Fluorine-free Photoacid Generators for 193 nm Lithography Based on Non-Sulfonate Organic Superacids

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We are introducing a new family of fluorine-free photoacid generators (PAGs) for use in 193 nm lithography. These PAGs are based on percyano-substituted cyclopentadienide anions and do not contain sulfonate groups. PAGs with these weakly coordinating anions generate photoacids of a similar strength as perfluoroalkylsulfonic acids. Triphenylsulfonium pentacyanocyclopentadienide (TPS CN₅) can be synthesized from inexpensive precursors, is stable in the presence of strong acids, has a low optical density at 193 nm and is well soluble in typical resist solvents. The performance of model resists formulated with TPS CN₅ approaches that of commercially offered photoresists for the 32 nm node.

Keywords: photoacid generator, 193 nm lithography, fluorine-free

1. Introduction

Optical lithography has been the mainstream approach used in patterning semiconductor devices. In current state of the art manufacturing tools, wafers in contact with water are illuminated with ArF laser light (193 nm). In the vast majority of all patterning processes, the wafers are coated with a photoresist and then exposed with such light through a mask that defines a particular circuitry pattern. Subsequent baking, followed by treatment of the wafer with a developer – most often an aqueous base solution – removes the photoresist from the exposed areas (positive tone photoresist).

Chemically amplified resists (CAR)¹, originally reported by IBM's Hiroshi Ito et al. in 1983,² remain the most commonly used resist platform. In such CARs, the photoacid generator³ (PAG) is one of the key components as it generates the catalytic amount of acid required to cleave protecting groups

from the polymer backbone and make it developer soluble. In most applications, PAGs are organic salts of an antenna cation (P⁺) that decomposes into a proton upon irradiation, and the anion of the photoacid (A⁻).

Typical antenna cations are triphenylsulfonium (TPS) or bisphenyliodonium (BPI) cations. It was shown that if the polymer contains aromatic moieties, like in 248 nm (DUV) resists or lithography nodes of earlier generations, it can assist the acid generation through excitation and energy transfer to the PAG. Resist polymers likely play a role in assisting acid generation in extreme ultraviolet (EUV) lithography as well.⁴ However, aliphatic resists used in 193 nm lithography are largely transparent to the ArF radiation, so that the PAG cation carries the entire burden of light

absorption and proton generation. At the same time, many protecting groups employed in ArF photoresists require a much stronger acid in order to be cleaved from the polymer than those used in 248 nm lithography and previous generation resists.

This requirement to generate a very strong acid or superacid drastically limits the choices of PAG anions. A further limitation is that this anion is preferred to be organic. Therefore, SbF_6^- was removed from photoresists due to concerns related to toxicity and metal contamination. Thus, most anions of PAGs used in current 193 nm photoresists are perfluoroalkyl sulfonates (PFAS).

For a long time, PAGs based on perfluorooctanesulfonates (PFOS), the anion of perfluorooctanesulfonic acid (PFOA), were used. Since the discovery of PFOS in global blood banks in 1997, it has become clear that this material is bioaccumulative.⁵ Though there is no direct evidence of toxicity to humans, animal studies indicate that at moderate to high levels, PFOS and PFOA can cause a series of health problems, ranging from developmental problems to benign tumors. Since this discovery, PFOS has largely been replaced by equivalent anions of shorter perfluorinated carbon chains, such as perfluorobutanesulfonate (PFBS) or, more recently, tetrafluoroethanesulfonates that are further substituted with non-fluorinated functional groups⁶.

The half-life time of such compounds in humans depends on the chain length and is reduced from 5.4 years in PFOS to 1 month in PFBS. PFOS and its derivatives were added to the "list of persistent and bioaccumulative chemicals under the Stockholm Convention"⁷. IBM recently eliminated PFOS from all manufacturing processes.⁸

The great majority of all PAG anions carry a sulfonate group that will generate a sulfonic acid after irradiation. The strength of this corresponding acid mainly depends on the delocalization of the negative charge in the sulfonate anion. In PFAS anions, this delocalization is driven by the strong negative inductive effect from the adjacent CF_2 groups. However, not every strong organic acid requires a sulfonic acid group, though it is most often employed to accomplish this goal. Although technically non-sulfonic acids, perfluoro-

alkylsulfonimides⁹ ($\text{R}_f\text{-SO}_2\text{NH}$) are closely related to those. In general, a key requirement in the design concept of an anion that will form a strong acid or superacid is to delocalize the negative charge of its anion as much as possible. In such anions, nucleophilicity, tendency of coordination and proton affinity are very small. This concept is therefore not limited to acceptor-substituted sulfonate groups. Examples of inorganic anions with delocalized negative charge are hexafluoroantimonate (SbF_6^-) or borane clusters¹⁰, both of which were either used or proposed as PAGs.

