Task Number: 425.029

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

Deliverable: Report on lithographic evaluation of new "Sweet" PAG Generation 2 materials

I. Summary/Abstract

We describe the development of new triphenylsulfonium photoacid generators (TPS PAGs) with fluorinated sulfonate anions containing glucose or other natural product groups, and their successful application to patterning sub-100 nm features using 193 nm and EUV lithography. The TPS PAGs with functionalized octafluoro-3-oxapentanesulfonate were synthesized efficiently in high purity and high yield by utilizing simple and unique chemistries on 5-iodooctafluoro-3-oxapentanesulfonyl fluoride. These new PAGs are very attractive materials for photoresist applications and they are particularly useful in addressing 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 are being 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 a number of current issues related to the lithographic performance and environmental impact of these key materials.

II. Technical Results and Data

Photoacid generators (PAGs) are photosensitive materials capable of releasing protons (H^+) upon exposure to UV irradiation.[1-2] 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.[3-5] Among the many types of PAGs, ionic materials based on the perfluorooctane sulfonate (PFOS) anion have been widely used because of its unique properties, including exceptional strength of the photo-released acid and good solubility in common processing solvents.[5-6] 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.[7-9] It is thus desirable to develop alternative PAGs which satisfy both environmental and materials performance issues.

We have investigated ionic PAGs based on non-PFOS backbones, for example, the 2-phenoxy tetrafluoroethanesulfonate anion.[10] 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 (Figure 1 and Figure 2).[11]

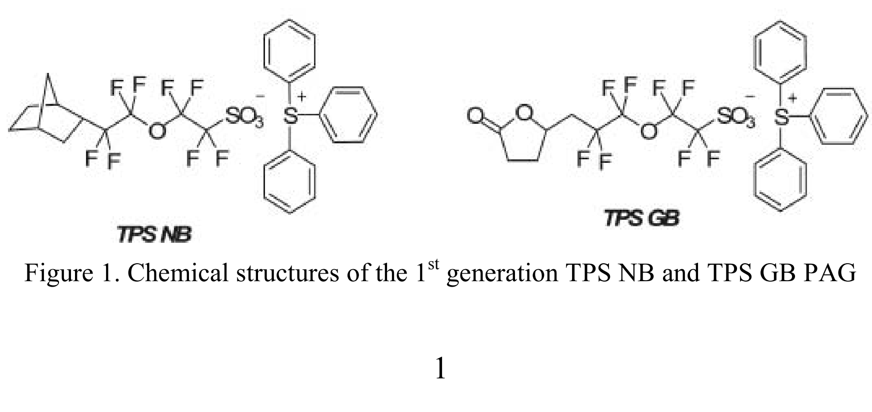

Figure 1. Chemical structures of the 1st generation TPS NB and TPS GB PAG

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 chemical structure and lithographic performance of the 1st generation glucose-based "Sweet" PAG are shown in Figure 2. The "Sweet" PAG was fully evaluated in terms of lithographic performance, environmental friendliness or toxicological impact. Sierra's group has been specially evaluated the susceptibility of xenobiotic chemicals to chemical and microbial degradation and the characterization of their toxic effects.

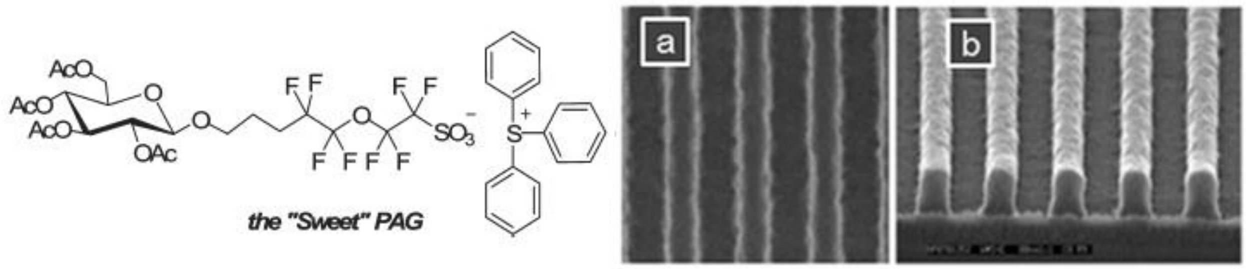

Figure 2. Chemical structure of the Sweet PAG and Top-down (a) and cross-sectional (b) SEM images of 90 nm dense lines (1:1 line/space) of resist films of poly(GBLMA-*co*-MAdMA) blended separately with the sweet PAG patterned by 193 nm lithography. E_{size} (mJ/cm^2): 27.3. LER (nm): 6.5.

