Efficiency of Photoacid Generators in Chemically Amplified Resists for 157nm Lithography

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The photoacid generation efficiency of six photoacid generators was measured upon exposure to 157nm light in a candidate polymer for 157nm resist formulations of poly(NBHFA-co-NBTBE) using a standard addition technique. The photoacid generators studied were triphenylsulfonium perfluoro-1-butanesulfonate (TPS-Nf), bis(4-tert-butylphenyl)iodonium trifluoromethanesulfonate (BBI-Tf), bis(4-tert-butylphenyl)iodonium perfluoro-1-butanesulfonate (BBI-Nf), bis(4-tert-butylphenyl)iodonium perfluoro-1-octanesulfonate (BBI-PFOS), N-hydroxy-5-norbomene-2,3-dicarboximide perfluoro-1-butanesulfonate (NDI-Nf), and bis(2-trifluoromethyl-6-dinitrobenzyl) 1,3-benzene sulfonate (TFMDNBS). For the four ionic salts the photochemical efficiency was in the order BBI-Nf > BBI-Tf > BBI-PFOS > TPS-Nf. The photoacid generators NDI-Nf and TFMDNBS exhibited extremely poor efficiency for photoacid generation in this resist system under exposure to 157nm radiation.

Keyword: photoacid generator, triphenylsulfonium perfluoro-1-butanesulfone, 157 nm lithography

1. Introduction

The continual increase in the speed and performance of microelectronic devices is a result of improvements to the resolution capabilities of photolithographic imaging since shrinking the size of transistors increases the speed of integrated circuits. The smallest printable feature into thin films of photoresist by an optical exposure system is directly proportional to the wavelength of light used in the exposure tool. Decreasing the wavelength of the exposure source increases the resolution of the exposure system. Current state-of-the-art lithographic processes use 193nm light to pattern features with dimensions less than 100nm. To push resolution limits to smaller dimensions, the wavelength of the exposure source used in optical lithography will likely be reduced to 157nm in the coming years. As with previous generations of photolithography, the improvement in resolution afforded by reducing the wavelength of light used in the exposure system cannot be realized until a photoresist has been designed and optimized to function at that wavelength.

The extension of optical lithography into the vacuum ultraviolet (VUV) at 157nm has introduced tremendous challenges to the design of photoresist materials. At this wavelength organic materials absorb light strongly. The large attenuation of 157nm light through a resist film limits its usable thickness, and for most organic materials that are commonly used in photoresists, the film thickness is limited to less than about 150nm. Another consideration in the design of 157nm photoresists is the energy of the exposure source. At 157nm (7.9eV) the photon energy becomes sufficiently large to excite, and possibly dissociate, common chemical bonds of polymer molecules used as the matrix of the resist. These processes may serve to delocalize the photochemistry of the resist and lead to extensive radiation damage of the polymer. These factors should be considered for the design and optimization of 157nm resist formulations.

Single layer resist processes for 157nm lithography will likely use chemical amplification to boost resist sensitivity to exposure. A chemically amplified...
photoresist uses the generation of a catalyst during exposure to perform chemical reactions within the resist matrix during a post-exposure bake that ultimately change the development rate of the exposed regions of the film. Chemical amplification is derived from the fact that one photogenerated molecule catalyzes numerous chemical reactions within the resist. The most common positive-tone chemically amplified photoresists rely on the generation of a strong photoacid by the decomposition of a photoacid generator (PAG) upon exposure to catalyze the removal of acid-labile protecting groups from the polymer. Photoacid catalyzes the deprotection of the polymer by a reaction-diffusion process within the resist matrix during a post-exposure bake (PEB). The removal of protecting groups increases the dissolution rate of the resist in a developing solution, typically aqueous base, and a pattern is formed by the difference in dissolution rates of the exposed and unexposed regions. The sensitivity of the resist (exposure dose required to develop) is therefore a combination of the efficiency of the decomposition of PAG to produce photoacid, the action of photoacid to deprotect the polymer, and the dissolution rate of the deprotected resist.