In the 1960s, Webster et al.¹¹ reported that diazatetracyanocyclopentadiene reacts with CuCN to pentacyanocyclopentadienide (CN_5^-) and other products. Since then, tremendous amounts of theoretical calculations were carried out that studied this anion and the acidity of its corresponding acid¹². This theoretical work showed that this class of anions is not necessarily limited to cyclopentadienide, but that larger, peracceptor-substituted aromatic anions should work in the same way¹³. In the same paper, Vianello et al., showed that the acid obtained by C-protonation of the CN_5^- anion has a theoretical pK_a value of -20.2.

Richardson *et al.* reported in 2004 for the first time about the protonation of the CN_5^- anion¹⁴. The authors also compared the coordination of the CN_5^- anion to silyl groups with those of other anions. The results indicate that the CN_5^- anion has about the same coordination properties as triflate, so that similar acid strengths as perfluoroalkylsulfonic acids can be expected in resist polymers. These anions are therefore promising candidates for the design of F-free PAGs.

2. Approaches to Fluorine-free ArF PAGs

For photolithography nodes using 248 nm or longer wavelengths, the mainly aromatic polymer platforms and lower activation energy protection groups allowed for somewhat more flexibility in the choice of the photoacid and therefore the PAG. Therefore, it was much easier to find suitable fluorine-free (F-free) PAGs for these lithography techniques¹⁵. PAGs with alkylsulfonate anions (Figure 1a) are chemically closest related to fluorinated PAGs. Octanesulfonate (Os) is directly derived from the PFOS anion by replacement of its fluorine atoms by hydrogen. Camphorsulfonate (Cs) is another example of this class of PAG anions. In

benzene sulfonates (Figure 1b), the negative charge is delocalized through the π -system of the benzene ring and the corresponding acids are therefore stronger than aliphatic sulfonic acids.

Examples are tosylate (Tos) and the three structural isomers of nitrobenzenesulfonate (NBS). In NBS, the negative charge is further stabilized by the electron withdrawing substituent, making the corresponding acid much stronger. However, the solubility of these PAGs in common resist solvents is quite poor. It was shown that even camphorsulfonic acid is strong enough to deprotect low-activation energy 248 nm photoresists¹⁵, though higher activation energy DUV resists like *tert*-butoxycarbonyloxy-protected poly(hydroxystyrene) can not even be cleared with the much stronger 2,4-dinitrobenzenesulfonic acid.

Figure 1. Structures of selected F-free PAG anions described previously: a) aliphatic F-free sulfonates. b) benzene sulfonates.

As aliphatic and most aromatic organic sulfonic acids are not strong enough to deprotect 193 nm photoresists under reasonable conditions, it is more difficult to find F-free PAGs for 193 nm lithography. Therefore, the simple removal of the fluorine atoms does not provide viable PAGs for ArF lithography.

We recently showed that PAGs based on acceptor-substituted thiophenesulfonate anions (Figure 2) exhibit very good performance in dry and immersion 193 nm lithography^{16,17}. In this concept, we used heteroaromatic ring structures with lower delocalization energy as the foundation for F-free PAGs. These thiophenesulfonates are more stable than furan and less basic than pyrrol, and the strong acceptor substituents like the nitro group lead to very strong corresponding acids. Formulations of these PAGs with typical 193 nm photoresists can resolve 75 nm lines and spaces under dry ArF conditions at 0.93 NA and 45 nm lines and spaces under immersion ArF conditions at 1.35 NA.

Figure 2. F-free PAG anions based on acceptor-substituted thiophenesulfonates^{16,17}.

In this work, we are introducing F-free PAGs based on acceptor-substituted aromatic anions that do not contain sulfonate groups¹⁸. Figure 3 shows two examples of these anions, pentacyanocyclopentadienide (CN5) and methoxycarbonyl-tetracyanocyclopentadienide (CN4-C1), both of which are already reported in the literature^{11,19}. However, they haven't been explored as PAGs yet.

Figure 3. F-free PAG anions based on peracceptor-substituted aromatic anions¹⁸.

3. Synthesis and Properties of Pentacyanocyclopentadienide PAGs

3.1 Synthesis

Figure 4 outlines the synthesis of the CN5 anion^{14,20}. In the first step, sodium cyanide adds to carbon disulfide in dimethylformamide (DMF) to afford sodium cyanodithioformate (**1**). This salt is not very stable and by stirring in water, it autooxidizes very smoothly to its dimer (**2**) under sulfur elimination. This intermediate can easily be further oxidized to the water-insoluble tetracyano-1,4-dithiin (**3**). In the last step, which is mechanistically not fully understood, (**3**) reacts with the sodium salt of methyl cyanoacetate to give Na CN5 (**4**) and disodium bis(2-mercapto-1,2-dicyanovinyl)sulfide (**5**), which can be separated by acidification of the reaction mixture, followed by filtration.