Design and Synthesis of the new PAGs

In addition to the 1st generation PAGs, we have designed and synthesized the 2nd generation linear type "Sweet" PAG and other natural units based on PAGs and study their structure-activity relationship in more detail.

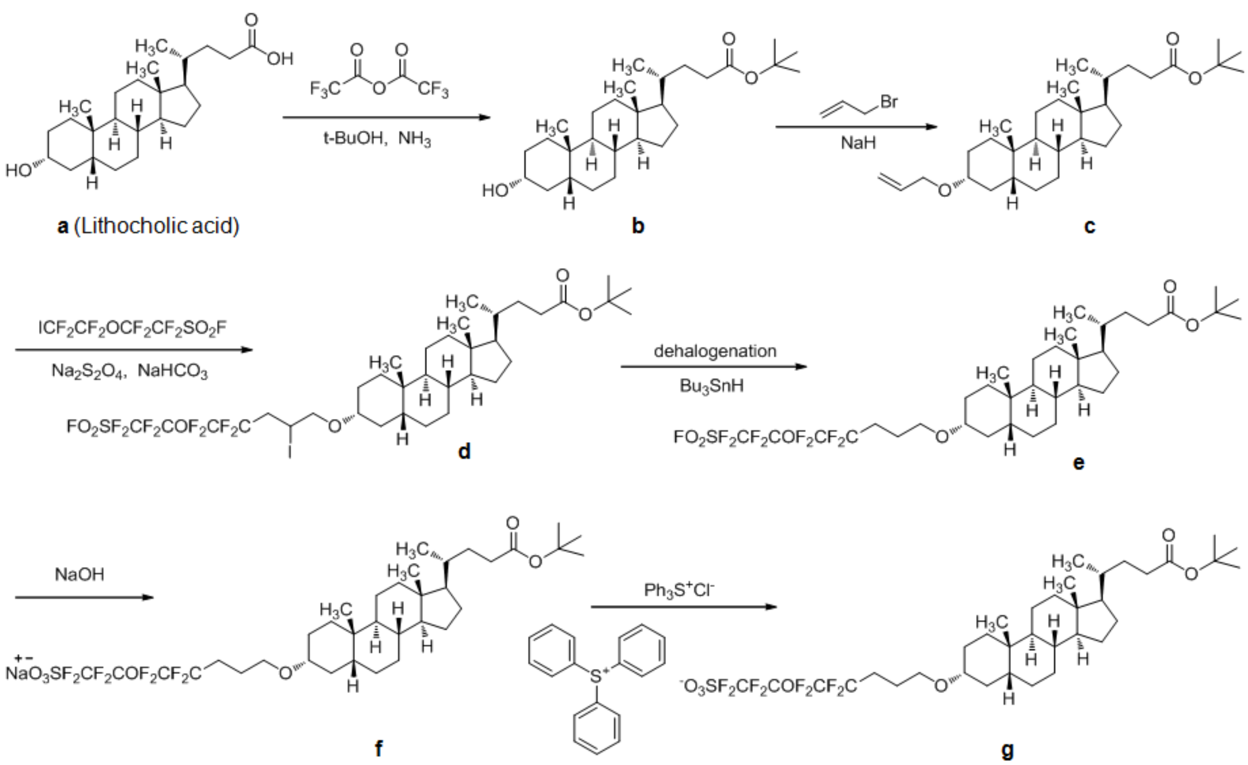

Figure 3. Synthetic scheme to the 2nd generation Biocompatible PAG based on lithocholic acid.

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 type "Sweet" PAG was thus designed based on D-glucose following a possible synthetic route shown in the last report. 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.[12] 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 type "Sweet" PAG.

We also designed additional PAG anions, each carrying either lithocholic acid or dihydrocholestrol units. Both of them have a multi-ring structure, which enables excellent thermal stability, a high melting point of the corresponding acid, and better control of acid diffusion. Moreover, these groups have biocompatible properties, thus they will be expected as an environmentally friendly materials. Along with sugar derivatives, other naturally occurring materials, such as bile acid, can be potential backbone materials for environmentally friendly PAGs.

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.

A PAG based on lithocholic acid was designed and its synthesis and materials properties were studied. The new PAG anion based on lithocholic acid was synthesized in 6 steps in the form of TPS sulfonate from the starting lithocholic acid as indicated in Figure 3. To get the final PAG based on lithocholic acid, sodium sulfonate and TPSCl were mixed together in 20 mL water. The mixture solution was stirred overnight and extracted with chloroform. The chloroform solution was separated and dried over anhydrous $MgSO_4$. After the evaporation of solvent, the new PAG based on lithocholic acid was obtained as a transparent viscous oil. Their chemical structures were confirmed by ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR.