In this work, we measured the efficiency of photoacid generation for six PAGs in a candidate polymer for 157nm resist formulations using a standard addition technique. Details of the standard addition technique and its validation have previously been published. In brief, the technique relies on the addition of a base quencher to the resist formulation that neutralizes a stoichiometric equivalence of photoacid generated by exposure. The exposure dose required to develop the resist increases as the base concentration increases since photoacid is neutralized. Experimental measurements of the dose to clear as a function of the added base concentration are fit using a model that describes the photoacid generation process and the neutralization of photoacid by base. The efficiency of photoacid generation is quantified by the resist C parameter, a parameter that is proportional to the quantum yield of the photodecomposition of PAG to form photoacid. Once the C parameter is known, the concentration of photoacid can be calculated for any exposure dose. Of the six PAGs examined in this work, iodonium salts exhibited the greatest efficiency for photoacid generation, but required a greater concentration of photoacid than sulfonium salts to render development.

![Chemical structures](image)

**Fig. 1.** Chemical structures for the resist materials used in this study: triphenylsulfonium perfluoro-1-butanesulfonate (TPS-Nf), bis(4-tert-butylphenyl)iodonium trifluoromethanesulfonate (BBI-Tf), bis(4-tert-butylphenyl)iodonium perfluoro-1-butanesulfonate (BBI-Nf), bis(4-tert-butylphenyl)iodonium perfluoro-1-octanesulfonate (BBI-PFOS), N-hydroxy-5-norbomene-2,3-dicarboximide perfluoro-1-butanesulfonate (NDI-Nf), bis(2-trifluoromethyl-6-dinitrobenzyl) 1,3-benzene sulfonate (TFMDNBS), tetrabutyl ammonium hydroxide (TBAH), and the poly(NBHFA-co-NBTBE) polymer.
2. Experimental

The photoacid generators triphenylsulphonium perfluoro-1-butanesulfonate (TPS-Nf), bis(4-tert-butylphenyl)iodonium trifluoromethanesulfonate (BBI-Tf), bis(4-tert-butylphenyl)iodonium perfluoro-1-butanesulfonate (BBI-Nf), bis(4-tert-butylphenyl)iodonium perfluoro-1-octanesulfonate (BBI-PFOS), and N-hydroxy-5-norbornene-2,3-dicarboximide perfluoro-1-butanesulfonate (NDI-Nf) were purchased from Midori Kagaku Co. (Tokyo, Japan). The photoacid generator bis(2-trifluoromethyl-6-dinitrobenzyl) 1,3-benzene sulfonate (TFMDNBS) was provided by Agere Systems (Murray Hill, NJ). A copolymer of bicyclo[2.2.1]hept-5-ene-2-(1,1,1-trifluoro-2-trifluoromethylpropan-2-ol (NBHFA) and bicyclo[2.2.1]hept-5-ene-2-carboxylic acid tert-butyl ester (NBTE) was provided by International SEMATECH in collaboration with researchers at University of Texas at Austin. The composition of the polymer was 70% NBHFA and 30% NBTE monomers. The average molecular weight was approximately 30,000 g/mol. The base quenchers, tetrabutyl ammonium hydroxide (TBAH) and 1-piperidineethanol (1PE) were purchased from Aldrich (Milwaukee, WI). TBAH was obtained as a 1M solution in methanol. Fig. 1 illustrates the chemical structures of the materials used in this study.