TPS CN5 is subsequently precipitated from the reaction mixture by addition of aqueous TPS bromide solution. The CN5 anion is stable in the presence of strong acids and no hydrogen cyanide is formed even from recrystallization of tetraethylammonium CN5 in concentrated nitric acid¹⁹. Some slow hydrolysis of the CN groups to amides might occur when Na CN5 is kept in aqueous basic

Figure 4 . Synthesis of TPS CN5.

solution for an extended period of time. Replacement of methyl cyanoacetate by dimethyl malonate gives TPS CN4-C1 instead, providing an easy handle for additional attachment of functionality to the anion.

Both TPS CN5 and TPS CN4-C1 are very soluble in standard resist solvents like propyleneglycolmonomethylether acetate (PGMEA) or cyclohexanone (CH).

3.2 Optical and Thermal Properties

To examine the optical properties of TPS CN5 and TPS CN4-C1, we formulated the model photoresists PR1, PR2 and PR3 using a polymer similar to poly(2-trifluoromethanesulfonylaminoethylmethacrylate-co-methyladamantane-methacrylate-co-norbornanelactonemethacrylate) (TFSM-MAdMA-NLM)²¹, the corresponding PAG in a concentration equimolar to 5 wt% TPS PFBuS and an aliphatic proprietary base quencher (PAG:quencher = 5:1 molar ratio). Wafers (3") were coated at 160 nm film thickness and the optical constants of these resist films were determined by ellipsometry. The results, summarized in Table 1, showed that TPS CN5 (PR2) and TPS CN4-C1 (PR3) are comparable to TPS PFBuS (PR1) in terms of optical density (OD). This means that the aromatic counterion does not add additional absorption at 193 nm to the

formulation. Interestingly, the OD of the formulation containing TPS CN5 is even lower than the reference formulation.

Table 1. Optical properties of TFSM-MAdMA-NLM films with TPS PFBuS, TPS CN5 and TPS CN4-C1 PAGs.

Resist	PAG	n	k	OD [μm^{-1}]
PR1	TPS PFBuS	1.70	0.04	0.99
PR2	TPS CN5	1.70	0.03	0.88
PR3	TPS CN4-C1	1.71	0.04	0.98

We determined the shelf life of these formulations after storage for 30, 60 and 81 days at room temperature. These experiments showed no change in their dose-to-clear (E_0) values even after 81 days.

TPS CN5 is also thermally very stable. TGA analysis showed only less than 1% weight loss at 200 °C, and a 5% loss at 350 °C.

3.3 Leaching Tests

To avoid tool contaminations, it is very important that resist components do not leach into the water used in state of the art immersion ArF scanners. Particularly the PAG as a low molecular weight component of the resist is prone to such leaching. We therefore extracted the PAG from sample wafers that were coated with the same model resist PR2 by purging the wafer with water in an IBM WEXA5 cell²². The PAG quantity in the water was then determined by HPLC-MS analysis and converted into mol PAG per cm^2 wafer surface. In this initial study, we only obtained leaching data for the resist before exposure. As summarized in Table 2, the PAG amount leached into the water was extremely small and passed IBM's leaching specification for immersion resists for the wafer with immersion top coat (TC) as well as without TC.

Table 2. Leaching data for the model resist PR2, containing TPS CN5 PAG equimolar to 5 wt% TPS PFBuS, without exposure.

Condition	PAG quantity [$\text{mol} \cdot \text{cm}^{-2}$]
with top coat	$2.08 \cdot 10^{-13}$
Without top coat	$5.53 \cdot 10^{-12}$

4. Basic Lithographic Performance of Fluorine-Free PAGs

4.1 Contrast Curves with a High Activation Resist

We evaluated the lithographic performance of various F-free PAGs at different levels of complexity and demand. At the very first stage, we obtained contrast curves from formulations of model ArF resist polymers, formulated with various F-free PAGs. Figure 5 shows 193 nm contrast curves of the ArF resist poly(methyladamantanemethacrylate-norbornanelactonemethacrylate) (MAdMA-NLM), formulated with 5 wt% TPS PFBuS and the equimolar amounts of triphenylsulfonium camphorsulfonate (TPS Cs), triphenylsulfonium octanesulfonate (TPS Os) and the new TPS CN5 PAGs. Tetrabutylammonium hydroxide (TBAH; 20% molar with respect to PAG) was used as a base quencher.

Typically, this high activation energy polymer platform requires a 120 °C post-exposure bake (PEB). TPS PFBuS (reference) has an E_0 of only 3.4 mJ under these conditions. In contrast, TPS Cs does not clear this resist at all, even under much more drastic conditions, like 140 °C PEB and more than 50 mJ exposure dose, and the F-free PFOS-equivalent TPS Os shows the onset of development at 40 mJ and 140 °C PEB, but is still not cleared either. The E_0 of TPS CN5 is comparable with TPS PFBuS, however, it also requires a PEB of 140 °C to reach this fast photospeed.

