PAG miscibility with resist polymers and help the biodegradation mechanism in the wastewater treatment process, rendering bioaccumulation no longer a serious problem. The 1st generation norbornyl, γ-butyrolactone, and glucose-based "Sweet" PAG are shown in Figure 2.

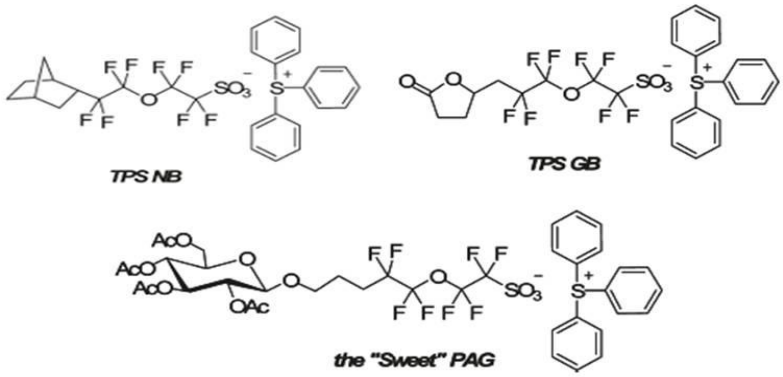

Figure 2. Chemical structure of the 1st generation TPS NB, TPS GB, and "Sweet" PAG based on acetyl glucopyranoside.

The "Sweet" PAG was fully evaluated in terms of lithographic performance, environmental friendliness or toxicological impact. Sierra's group has specially evaluated the susceptibility of xenobiotic chemicals to chemical and microbial degradation and the characterization of their toxic effects. In addition to the 1st generation PAGs, we have designed and synthesized the 2nd generation linear type "Sweet" PAG and study their structure-activity relationship in more detail.

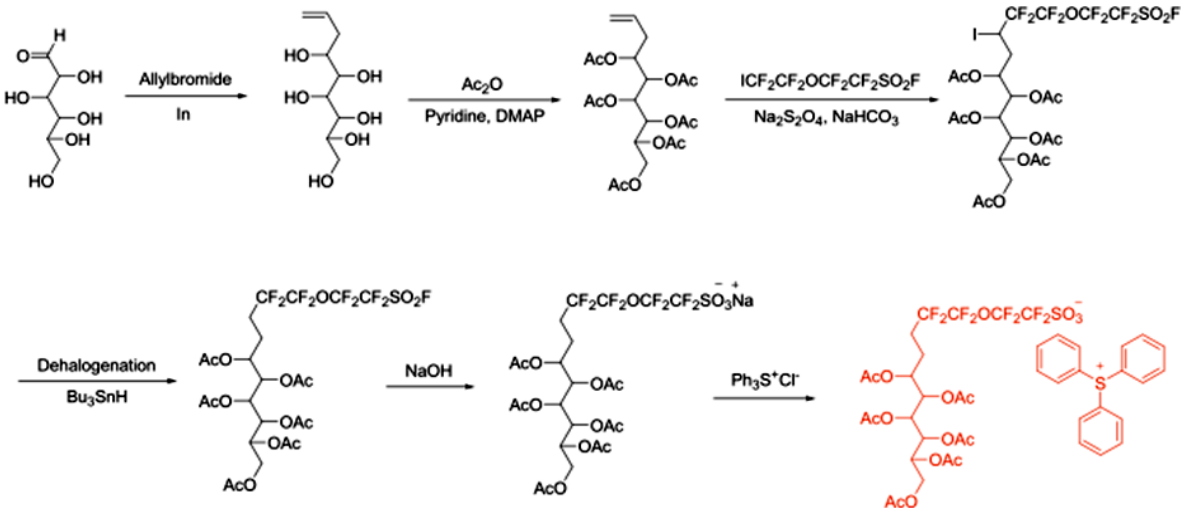

Figure 3. Synthetic pathway to the 2nd generation Linear typed "Sweet" PAG based on D-glucose.

One of the concerns on the 1st generation "Sweet" PAG is its possible deterioration before lithographic processing (short shelf-life) because of the acetal linkage inside the glucose unit. In general, acetals or ketals are acid-sensitive particularly in the presence of moisture. This situation can be improved by replacing the alicyclic sugar structure with a non-acetal containing linear derivative. The 2nd generation Linear typed "Sweet" PAG was thus designed based on D-glucose following a possible synthetic route

shown in Figure 3. This sugar derivative is also expected to be environmentally friendly and readily available at a lower cost than allyl-*tetra*-*O*-acetyl-*β*-D-glucopyranoside the starting material of the 1st generation "Sweet" PAG.[6] Following acetylation of the hydroxyl groups makes compound soluble in common processing solvents and compatible with resist polymers. Hydrolysis of the resulting sulfonyl fluoride follows and a salt exchange reaction with triphenylsulfonium chloride completes the synthesis of the 2nd generation linear typed "Sweet" PAG.