Resist solutions were formulated for each of the six PAGs in the poly(NBHFA-co-NBTBE) polymer from stock solutions of individual components. Stock solutions of PAG components were made in ethyl lactate, and the polymer was dissolved in propylene glycol methyl ether acetate (PGMEA). Stock solutions of TBAH and 1-PE were prepared by dilution with PGMEA. The concentration of PAG in each resist formulation was 100 µ mol/g resist based on solids content. For each PAG, a series of resist formulations was prepared that differed only in the concentration of base quencher. For TPS-Nf, two series of resist formulations were prepared using 1-PE and TBAH as the base quenchers. For all other PAGs only TBAH was used. The base concentration ranged from zero to 25 µ mol/g (0.0 to 0.25 ratio to the initial PAG concentration). Each resist solution was diluted to 5 wt% solids with PGMEA.

All samples were prepared on eight-inch silicon test wafers using a Polaris 2000 microlithography cluster (FSI International). Substrates were coated with Shipley AR19-820 anti-reflective coating for a nominal thickness of 82.5 nm. Resist solutions were spin cast on top of the ARC and baked at 140°C for 60 seconds. Film thickness was controlled to yield an average film thickness of 125 ± 5 nm. The optical constants (n and k) for resist films were determined from measurements on a vacuum ultraviolet-variable angle spectroscopic ellipsometer (VUV-VASE) (JA Woollam Co., Inc.) using silicon substrates without ARC. Exposures were performed using a 157nm microstepper (Exitech Limited). A 10x10 dose array was exposed on each sample without a mask (open frame). The post-exposure bake (PEB) for exposed resist samples was 110°C for 60 seconds for all resists except the TFMDNBS series for which the PEB was increased to 130°C for 90 seconds. Resist films were then developed in Shipley LDD-26W (0.26N tetramethylammonium hydroxide) developer for 20 seconds. The minimum exposure dose required to completely dissolve the resist film after development (dose to clear) was recorded for each sample.

3. Results

A. Resist absorption in the vacuum ultraviolet

Table 1 lists the average absorption coefficients (base e) for the poly(NBHFA-NBTBE) polymer and six resist formulations. The absorption coefficients for the resist formulations were greater than for the polymer alone. The absorbance of the sulfonium resist was larger than the three iodonium and the dicarboximide formulations. The absorbance of iodonium resists increased slightly as the size of the anion increased. The resist containing TFMDNBS exhibited the greatest transparency of the six resists. Within the error of replicate measurements, the absorbance did not change for formulations containing the base quencher TBAH.

Table 1. Resist absorption coefficients

<table>
<thead>
<tr>
<th>Photoacid Generator</th>
<th>Absorption Coefficient (µm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(NBHFA-co-NBTBE)</td>
<td>9.55</td>
</tr>
<tr>
<td>TPS-Nf</td>
<td>10.89</td>
</tr>
<tr>
<td>BBI-Tf</td>
<td>10.31</td>
</tr>
<tr>
<td>BBI-Nf</td>
<td>10.45</td>
</tr>
<tr>
<td>BBI-PFOS</td>
<td>10.70</td>
</tr>
<tr>
<td>ND-Nf</td>
<td>10.13</td>
</tr>
<tr>
<td>TFMDNBS</td>
<td>10.11</td>
</tr>
</tbody>
</table>
B. Measurement of Dose to Clear Values for Resist Systems Containing Base Quenchers

The dose to clear was measured for a resist system consisting of the TPS-Nf PAG in poly(NBHFA-co-NBTBE) using the base quencher 1PE. Two post-exposure bake conditions at 110°C for 60 seconds and 130°C for 60 seconds were used. As the concentration of base was increased, the dose to clear remained constant at values of 3.5 mJ/cm² and 1.05 mJ/cm² for the two PEB processes at 110°C and 130°C, respectively. Surprisingly, the 1PE base quencher did not appear to neutralize photoacid within the resist. These effects were not explored further, and the 1PE base quencher was not used in additional formulations.