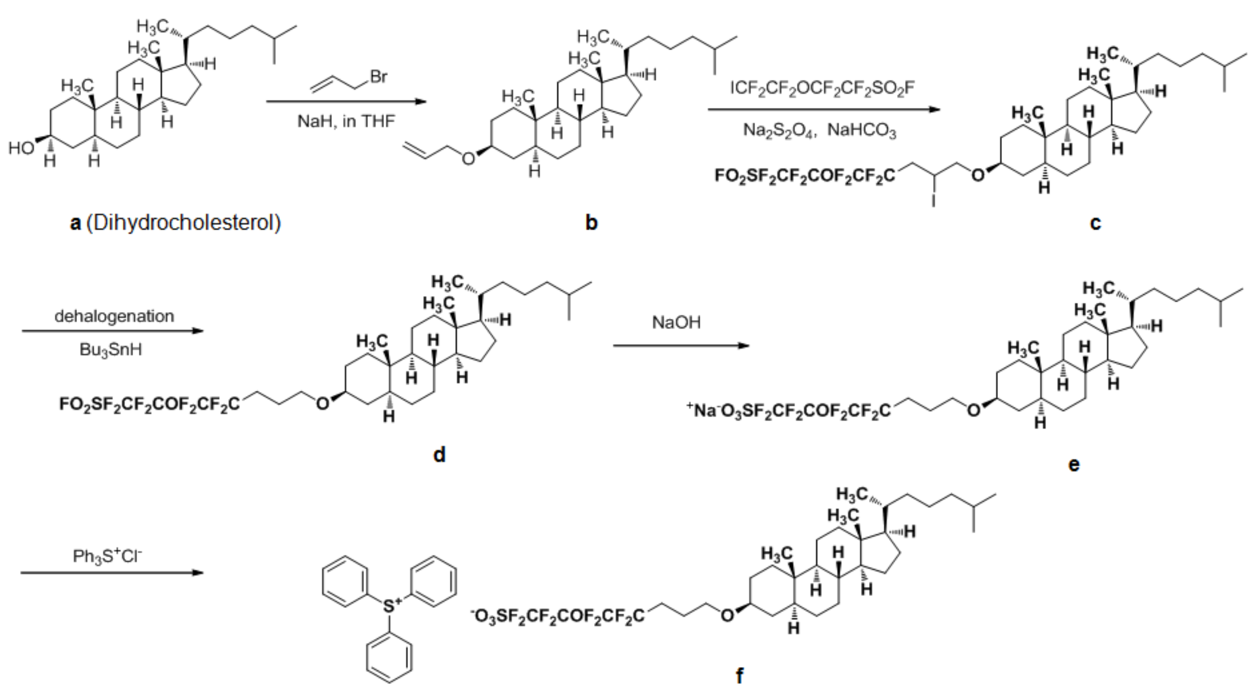

Figure 4. Synthetic scheme to the 2nd generation Biocompatible PAG based on dihydrocholesterol.

The new PAG anion based on dihydrocholesterol was synthesized in 5 steps in the form of TPS sulfonate from the starting dihydrocholesterol as indicated in Figure 4. This synthetic scheme is similar with the synthetic pathway of the biocompatible PAG based on lithocholic acid.

Lithographic performance of the Linear type Sweet PAG

The 1st 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).[11] TPS GB, TPS NB, TPS PFBS, and TPS PFOS were separately blended with poly(GBLMA-*co*-MAdMA). The four resists were evaluated at 193 nm and 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.[13] We reported about it in the last report. For example, 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.

A typical resist solution was prepared by dissolving the ESCAP (100mg) and the linear type Sweet PAG (5 wt% relative to the polymer, 5mg) in propylene glycol methyl ether acetate (PGMEA) (2.0g). The solutions were stirred until complete dissolution of components was observed. After the ESCAP and the linear type Sweet PAG dissolved, the clear solution was filtered through a 0.45μm PTFE filter (Whatman). Photoresist films were spin-coated onto 1,1,3,3,3-hexamethyldisilazane (HMDS) vapor primed silicon wafer at 2500rpm for 60s, and prebaked at 130℃ for 60s. The resist film thickness was in 110±10nm. Resist-coated wafers were then exposed to EUV irradiation. The exposed films were then baked at 130℃ for 60s. The films were developed in aqueous tetramethylammonium hydroxide solution (TMAH, 0.26N) for 60s, then rinsed in distilled water, and dried with a stream of nitrogen. After development, the patterns were examined with the optical microscopy and a high resolution scanning electron microscope.

Figure 5 shows the chemical structure of the 2nd generation linear type "Sweet" PAG based on D-glucose and their SEM micrographs obtained with ESCAP film containing the linear type Sweet PAG. The sensitivity of the resist containing the linear type Sweet PAG is 28 mJ/cm^2 at 254nm. It is more sensitive than TPS PFOS resist (31.2 mJ/cm^2).