When a sensitizer like 1-naphthol is blended (15 wt%) with the resist polymer, TPS Cs nearly clears the resist at 30 mJ and 140 °C PEB, but some residue remains. Finally, when the naphthol sensitizer is integrated into the resist polymer, clearing occurs at ~15 mJ at 140 °C. However, neither one of these processing conditions is viable for a real lithographic process, as patterned features require a three to five times higher dose to size (E_{size}) than the E_0 values in the contrast curves. In addition, the sensitizer increases the optical density of the resist to the extent that the contrast starts to degrade (tailing at the end of the contrast curves).

Nevertheless, these results provide some insight on how the PAG structure and the interaction of PAG and matrix impact the deprotection of the resist polymer and therefore the lithographic performance. Even though both TPS Cs and TPS Os generate primary alkylsulfonic acids of presumably similar acid strength, the less bulky octanesulfonic acid (OsA) clears the resist much easier than camphorsulfonic acid (CsA). One possible explanation for this behavior is that the diffusion of TPS Cs (and CsA) within the resist is much slower

Figure 5. ArF Contrast curves of poly(methyladamantanemethacrylate-co-norbornanelactonemethacrylate) with TPS Cs, TPS Os and TPS CN5 PAGs, compared to TPS PFBuS, under various conditions.

than the linear TPS Os (and OsA).

The significant impact of sensitizers on the photospeed of these resists demonstrates that there is a sensitization pathway via the polymer or sensitizers even for 193 nm radiation, in addition to the direct PAG decomposition pathway. It is yet to be determined if the additional increase in photospeed found for resists having naphthol groups attached to the polymer backbone is due to a better sensitization or increased dissolution due to the naphtholic OH group.

4.2 Contrast Curves with a Low Activation Resist

As most commonly used in ArF resist platforms use low activation energy protecting groups, we repeated the contrast curve experiments with the model resist polymer poly(ethylcyclopentane-methacrylate-co-norbornanelactonemethacrylate) (EcPMA-NLM). In this study, we included two F-free PAGs based on benzene sulfonates, two heteroaromatic F-free PAGs (TPS TN, TPS TBNO) and the novel TPS CN5 PAG. The results are shown in Figure 6. As expected, this resist is much faster than MAdMA-NLM, and the dose-to-clear value (E_0) of the reference formulation using TPS PFBuS is 1.3 mJ. The general trends, as discussed above for MAdMA-NLM, were very similar when EcPMA-NLM was used. TPS Cs required very drastic conditions, 25 mJ at 140 °C PEB, to clear this low activation resist. TPS Os is somewhat faster and

requires 23 mJ and 130 °C PEB. This can again be explained by the faster diffusion of the less bulky, linear Os anion.

For the reasons discussed above, aromatic sulfonic acids are stronger than aliphatic sulfonic acids. Therefore, both TPS tosylate (TPS Tos) and TPS 2-nitrobenzenesulfonate (TPS 2NBS) have much lower E_0 values than TPS Cs and TPS Os. TPS Tos clears at ~20 mJ at 110 °C and is slower than TPS 2NBS (3.5 mJ, 110 °C PEB), which has the additional electron-withdrawing nitro substituent on the benzene ring. Both TPS TN (2 mJ at 110 °C) and TPS TBNO (5 mJ at 110 °C) provide a fast photospeed with this resist.

Figure 6. Contrast curves of poly(ethylcyclopentane-methacrylate-co-norbornenelactonemethacrylate) with a) TPS Tos, TPS Os and TPS Cs, b) TPS 2NBS, TPS TN, TPS TBNO and TPS CN5, each compared to TPS PFBuS, under various PEB conditions.

The new TPS CN5 PAG exhibits an E_0 of 3.5 mJ as well and has therefore a similar photospeed as TPS 2NBS. However, as discussed above, the coordination tendency of the CN5 anion is similar to triflate¹⁴ and subsequently, the conjugated acid of CN5 should be just as strong as triflic acid or perfluorobutanesulfonic acid.

It was therefore expected that the photospeed of this resist formulated with TPS CN5 should be comparable to TPS PFBuS, rather than TPS 2NBS. As shown in the comparison of TPS Cs and TPS Os, there are other factors than just the acid strength that impact the actual dose-to-clear value of a resist. One reasonable explanation could be that the diffusion of TPS CN5 and its corresponding acid is somewhat slower than TPS PFBuS and perfluoroalkylsulfonic acids (PFAA). Most likely, the cyclic aromatic anion does not diffuse through aliphatic ArF resists as quickly as linear alkylsulfonates, whether they are fluorinated or not. If true, this would be an important benefit of the CN5 anion, as the fast diffusion of PFAS without bulky substituents may become problematic when features as small as 45 nm lines should be resolved.