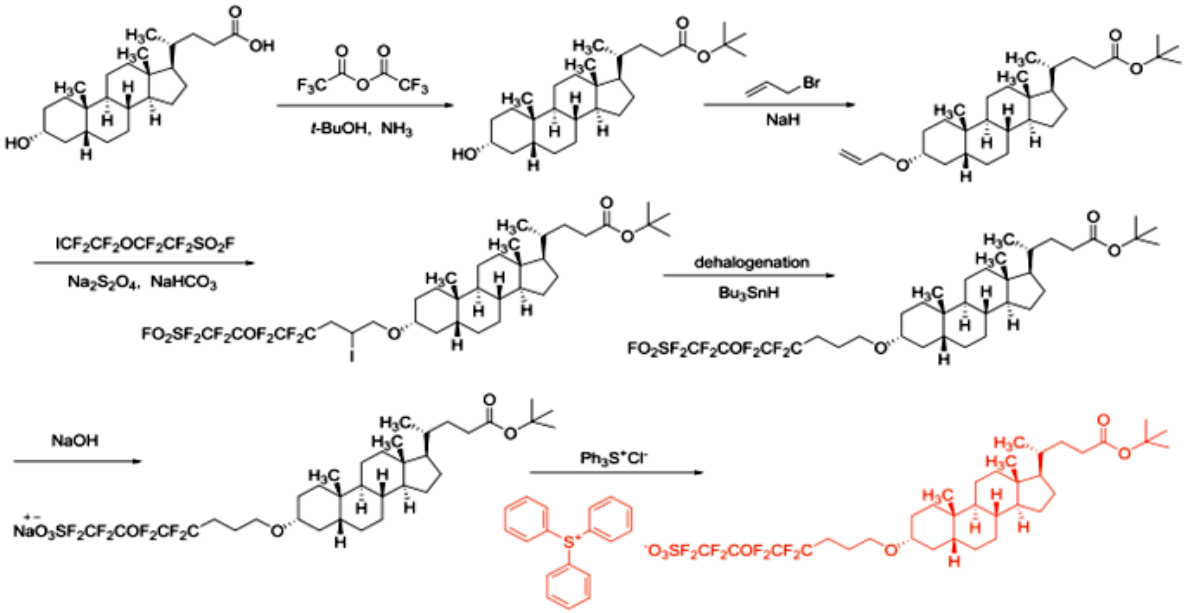

Figure 4. Synthetic pathway to the 2nd generation Biocompatible PAG based on lithocholic acid.

In the current synthetic process, there is one step which requires improvement. The second high priority issue of this study enables us to build not only environmentally friendly materials, but environmentally friendly synthetic processes. Along with sugar derivatives, other naturally occurring materials, such as bile acid, can be potential backbone materials for environmentally friendly PAGs. A PAG based on lithocholic acid was designed and its synthesis and materials properties were studied (Figure 4).

Lithographic performance of the new PAGs

The 1st and 2nd generation PAGs showed good lithographic performance at 193 nm wavelength with a series of resists selected from commercial and experimental resists for 193 nm patterning (both under dry and immersion conditions). TPS GB, TPS NB, TPS PFBS, and TPS PFOS were separately blended with poly(GBLMA-*co*-MAdMA). The four resists were initially evaluated at 193 nm. Figure 5 compares their sensitivities for 90 nm (1:1) dense lines and spaces. The resist compositions containing TPS GB and TPS NB have very close sensitivity, 28.2 mJ/cm^2 for TPS GB formulation and 27.1 mJ/cm^2 for TPS NB formulation. They are more sensitive than TPS PFOS resist (31.2 mJ/cm^2) and less sensitive than TPS PFBS loaded resists (24.1 mJ/cm^2). The PFOS resist has the largest LER value of 9.8 nm, while the resists containing TPS PFBS, TPS GB, and TPS NB have values of 8.6, 8.5, and 8.4 nm, respectively. The smaller LER of TPS GB and TPS NB resists is due to the more homogeneous distribution of the new PAGs. As the corresponding acids of TPSGB and TPSNB have a larger size, they can provide better control of acid diffusion than TPS PFBS. The performance of the new PAGs can be further improved through optimization of resist process conditions. The resist compositions with TPS NB and the sweet PAG demonstrate fine 90 nm patterns with significantly reduced LER (Figure 6).