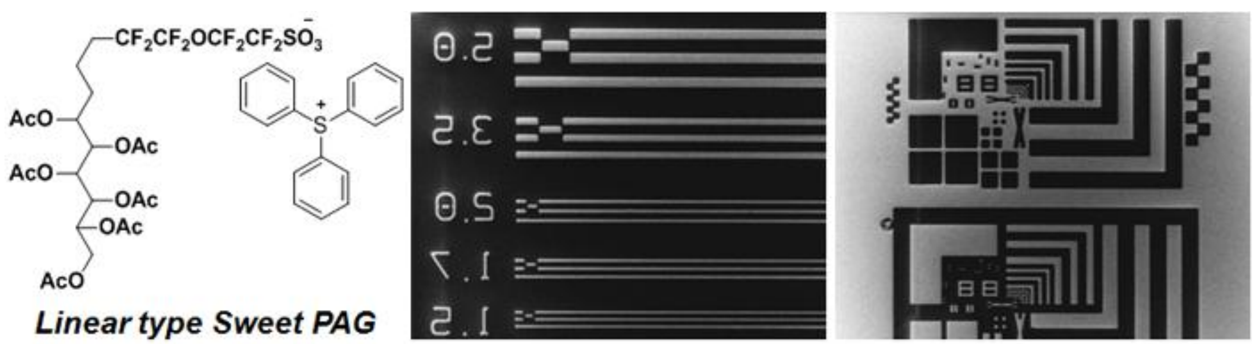

Figure 5. The chemical structure of the 2nd generation linear type "Sweet" PAG based on D-glucose and their SEM micrographs obtained with ESCAP film containing the linear type Sweet PAG. Processing condition: PAB=130℃/60s; PEB=130℃/60s; development=0.26N TMAH(AZ MIF 300)/60s.

The SEM images of the fine features are shown in Figures 5. On the basis of their excellent lithographic performance, we believe the new linear type Sweet PAG is capable of achieving higher resolution with low LER after resist processing conditions are optimized. Lithographic performance of the linear type Sweet PAG together with TPS PFOS and triphenylsulfonium perfluorobutanesulfonate (TPS PFBS) is being evaluated at both 193 nm and EUV wavelength.

Summary

We have efficiently synthesized the 2nd generation PAGs based on D-glucose, lithocholic acid, and dihydrocholesterol 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. Some of the new PAGs may be degraded by the chemicals and microorganisms. Initially, the linear type Sweet PAG showed excellent lithographic performance. Therefore, the new PAGs are promising candidates for environmentally friendly high-resolution lithography. Further studies on 193nm and EUV lithography as well as the environmental compatibility of novel PAGs such as the bioaccumulation potential and toxic effects are underway.

References

[1] Shirai, M.; Tsunooka, M. *J. Prog. Polym. Sci.* **1996**, *21*, 1.
[2] Shirai, M.; Tsunooka, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2483.
[3] Crivello, J. V. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 4241.
[4] Ito, H. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3863.
[5] Ito, H. *Adv. Polym. Sci.* **2005**, *172*, 37.
[6] Suzuki, Y.; Johnson, D. W. *Proc. SPIE.* **1998**, *3333*, 735.
[7] Kannan, K.; Koistinen, J.; Beckmen, K.; Evans, T.; Gorzelany, J. F.; Hansen, K. J.; Jones, O. P. D.; Helle, E.; Nyman, M.; Giesy, J. P. *Environ. Sci. Technol.* **2001**, *35*, 1593.
[8] Kannan, K.; Newsted, J.; Halbrook, R. S.; Giesy, J. P. *Environ. Sci. Technol.* **2002**, *36*, 2566.
[9] Kannan, K.; Newsted, J.; Halbrook, R. S.; Giesy, J. P. *Environ. Sci. Technol.* **2004**, *38*, 1264.
[10] Ayothi, R.; Yi, Y.; Cao, H. B.; Yueh, W.; Putna, S.; Ober, C. K. *Chem. Mater.* **2007**, *19*, 1434.
[11] Yi, Y.; Ayothi, R.; Wang, Y.; Li, M.; Barclay, G.; Sierra-Alvarez, R.; Ober, C. K. *Chem. Mater.* **2009**, *21*, 4037.
[12] Balla, E.; Zamyatina, A.; Hofinger, A.; Kosma, P. *Carbohydr. Res.* **2007**, *342*, 2537.
[13] Chauhan, M. M.; Nealey, P. J. J. *Vac. Sci. Technol. B* **2000**, *18*, 3402.