4.3 Patterning of 150 nm Lines/Spaces

In the next stage of the lithographic evaluation of F-free PAGs, we generated 150 nm/150 nm line/space (L/S) patterns, using a 0.75 NA dry 193 nm scanner. For this evaluation, we only selected F-free PAGs with reasonable contrast curves from the experiments discussed above. In addition, F-free PAGs based on heteroaromatic sulfonates, such as TPS TN and TPS TBNO (Figure 2)¹⁶, were included. We therefore excluded TPS Cs, TPS Os and TPS Tos from this evaluation. The model resist composed of a polymer similar to TFSM-MAdMA-NLM, the PAG (equimolar to 5wt% TPS PFBuS) and a proprietary aliphatic quencher (PAG:quencher = 5:1 molar) was used as resist platform. The components were dissolved in either PGMEA alone or with 30 wt% CH as a co-solvent. All resists were coated onto 90 nm of a commercial organic BARC to achieve 160 nm resist thickness. PEB was 120 °C, except for TPS CN5, where PEB was 140 °C.

Figure 7. Cross-sections of 150 nm L/S E_{size} patterns, obtained with F-free PAG formulations using the TFMS-MAdMA-NLM resist.

Figure 7 shows cross-sections of the dose-to-size (E_{size}) fields obtained from these F-free PAG formulations. As the formulations were not optimized, all features, including those obtained from the TPS PFBuS reference formulation (a) are somewhat tapered. However, the worst tapering was found for the smaller aromatic sulfonates, particularly TPS 2NBS (b) and TPS 4-cyanobenzenesulfonate (TPS CN, c). The best profiles were obtained for TPS PFBuS, TPS TBNO (e) and TPS CN5 (f). Both TPS TBNO and TPS CN5 were slower than TPS PFBuS, as well as TPS 2NBS, TPS CN and TPS TN. The contrast curve results discussed in the previous section already indicated that TPS CN5 had a slower photospeed than TPS PFBuS, despite the higher than normal PEB temperature used here.

5. Performance of TPS CN5 under Advanced ArF Patterning Conditions

5.1 Patterning of 100 nm and 45 nm Lines/Spaces

The excellent profiles of the TPS CN5 formulation in the previous experiment were promising enough to evaluate this new PAG under more challenging lithographic conditions. We started the evaluation with the same model resists *PR1* and *PR2* that were then either coated onto an organic BARC and exposed with a 0.93 NA dry 193 nm tool or used in the trilayer scheme with a 1.35 NA immersion 193 nm scanner. The performance was studied with test patterns of 100 nm/100 nm L/S (Figure 8). The *PR2* resist containing TPS CN5 was benchmarked against *PR1* (TPS PFBuS) under the exact same condition, except that the PEB

temperature for *PR2* was 140 °C and for *PR1* 120 °C.

The results clearly indicate that the resist containing TPS CN5 can easily achieve this resolution under both exposure conditions. Overall, TPS PFBuS gives slightly less residue in the trenches, particularly on the trilayer stack (silicon ARC). This could have various reasons, such as segregation of the TPS CN5 towards the top of the film (unlikely, as the PAG is F-free) or that PFBuS has a stronger affinity to the silicon ARC interface than CN5. Also, the photospeed of *PR2* is about 6 mJ slower than that of *PR1*, although the PAB of *PR2* was 20 °C higher than *PR1*.

We subsequently obtained 45 nm/45 nm L/S patterns with the 1.35 NA immersion 193 nm tool for both of these resists, under the otherwise same processing conditions. Here, we clearly approach the resolution limit of the resist platform, as both formulations have problems resolving 45 nm lines (Figure 9). The reference resist *PR1*, containing TPS PFBuS, shows line collapse at this line width, though the features otherwise look decent and the trenches are clear. The F-free PAG resist *PR2*, containing TPS CN5, can still resolve this feature size, but there is significant footing, residue and top loss of the features. The E_{size} values are about 9 mJ higher for *PR2* than for *PR1*, despite the higher PEB temperature for *PR2*. Clearly, this higher PEB temperature also accounts for the feature

Figure 8. Slightly overexposed 100 nm/100 nm L/S patterns of the model resists *PR1* (TPS PFBuS) and *PR2* (TPS CN5), obtained with a 0.93 NA 193 nm tool on an organic BARC or with a 1.35 NA immersion 193 nm tool on trilayer stack.

Figure 9. 45 nm/45 nm L/S patterns of the resists *PR1* (TPS PFBuS) and *PR2* (TPS CN5), obtained with a 193 nm immersion tool on trilayer.

degradations, like the top loss, seen in the cross-sections.