Using TBAH as the base, the dose to clear was measured for each series of resist formulations containing the six different PAGs. A PEB process was at 110°C for 60 seconds for each series except TFMDNBS in which the PEB temperature was increased to 130°C and baked for 60 seconds. In Fig. 2 the dose to clear for each system is plotted as a function of the added base concentration. The dose to clear values increased as the concentration of base quencher increased for resists containing sulfonium and iodonium salts. The dose to clear values for resists containing NDI-Nf increased rapidly for small additions of base quencher and as the concentration of base increased above 13 μ mol/g (0.13 [Base]/[PAG]₀) the resist formulations did not develop, even for very large exposure doses above 100 mJ/cm². The TFMDNBS resist series exhibited a maximum in the dose to clear value at a concentration of base of approximately 15 μ mol/g (0.15 [Base]/[PAG]₀), and then decreased slightly as additional base was added.

4. Discussion

A. Resist Absorbance in the Vacuum Ultraviolet

As expected by the strong absorbance of phenyl groups in the VUV, the absorbance of the resist formulations appeared to increase with increasing phenyl content. As follows, the sulfonium PAG increased the resist absorbance more than the iodonium PAG. Accordingly, the incorporation of sulfonium or iodonium PAGs to poly(NBHFA-co-NBTBE) increased the absorption coefficient to a greater degree than the NDI-Nf PAG. The exception to this trend appeared to be the resist containing TFMDNBS, as the absorbance of this resist was lower than the other five. The incorporation of fluorinated groups on carbonaceous materials is known to decrease the absorption of light in the VUV. The presence of the fluorinated groups on this PAG likely decreased its contribution to the overall absorption of light by the resist. Contrary to this observation, the absorption coefficient of the iodonium resists slightly increased with increasing size of fluorinated alkyl anions.

B. Base Quencher Selection

For the resist series containing the TPS-Nf PAG and the 1-PE base quencher the dose to clear did not increase as the concentration of base quencher increased. This suggested that the 1PE base quencher did not act to neutralize photogenerated acid within the poly(NBHFA-co-NBTBE) resin. The 1PE base quencher was previously validated and implemented with the standard addition technique in a matrix of poly(p-t-butoxy-carbonyloxystyrene –co–p-hydroxystyrene) (PTBOCST) In that work, the 1PE base quencher was shown to neutralize photoacid and operate in accordance with the assumptions of the standard addition technique. No definite conclusions could be drawn from these observations, but 1PE did not appear to function as a base quencher within the poly(NBHFA-co-NBTBE) copolymer.

It is important to note that the role of TBAH in the poly(NBHFA-co-NBTBE) has not been thoroughly examined nor proven to meet the assumptions of the
standard addition technique. The experiments used to evaluate 1-PE in PTBOCST cannot be easily applied to this resist system. Due to the strong absorbance of 157nm radiation by these resists, ultra-thin films of resist must be used. Measurements of the resist dissolution rate and infrared absorbance are difficult to perform in ultra-thin films. We recognize TBAH could effect resist performance beyond neutralization of photoacid, and these effects could lead to errors in the C parameter estimates. However, we believe that these effects will not alter the observed trends and will still permit characterization of the photoacid generators used in this work.

C. Measurement of the Efficiency of Photoacid Generation Using the Standard Addition Technique

In accordance with the methods of the standard addition technique, the dose to clear for a resist system was measured as a function of the concentration of base quencher in the resist formulation. Each formulation in the series was prepared, exposed and developed under the same processing conditions. The efficiency of photoacid generation for the resist, described by the resist C parameter (cm²/mJ), was determined by fitting this experimental data to the standard addition model, written as

\[ A_{\text{Free}} = \frac{P_0}{x_0} \int_0^\infty \left( 1 - \exp \left\{ -CD_x e^{-\alpha x} \right\} \right) dx - B \]  

(1)

where \( A_{\text{Free}} (\mu \text{mol/g}) \) is the free acid concentration, \( P_0 (\mu \text{mol/g}) \) is the initial concentration of PAG, \( x_0 (\mu \text{m}) \) is the film thickness, \( \alpha (\mu \text{m}^2) \) is the absorption coefficient of the resist, \( D_0 (\text{mJ/cm}^2) \) is the dose to clear value, and \( B (\mu \text{mol/g}) \) is the concentration of base quencher. Assuming that at each value of the dose to clear the free acid concentration is equivalent, experimental data for the dose to clear as a function of the base quencher concentration was fit to eq. (1) by nonlinear minimization to determine the values of the C parameter and the free acid concentration.