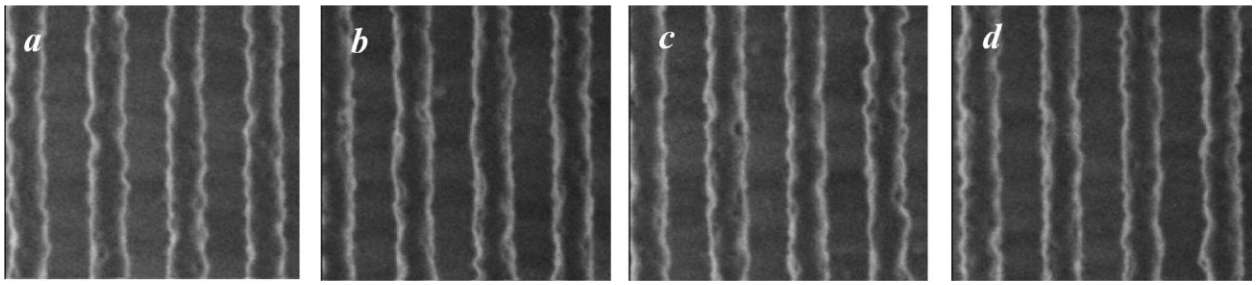

Figure 5. Top-down SEM images of 90 nm dense lines (1:1 line/space) of resist films of poly(GBLMA-*co*-MAdMA) blended separately with TPS PFOS (a), TPS PFBS (b), TPSGB(c), and TPSNB(d) patterned by 193nmlithography. E_{size} (mJ/cm^2): a, 31.2; b, 24.1; c, 28.2; d, 27.1. LER(nm): a, 9.8; b, 8.6; c, 8.5; d, 8.4.

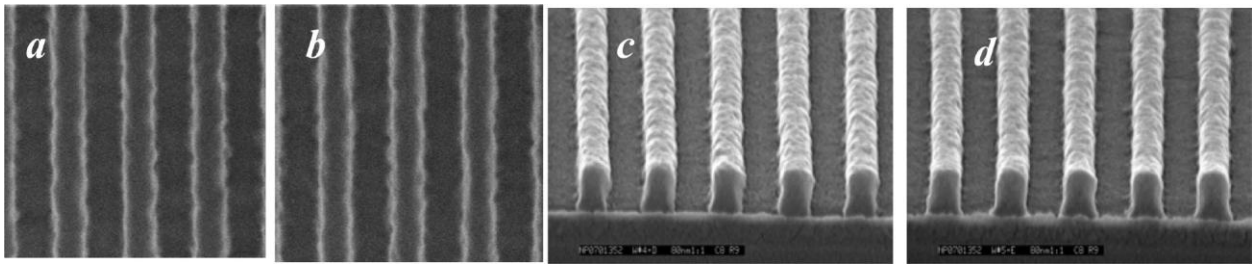

Figure 6. Top-down and cross-sectional SEM images of 90 nm dense lines (1:1 line/space) of resist films of poly(GBLMA-*co*-MAdMA) blended separately with TPS NB (a and c) and the sweet PAG (b and d) patterned by 193 nm lithography. E_{size} (mJ/cm^2): a, 23.8; b, 27.3. LER (nm): a, 5.8; b, 6.5.

As EUV imaging optics operate under vacuum, one concern for resist materials is outgassing products that are released during exposure. Such outgassing products adsorb on the optical surfaces and thus can contaminate the imaging optics and lower the tool's performance and lifetime. Therefore, outgassing fragments should be minimized to protect the imaging optics. According to previous studies, the major outgassing contaminants are deprotected groups from polymers and decomposition products from PAGs.[7] An outgassing limit of $6.5*10^{13}$ molecules/cm^2 is suggested by Intel for microexposure tools, while a limit of $5*10^{13}$ molecules/cm^2 is required by ITRS 2005. We evaluated the outgassing properties of TPS GB and TPS NB prior to EUV lithography. The environmentally stable chemically amplified photoresist (ESCAP) type polymer was selected as the polymer matrix because ESCAP type polymers have shown lower outgassing compared to the other types of polymers.[8] The major fraction from TPS GB and TPSNB is benzene, which is the main decomposition product of the TPS cation. No significant fragments from the GB and NB anions were detected. The total measured outgassing concentration was $3.2*10^{13}$ molecules/cm^2, which is below the limit suggested by ITRS 2005.