5.2 Comparison of the TPS CN5 Formulation *PR4* with Commercial 32 nm Resists

The comparably poor results obtained for 45 nm/45 nm L/S patterns with the *PR1* and *PR2* resists indicated that an improved resist platform was required. Optimizations led to a proprietary low activation resist, containing ethyl-cyclooctane-methacrylate (EcOMA) moieties²³. The PEB temperature for this resist is only 90 °C. For this evaluation, the resist *PR4* was formulated in PGMEA to achieve 120 nm film thickness, with 5 wt% TPS CN5 and a molar ratio of PAG : quencher of 5 : 1. In addition to the polymer platform, the base quencher was also changed from aliphatic to aromatic, assuming that an aromatic quencher should be compatible with an aromatic PAG. We

Table 3. Lithographic performance of the commercially available resists A, B, C and the F-free PAG formulation *PR4*, containing the TPS CN5 PAG.

Resist	E _{size} [mJ]	MEEF	LWR	P100 L/S
	<30	<3	P100 L/S	DOF at 5% EL
A	14.3	2.2	7.5	0.24
B	25.8	2.24	6.0	0.29
C	21.2	2.4	6.5	0.21
<i>PR-4</i>	15.4	2.26	9.6	0.22

Resist	P90 L/S	Iso space (CD=78nm)	Iso line (CD=78nm)
	DOF at 5% EL	DOF at 5% EL	DOF at 5% EL
A	0.15	0.15	0.13
B	0.15	0.15	0.16
C	0.13	0.13	0.15
<i>PR-4</i>	0.15	0.15	0.13

chose three commercially available L/S resists offered for usage in the 32 nm node and benchmarked the F-free PAG formulation *PR-4* against these materials. Again, we used a 1.35 NA immersion 193 nm scanner, and the trilayer stack.

The lithographic performances of the three commercial resists and the F-free PAG formulation *PR4* with TPS CN5 are summarized in Table 3. Profiles of 55nm/45nm and 45nm/45nm L/S patterns are shown in Figure 10 and Figure 11, respectively. These data clearly shows that the performance of the *PR4* formulation is comparable to that of the commercial samples. This is particularly remarkable, as the *PR4* formulation is not further optimized and contains only one PAG component. Most commercial resists have PAG mixtures to fine-tune their performance.

The E_{size} of *PR4* (15.4 mJ) is at the lower end of the four resists compared in this study, even though TPS CN5 is not as fast as PFAS PAGs. Most modern formulations use PAGs with slower acid diffusion than PFBuS to achieve a higher resolution at tight pitches. TPS CN5 is most likely also a PAG with slower diffusion than TPS PFBuS, as discussed above. The mask error enhancement factor (MEEF) for *PR4* is in the same range as resists A and B and better than resist C. Line width roughness (LWR) is slightly worse for *PR4* than for the commercial resists and the depths of focus (DOF) for 100 nm and 90 nm dense L/S patterns as well as 78 nm isolated line and 78 nm isolated space at 5% exposure latitude (EL) are comparable to them.

Figure 10. Cross-sections of 55 nm/45 nm L/S patterns, obtained from three commercially available formulations A, B and C, and compared to the F-free PAG formulation *PR4* containing the TPS CN5 PAG.

Figure 11. Cross-sections of pitch 90 nm/space 45 nm patterns, obtained from three commercially available formulations A, B and C, and compared to the F-free PAG formulation *PR4* containing the TPS CN5 PAG.

The profiles for 55nm/45nm L/S patterns (Figure 10) of *PR4* are excellent. The TPS CN5 resist *PR4* exhibits even less footing than resists A and B. For 45nm/45nm L/S (Figure 11), there is an onset of residue formation between the lines of *PR4*, but overall, the profiles look very good here as well.

Overall, the *PR4* resist can compete with the commercial samples for the 32 nm node. The TPS CN5 PAG has the potential to outperform many PAGs in current formulations, as further optimizations to the *PR4* formulation, such as the choice of the polymer platform, the quencher and the PAG loading can further be performed.

5.3 Comparison of TPS CN5 and TPS CN4-C1

The data discussed so far focused on the PAG containing the CN5 anion. While the results clearly showed that this PAG has excellent performance, it is structurally limited in the sense that any change to the five CN groups on the ring may alter its performance. In the PAG TPS CN4-C1, one of the CN groups is replaced by a methyl ester group. An ester group is a slightly weaker electron accepting group than a cyano group, which might lead to a reduced acid strength and therefore slower photospeed or modified overall lithographic performance. On the other hand, the methyl group could be replaced by any other alkyl group, so that such a PAG has much more flexibility to fine tune its properties.