Table 2. Calculated values for the resist C parameter and free acid concentration

<table>
<thead>
<tr>
<th>Photoacid Generator</th>
<th>C Parameter (cm²/mJ)</th>
<th>Free Acid Concentration (µmol/g)</th>
<th>Sensitivity (mJ/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPS-NF</td>
<td>0.077 (0.071, 0.084)</td>
<td>142 (124, 162)</td>
<td>3.7</td>
</tr>
<tr>
<td>BB1-TF</td>
<td>0.170 (0.140, 0.199)</td>
<td>176 (134, 218)</td>
<td>21</td>
</tr>
<tr>
<td>BB1-NF</td>
<td>0.204 (0.118, 0.290)</td>
<td>364 (230, 498)</td>
<td>39</td>
</tr>
<tr>
<td>BB1-PFOS</td>
<td>0.124 (0.062, 0.186)</td>
<td>289 (139, 440)</td>
<td>46</td>
</tr>
<tr>
<td>NDI-NF</td>
<td>0.02 estimated</td>
<td>—</td>
<td>76</td>
</tr>
<tr>
<td>TFMDNBS</td>
<td>0.01 estimated</td>
<td>—</td>
<td>76</td>
</tr>
</tbody>
</table>

95% Confidence intervals are shown in parentheses

The experimental data for the sulfonium and iodonium PAGs were fit to eq. (1) by non-linear minimization using Mathematica (Wolfram Research). Table 2 lists the values of the extracted parameters and their 95% confidence intervals. The experimental data and best-fit solutions for the ionic salts are shown in Fig. 3. The model was unsuccessful in predicting reasonable parameter estimates for the NDI-NF and TFMDNBS PAGs. Results for the various PAGs are discussed in the following sections.
D. Comparison of Sulfonium and Iodonium Salt Photoacid Generators

The sensitivity of photoresist is often characterized by its dose to clear. A resist with a low dose to clear exhibits a good sensitivity. Table 2 tabulates the dose to clear value at zero loading of base quencher for each photoacid generator. For the iodonium salts the dose to clear increased with increasing length of the PAG anion. This decrease in sensitivity was expected due to diffusion of the photoacid through the polymer. Increasing the size of the anion was expected to decreases the diffusion coefficient of the acid. Additional acid was required to complete sufficient deprotection of the polymer during the PEB, increasing the dose to clear.

The values of the C parameter calculations using the standard addition technique are presented in Table 2. The photoacid generation efficiency for the ionic salts was determined to be in the order BBI-Nf > BBI-Tf > BBI-PFOS > TPS-Nf. TPS-Nf was found to be much less efficient at generating photoacid than the iodonium salts. Since the difference in efficiency between TPS-Nf and the iodonium salts is much greater than the differences among the various iodonium compositions, it is likely that sulfonium salts containing similar anion variations would likewise be less efficient than their iodonium counterparts.

The lower efficiency for photoacid generation for BBI-PFOS as compared to BBI-Tf and BBI-Nf was not understood. Solution-based experiments of triphenylsulfonium salts exposed to deep ultraviolet radiation found that the composition of the anion can affect the overall efficiency and product distributions during PAG photolysis. Strong nucleophilic anions were shown to reduce the total generation of acid by interfering with reactive intermediates. We do not expect this process to be important in these resist systems since the length of the fluorocarbon chain only mildly effects the nucleophilic strength of the anion and a trend with chain length was not observed. Previous work using the standard addition method measured a greater C parameter for a resist containing BBI-PFOS as compared to a BBI-Tf formulation in a phenolic resin when exposed to 248nm light. The same resist formulations displayed the opposite trend, where BBI-Tf was more efficient than BBI-PFOS, when exposed to 157nm and ionizing forms of radiation (extreme ultraviolet, x-ray, and e-beam). The experimental results of the present study qualitatively agree with those from previous work.