Poly(HSt-*co*-St-*co*-tBA), and poly(GBLMA-*co*-MAdMA) were used in our EUV lithography studies. TPS NB and TPS GB were separately blended with poly(HSt-*co*-St-*co*-tBA) and poly(GBLMA-*co*-MAdMA). The other two resist compositions containing TPS PFBS and the polymers were also prepared as controls. The resist thin films were spin-coated onto silicon wafers and, then, exposed to EUV irradiation. The range of dose is between 3.2 and 5.8 mJ/cm^2. After the exposed thin films were developed, the patterns were examined, and their images were obtained by a Zeiss Supra SEM. Important resist parameters including the resist resolution, sensitivity, and the LER of 100 nm (1:1 line/spacing) dense lines were then measured. All of the resist compositions studied have sensitivity values (E_{size} for 100 nm (1:1 line/spacing) dense lines) of no more than 5 mJ/cm^2, which indicates that the new PAGs are as highly sensitive as the control PAG. The SEM images of the smallest features are shown in Figures 7. It is evident that all resist compositions studied can reach a resolution of 60 nm dense lines. For elbow features, the resist compositions of TPS GB blended with poly(HSt-*co*-St-*co*-tBA) and poly(GBLMA-*co*-MAdMA) demonstrated a higher resolution of 60 nm, while the resist compositions of TPS NB and TPS PFOS achieved 70 nm for poly(HSt-*co*-St-*co*-tBA) and 80 nm for poly(GBLMA-*co*-MAdMA). On the

basis of their excellent lithographic performance, we believe the new PAGs are capable of achieving higher resolution with low LER after processing conditions are optimized. Lithographical performance of the new PAGs together with TPS PFOS and triphenylsulfonium perfluorobutanesulfonate (TPS PFBS) was successfully evaluated at both 193 nm and EUV wavelength.

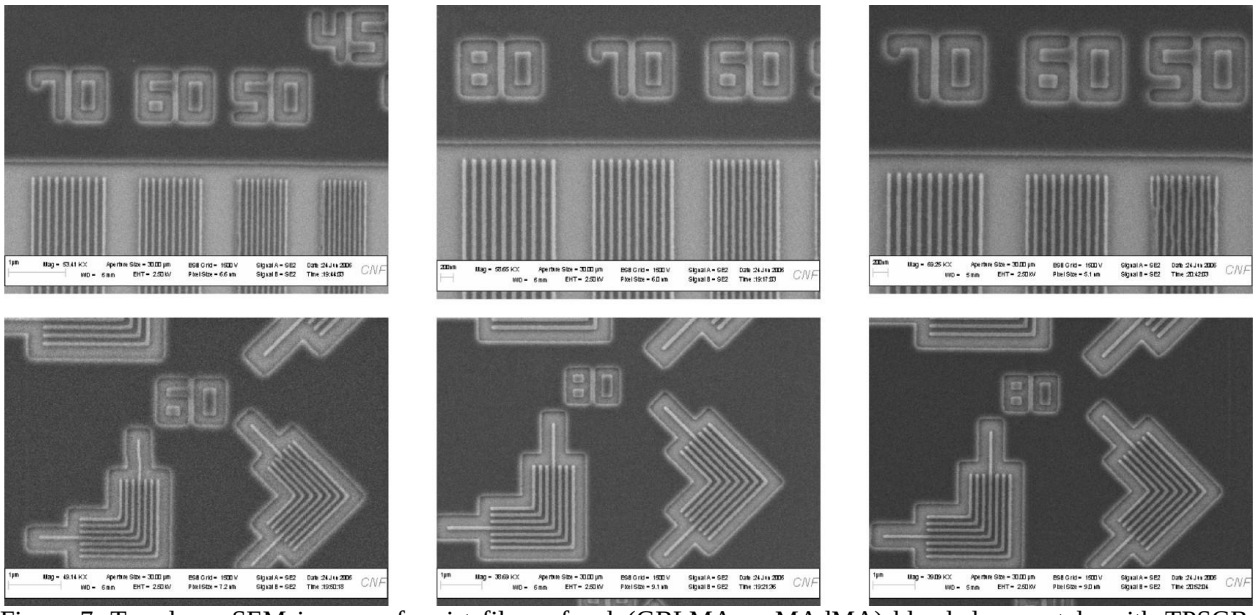

Figure 7. Top-down SEM images of resist films of poly(GBLMA-co-MAdMA) blended separately with TPSGB (left column), TPSNB (middle column), and TPSPFBS (right column) patterned by EUV lithography.