We therefore created two new formulations, using the same polymer platform and quencher as in *PR4*, but with a 7 wt% PAG loading, using TPS

CN5 (*PR5*) and TPS CN4-C1 (*PR6*) as PAGs. Figure 12 shows cross-sections of 45 nm/45 nm L/S features, obtained by immersion ArF radiation from these two resists on the trilayer stack. Clearly, there is no significant difference, if any, between the profiles of these two resists.

The E_{size} of *PR-6* at 90 °C PEB, containing TPS CN4-C1 is 16.5 mJ, that of *PR-5* (TPS CN5) is 15 mJ, which is an almost negligible difference. Therefore, ester-substituted CN4-Cx PAGs are generally expected to perform similarly as TPS CN5.

Figure 12. 45 nm/45 nm L/S patterns obtained from *PR5* (TPS CN5) and *PR6* (TPS CN4-C1) formulations.

6. Experimental Section

6.1 Materials and Material Property Measurements

All chemical precursors and solvents were obtained from Sigma-Aldrich in at least 95% purity. NMR spectra were recorded in solution on a Bruker Avance 400, with tetramethylsilane as internal standard.

Thermal gravimetric analysis (TGA) was performed with a Hi Res TGA 2950 Thermogravimetric Analyzer from TA Instruments. Samples were heated at a rate of 10 °C under a nitrogen flow of 5 mL/min. For optical property measurements, thin solid films were then prepared by spin-coating formulations over 5 inch silicon wafers at the spin rate of 1500 rpm for 60 seconds and baked at 110 °C for 60 seconds. n and k were measured by VASE ellipsometry, OD values were then calculated from k . For leaching experiments, same resist formulations were spin-coated on bare silicon wafer at 1500 rpm for 60 seconds and baked at 110 °C for 60 seconds.

An immersion top coat typically used in the industry was spin-coated onto the resulting resist film at 1500 rpm for 30 seconds and soft baked at 90 °C for 60 seconds. A water sample was collected from resist thin film without exposure according to IBM WEXA5 condition. The anion concentration

was analyzed by HPLC-MS by MPI Research, State College, PA, against a standard sample.

6.2 Photolithographic Experiments

For initial 193 nm lithography screening, the prepared photoresist formulation (typically in PGMEA or PGMEA/CH 70/30, with a PAG loading equimolar to 5 wt% TPS PFBuS and a PAG:quencher ratio of 5:1) was spin-coated for 30 seconds to achieve 150 nm film thickness onto an organic ARC layer, pre-applied onto 8" silicon wafers at a film thickness of 90 nm. The resist films were baked at 110°C for 60 seconds. The wafers were then exposed to 193 nm radiation (ASML scanner, 0.75 NA). Contrast curves were obtained from a dose meander of 1 + 0.1 mJ or 1 + 0.2 mJ, applied to 1x1 cm² fields on the wafer. The wafers were then baked for 60 s (PEB) at the temperature specified in the discussion section and subsequently puddle developed by 0.26 N tetramethylammonium hydroxide (TMAH) developer for 60 s.

The film thicknesses of each dose step were then measured with a NanoSpec (Model 4000; Nanometrics, Inc.). 150 nm/150nm L/S patterns were obtained under the same conditions, but typically a dose meander of 5 + 1 mJ was used. The resulting patterns of the photoresist imaging layers were examined by top-down scanning electron microscopy (SEM).

For formulation optimization for 193 nm non-immersion lithography, resist formulations were prepared with PGMEA or PGMEA/CH (70% wt./30% wt.) as solvent. PAG loading was equimolar to 5 wt% of TPS PFBuS to polymer and quencher loading was 20% molar ratio to PAG. The prepared resist formulations (film thickness of 120 nm at 1500 rpm) was spin-coated for 30 seconds onto an organic ARC layer (90 nm), pre-applied onto 12" silicon wafers. The resist films were baked at 110 °C for 60 seconds. The wafers were then exposed to 193 nm radiation (ASML scanner, 0.93 NA). The exposure pattern was an array of lines and spaces of various dimensions down to 70 nm. The exposed wafer was then post-exposure baked for 60 seconds at the temperature specified in the discussion section. The wafer was puddle developed by 0.26 N TMAH developer for 60 seconds. The resulting patterns of the photoresist imaging layers were examined by top-down SEM and obtained the images of 75 nm line and space.

In the case of 193 nm immersion lithography, resist formulations were prepared with PGMEA or PGMEA/GBL (1.5% wt. GBL) as solvent. PAG loading is 5 wt% to polymer and quencher loading is 20% molar ratio to PAG. The prepared resist formulation (film thickness of 120 nm at 1500 rpm) was spin-coated for 30 seconds onto a tri-layer stack (resist / 35 nm Si ARC / 200 nm spin-on carbon), applied on 12" silicon wafers. The resist films were baked at desirable temperatures for 60 seconds and then coated with 90 nm of an immersion top coat typically used in the industry. The wafers were then exposed to 193 nm radiation (ASML scanner, 1.35 NA). The exposure pattern on a binary mask was an array of lines and spaces of various dimensions down to 40 nm. The exposed wafer was then post-exposure baked at desirable PEB temperatures for 60 seconds. The wafer was puddle developed by 0.263 N TMAH developer for 60 seconds.