Direct comparisons of the free acid concentration required to develop resists may be made since all processing conditions were equivalent for each PAG. The required free acid concentration of the TPS-Nf resist was lower than all the iodonium formulations, including BBI-Tf. This was surprising since the acid generated by BBI-Tf, triflic acid, is smaller than the molecule of perfluorobutane sulfonic acid generated from TPS-Nf. Based on diffusion arguments, a smaller acid should more readily diffuse through the resist film during the PEB. The increased concentration of photoacid required to develop formulations containing iodonium PAG may be related to dissolution inhibition. Strong dissolution inhibitors may increase the required extent of deprotection to achieve the same development rate, increasing the required free acid concentration. Additionally, the diffusivity of the photoacid may be affected by the chemical composition of PAG or photodecomposition products if these species alter the physical properties of the resist film. Small differences in the density, glass transition temperature, or concentration of residual casting solvent may alter the diffusion of small molecules within the resist. Further investigation is required to determine if any of these processes were in effect.

The free acid concentration required for development for the resists containing iodonium PAGs was determined to follow the order BBI-Nf > BBI-PFOS > BBI-Tf. The lesser concentration of free acid required by the BBI-Tf resist follows expectations based on diffusion. The slightly greater acid concentration required by the BBI-Nf resist as compared to the BBI-PFOS resist does not follow the expected trend. Since the confidence intervals of the calculations for the BBI-Nf and BBI-PFOS systems overlap, it is possible that these experiments cannot discern small differences between these photoacids with sufficient resolution. Alternatively, the lower concentration of acid found in the BBI-PFOS resist could be related to the photochemical processes that reduce its efficiency compared to the other iodonium PAGs. The results provided by these studies only allow speculation, and further investigation is required.
E. Inefficient Photoacid Generation by Dicarboximide Photoacid Generators

Dose to clear values for the NDI-Nf resist system could not be measured above a concentration of base of 13 μmol/g. For the dose to clear values that could be determined, the standard addition technique was applied to calculate the C parameter and free acid concentration for this system (Fig. 4). However, unsatisfactory results were obtained, and the model was unsuccessful at predicting the process of photoacid generation for this system. Since the exposure dose required to develop NDI-Nf resists under these conditions was large, it is plausible that radiation damage may be affecting resist development. Cross-linking of poly(hydroxystyrene) was found to occur during exposure to 157nm radiation at exposure doses less than 50 mJ/cm². It is unknown if similar reactions occur in poly(NBHFA-co-NBTBE), however if such negative-tone reactions did exist, the required acid concentration to enable development would increase. Once sufficient damage has occurred, the resist film would then become completely insoluble in developer. This behavior may explain the inability to develop the NDI-Nf resist films above a concentration of base of 13 μmol/g.

A linear approximation was employed to estimate the order of magnitude of the C parameter. By using a linear fit to only the first two data points, the effects at high base concentration were avoided. We recognize that this linear approximation contains significant uncertainty and has been shown in previous work to limit the accuracy of parameter estimations. However, it was useful in this case to obtain an order of magnitude estimate of the C parameter. By the linear approximation, a C parameter of the order 0.02 cm²/mJ was calculated, making the photodecomposition of NDI-Nf much less efficient than the sulfonium or iodonium salts during exposure to 157nm radiation.