Chemical and microbial degradation

Chemical substitutions that facilitate the degradation of PAG compounds under biotic and abiotic conditions were identified to aid in the design of environmentally compatible PAG compounds. The PAG compounds were tested for microbial degradation (aerobic and anaerobic conditions) and for chemical degradability under oxidizing conditions (Fenton's reaction) as well as reducing conditions (reaction with zero-valent iron).

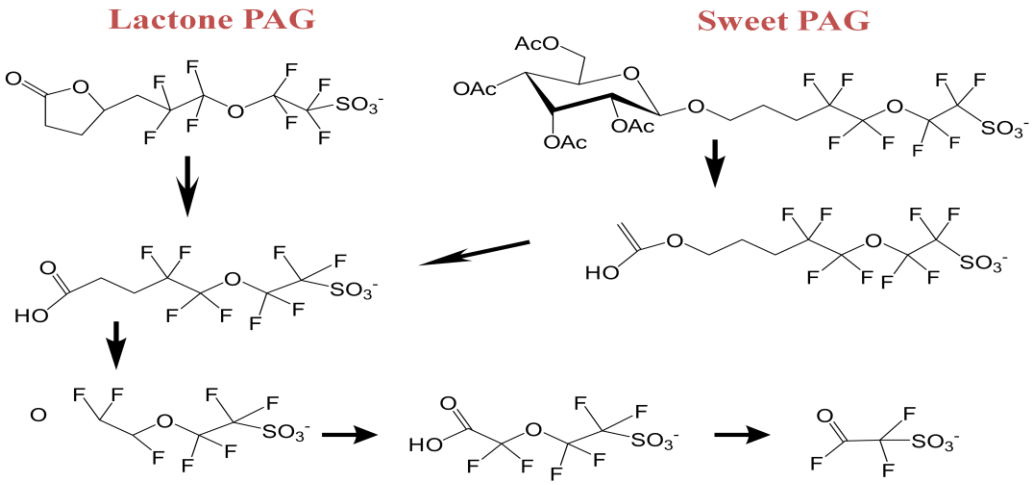

Figure 8. The proposed degradation mechanism based on mass spectrometry (MS) data.

Fenton's treatment is effective in removing the new generation non-PFOS PAGs (Table 1). The proposed degradation mechanism based on mass spectrometry data is shown in Figure 8. However, the

reductive treatment with Zero-Valent Iron (ZVI) is not effective in removing the biomolecule-based non-PFOS PAGs (Table 2).

Microbial degradation of lactone PAG and sweet PAG was confirmed by ion chromatography and mass spectrometry (MS) analysis in the forms of several unindentified degradation products. Lactone and glucose-based PAGs are degraded by aerobic- and anaerobic microorganisms in wastewater treatment sludges (Table 3).

Fenton's reaction: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^{-}$, $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^{\cdot}OOH + H^{+}$

PAG + radicals → Oxidized products

Table 1. The chemical degradation of new generation PAGs in advanced oxidation, Fenton's reaction.

Compounds	Degradation	PAG Removed (%)	Fluoride Released (%)
Lactone PAG	YES	100	5.7
Sweet PAG	YES	100	8.7
PFOS	NO	0.8	0.6
PFBS	NO	0.5	0.4

Redox degradation by ZVI: $Fe^{0} \rightarrow Fe^{2+} + 2\,e^{-}$, **PAG** + $2e^{-}$ ----> **Reduced PAG**

Table 2. The chemical degradation of new generation PAGs in reductive attack with ZVI.

Compounds	Degradation	PAG Removed (%)	Fluoride Released (%)
Lactone PAG	NO	1.0	0.3
Sweet PAG	NO	1.0	0.8
PFOS	NO	0	0
PFBS	NO	0	0

Table 3. The microbial degradation of new generation PAGs in activated sludge.

Compounds	Aerobic Degradation	Anaerobic Degradation
Lactone PAG	YES	NO
Sweet PAG	YES	YES
PFOS	NO	0
PFBS	NO	0

Results

We have efficiently synthesized a new generation PAGs of TPS salts with functionalized octafluoro-3-oxapentanesulfonate anions. Compared with conventional TPS PFOS, the new PAGs with reduced CF_2 content are environmentally friendly. Their capability to achieve high-resolution patterning was confirmed by excellent performance at 193 nm and at EUV wavelength. Moreover, they show comparable performance with TPS PFBS and better performance than TPS PFOS. Some of the new PAGs are degraded by the chemicals and microorganisms. Therefore, the new PAGs are promising candidates for environmentally friendly high-resolution lithography. Further studies on the environmental compatibility of novel PAGs such as the bioaccumulation potential and toxic effects are underway.

References

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