The resulting patterns of the photoresist imaging layers were examined by CD-SEM. CD-SEM images were completed on Verity 4i with CD bias of 5nm. For 50 nm line and space mask feature, physical CD target was 50 nm while for 45 nm line and space mask feature, physical CD target was 45 nm. For isolated space, physical CD target was 78 nm. For isolated line mask feature, physical CD target was 78 nm.

6.3 Chemical Synthesis

Sodium cyanodithioformate (1)^{20b}

To 0.61 mol (30 g) of sodium cyanide, finely dispensed in 150 mL dimethylformamide (DMF), was added drop-wise 38 mL (0.63 mol) carbon disulfide over the course of 90 min. The reaction temperature was allowed to rise to 40 °C during the addition process (below the boiling point of CS₂). Towards the end of the reaction, the product precipitated as dark brown crystals with 3 eq of DMF. Subsequently, 60 ml of 2-butanol was added and the mixture heated to 110 °C. The product crystallized upon cooling to room temperature under stirring, was filtered and washed with cold 2-butanol. More product was obtained from the filtrate by storage at 4 °C overnight. The salt was usually used immediately in the next step, without further analysis.

¹³C NMR (CD₃CN, 100 MHz): δ = 118.7; 211.1.

Disodium dimercaptomaleonitrile (2)^{20b}

Crude compound 1 was dissolved in 1 L water and stirred for 72 h at room temperature. The originally dark brown solution turned yellow-orange during the course of the oxidation. Elemental sulfur precipitated and was filtered off. The obtained aqueous solution of 2 was used in the next step without further purification.

¹³C NMR (D₂O, 100 MHz): δ = 122.7; 126.1.

Tetracyano-1,4-dithiin (3)¹⁴

150 g (0.66 mol) of ammonium peroxodisulfate was dissolved in 300 mL water and slowly added to the aqueous solution of compound 2. The reaction mixture turned dark red and then, a bright brownish mixture of 3 and elemental sulfur precipitated. The product mixture was filtered, thoroughly washed with water and dried in oil pump vacuum. It was then placed into an extraction thimble, which was transferred into a soxhlet extractor. Sulfur was extracted over the course of three days with carbon disulfide, after which time the product was removed from the thimble and dried.

Typical overall yields for these three steps are 75 – 90 %. ¹³C NMR (acetone-d₆, 100 MHz): δ = 111.5; 124.5.

Triphenylsulfonium pentacyanocyclopentadienide (TPS CN5)

To 1.2 g NaH (60% in min. oil; 30 mmol) in 40 ml dry tetrahydrofuran was added 0.6 g (6.1 mmol) methyl cyanoacetate under N₂. Once hydrogen evolution had ceased, 2.16 g (10 mmol) of tetracyano-1,4-dithiin (3) was added. The mixture was stirred at 110 °C for 12 h, then heated up to 160 °C until the solvent was evaporated. Remaining traces of solvents were removed in oil pump vacuum, until a dark brown, dry solid was formed. This solid was dissolved in 100 mL of water, followed by addition of 5 mL conc. H₂SO₄. Filtration from the dark brown solids yielded a reddish solution that was discolored by addition of 10 mL of aqueous 6% sodium hypochlorite solution. Further red-brownish precipitate was filtered off. Addition of an aqueous solution of triphenylsulfonium bromide (or chloride) gave a yellowish precipitate that was filtered and thoroughly washed with water until the pH of the filtrate reached pH = 5. The PAG was then dried, dissolved in dichloromethane, filtered through a 20

µm syringe filter and precipitated into hexanes. Yield: 0.93 g (2.05 mmol; 41% theoretical yield).

¹H NMR (acetone-d₆, 400 MHz): δ = 7.94-7.85 (m, 15H); ¹³C NMR (acetone-d₆, 100 MHz): δ = 134.8; 131.6; 131.3; 124.9; 113.0; 102.1.

Triphenylsulfonium methoxycarbonyltetracyanocyclopentadienide (TPS CN4-C1)

TPS CN4-C1 was synthesized in the exact same fashion as TPS CN5, except that dimethyl malonate was used in the place of methyl cyanoacetate.

¹H NMR (acetone-d₆, 400 MHz): δ = 7.94-7.85 (m, 15H); 3.82 (s, 3H).

¹³C NMR (acetone-d₆, 100 MHz): δ = 134.8; 131.6; 131.3; 124.9; 114.5; 114.0; 113.0; 102.5; 100.3; 50.8.

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