Previous work using the standard addition technique in phenolic polymers found the photochemical efficiency of another dicarboximide PAG, N-hydroxy-5-norbornene-2,3-dicarboximide trifluoromethanesulfonate (NDI-Tf), to be comparable to sulfonium and iodonium salts of the same anion. The dramatic decrease in the efficiency of the dicarboximide PAG with respect to the ionic PAGs found in this study was attributed to the composition of the polymer. In a resist film, the polymer generally composes greater than 90% of the film. The interaction of radiation with the polymer and its subsequent energy transfer or chemical dissociation to form radicals was expected to greatly affect the photochemistry of PAG in the resist. The incorporation of fluorine into the polymer is known to increase transparency of the resin. Additionally, the σ molecular orbital is greatly stabilized by the substitution of fluorine for hydrogen. This stabilization increases the binding energy of the C-F bond as compared to a C-H bond. The combination of these effects may reduce the transfer of energy from the polymeuer to the PAG or the production of radicals along the polymer backbone. The large increase in photochemical efficiency for the dicarboximide PAGs within phenolic matrixes as compared to poly(NBHFA-co-NBTBE) suggests such processes are important for acid generation by this class of PAG. This suggests that the direct photolysis of the dicarboximide PAG was not the primary mechanism for photoacid generation, and the reaction pathway depends on energy transfer from the matrix.

F. Inefficient Photoacid Generation in Resists Containing TFMDNBS

Dose to clear measurements for the TFMDNBS system were first attempted using a post-exposure bake temperature of 110°C, however the dose to clear value without added base was in excess of 15 mJ/cm². To avoid extremely high doses that were expected to be

![Figure 4](image-url)
necessary to develop solutions at high base concentration, the PEB temperature was raised to 130°C. Since the post-application bake was 140°C, no complications were expected at this elevated temperature. As shown in Figure 2 the TFMDNBS resist series reached a maximum in the dose to clear at high levels of base. This behavior cannot be explained by the photoacid generation model described in eq. (1). It follows from the exposure kinetics that the dose to clear the resist film should always increase with increasing base concentration since base neutralizes an equivalence of photogenerated acid. Adding complexity to the exposure model by considering the generation of multiple molecules of acid or competing reactions of PAG to generate species other than photoacid also cannot explain the decrease in dose. In either of these models the concentration of photoacid created during exposure will always increase with increasing dose. The cause of the decrease in dose to clear at high loadings of base quencher remains unknown. Since the other PAGs screened in this study did not indicate this effect, and all systems were formulated from the same batch of polymer, we believe the TFMDNBS PAG is responsible for this behavior. By using a linear approximation the $C$ parameter of the TFMDNBS system was calculated as approximately 0.01 cm$^2$/mJ. Based on this estimation, the resist system containing the TFMDNBS PAG was inefficient at generating photoacid.

4. Conclusions
The standard addition technique was used to evaluate the photochemical efficiency of six photoacid generators in a candidate polymer for 157nm lithography. Of the PAGs investigated, bis(t-butylphenyliodonium) salts exhibited the greatest efficiency for photoacid generation. Furthermore, the photochemical efficiency of triphenylsulfonium PAGs was approximately half that of bis(t-butylphenyliodonium) salts. Slight differences in the $C$ parameter were determined for the iodonium salts containing different anions. Although consistent with previous studies, the source of these anion effects remains unknown. PAGs based on dicarboximide and on a fluorinated benzene sulfonate derivative were found to be extremely inefficient generators of photoacid at 157nm. For both of these systems, the model for photoacid generation from the decomposition of PAG upon exposure did not adequately explain the experimental data. The free acid concentration required to develop the TPS-Nf resist was found to be less than the resist containing BBI-Tf, despite the much smaller photoacid molecule and identical processing conditions. These results suggest that the physical properties of photoresist may be affected by the composition of the PAG.

The sensitivity of a photoresist formulation to exposure radiation is a complex combination of the photochemical efficiency and the utilization of the free acid to drive polymer deprotection. Dose to clear values alone cannot indicate how these parameters interrelate. The standard addition model provides a useful tool for screening candidate materials by simultaneously determining these parameters using fast and simple experimental methods.

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References