CHEMISTRY OF MATERIALS
Article

Chem. Mater. **2010,** *22,* 5609–5616 5609
DOI:10.1021/cm101867g

Catalytic and Autocatalytic Mechanisms of Acid Amplifiers for Use in EUV Photoresists

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Received July 5, 2010

Twelve fluorinated acid amplifiers (AAs) were synthesized and studied for use in photoresists exposed to 13.5 nm, extreme ultraviolet (EUV) light. Acid amplifiers are compounds that decompose in the presence of acid to generate more acid via catalytic or autocatalytic mechanisms. These AAs are composed of a body, trigger, and an acid precursor. Thermal decomposition rates of solutions of the AAs in C_6D_6/*m*-ethylphenol (50/50 wt %) at 100 °C were monitored by ^{19}F NMR with and without 1.2 equiv. of 2,4,6-tri-*t*-butylpyridine. All of the AAs in the presence of base decompose according to first-order kinetics with rate constants k_{Base}. The rate constants, k_{Base}, at various temperatures yielded the activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$. The enthalpy of activation, $\Delta H,^{\ddagger}$, was in a narrow range of 16.6−19.1 (kcal/mol), whereas the entropy of activation, $\Delta S^{\ddagger}$, spanned from 0 to −12 (cal/(mol K)). When acid is allowed to build up in solution (in the absence of base), six of the AAs with tertiary triggers (Body-3) decompose autocatalytically, but the six with secondary triggers (Body-2) are unaffected. Although Body-2 AAs do not decompose autocatalytically, nonaflate acid does catalyze their decomposition. Lithographic evaluation showed that some AAs are capable of simultaneously improving the resolution, line-edge-roughness, and sensitivity of a control EUV photoresist. This simultaneous improvement was quantified using the *Z*-Parameter. The AAs investigated here were found to improve the *Z*-Parameter by as much as a factor of 3.

Introduction

High-resolution, positive chemically amplified photoresists[1] are central to the manufacture of today's integrated circuits. These thin film resists are composed primarily of organic polymers and photoacid generators (PAGs). During exposure to 193 or 13.5 nm light, the PAGs produce strong acids. During a subsequent bake step, these strong acids typically catalyze reactions of the organic polymer. For positive resists, these acid-catalyzed reactions transform the resist from a material that is insoluble in aqueous alkaline developer into a material that is now soluble in this developer. Development reveals patterns of photoresist features in which the exposed regions have been removed and the unexposed regions remain behind.

The development of chemically amplified photoresists for use with extreme ultraviolet (EUV, 13.5 nm) light is critical to meet the future photolithographic requirements of the microelectronics industry. These resists must simultaneously exhibit three properties: high resolution, low line edge roughness (LER),[2] and high sensitivity.[3] We have proposed that the best way to simultaneously improve these three properties in an EUV resist is to increase the number of strong acids generated during exposure,[4] and we assert that acid amplifiers may be one of the best ways to achieve this goal. Acid amplifiers (AAs) are compounds that decompose via acid-catalyzed mechanisms to produce more acid.[5] When the product acid is strong enough to catalyze the decomposition of the AA, the decomposition occurs autocatalytically (Scheme 1).[6]

Previous work shows that to improve the imaging in a modern photoresist, AAs must meet the following requirements.[7,8] First, AAs must be thermally stable in the absence of acid, at least within the process conditions of photolithography. Second, AAs must rapidly decompose autocatalytically in the presence of catalytic acid. Third, AAs must generate strong (fluorine-containing sulfonic) acids capable of participating in the photoresist chemistry. Prior to our first communication on this topic,[9] there were 26 acid

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Published on Web 09/20/2010

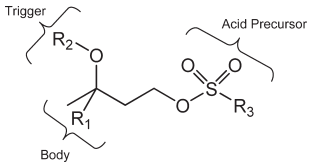
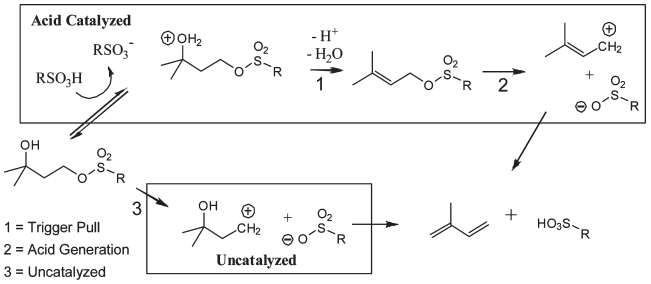


Figure 1. Acid amplifiers described here consist of three parts: a trigger, an acid precursor, and a body. Six AAs have bodies resulting in tertiary triggers (R_1 = CH_3) and six AAs have bodies resulting in secondary triggers (R_1 = H).

Scheme 1. Our Proposed Reaction Mechanism for the Acid-Catalyzed and Uncatalyzed Decomposition of Tertiary Acid Amplifiers



amplifiers in the literature. The AAs previously reported consist of acetoacetate derivatives,[7] cyclohexane-1,2-diol monosulfonates,[10,11] a trioxane derivative,[12] ketal sulfonates,[13] pinane-1,2 diol monosulfonates,[14,15] cyclohexane-1,4-disulfonates,[16] and benzyl sulfonates.[17] Only two of the AA's described in the literature produce fluorinated acids.[16] In addition, only five of the AAs were evaluated for their additive effects on photoresist imaging. Nonfluorinated AAs were incorporated into acrylate based ArF resists[11,15] and phenolic KrF resists.[18] The results of these experiments show that AAs designed for lithographic applications must generate strong acids and be thermally stable. Our efforts focus on designing thermally stable AAs that produce fluorinated sulfonic acids for use in phenolic EUV resists.

In this work, we report on the synthesis, thermal decomposition kinetics, and lithographic performance of 12 acid amplifiers. We systematically vary the chemical structures to give a range of reactivities. These acid amplifiers consist of three parts (Figure 1), a body, an acid-sensitive trigger (**T**, either hydroxyl or methoxy), and a fluorinated sulfonic acid precursor (**A**). During autocatalysis, the trigger undergoes acidolysis[8] yielding an allylic sulfonic ester (E_1 or E_2) (Scheme 1). This allows the sulfonic ester to thermally decompose via an E_1 or E_2 elimination reaction more rapidly than the starting AA, yielding a second double bond and a sulfonic acid. Surprisingly, we found that the AA's with tertiary triggers react with these product acids to undergo autocatalytic reaction kinetics, whereas the AAs with secondary triggers do not generate acids that are strong enough to catalyze their own decomposition. Instead, we found that the decomposition of AAs with secondary triggers can be catalyzed by an added super acid.

Additionally, the performance of these twelve acid amplifiers was also evaluated for their performance in EUV photoresists using a global performance constant called the *Z*-Parameter.[19−22] We found that AAs with both secondary and tertiary triggers can enhance the lithographic performance of EUV resists. The best AA can improve the *Z*-Parameter of our control resist by a factor of 3.

Experimental Section

General Procedures. All nuclear magnetic resonance spectra were recorded on Bruker 400 spectrometer and the chemical shifts are reported in parts per million. ^{1}H NMR data are referenced to $CDCl_3$ (7.24 ppm) and ^{19}F data are referenced to C_6F_6 (−164.9 ppm). All reagents were purchased from commercial suppliers and used without further purification. Kinetic experiments were run in flame-sealed NMR tubes and the solvent system was a 50/50 wt % mixture of C_6D_6 and *m*-ethyl phenol with a trace amount of C_6F_6 as a fluorine reference. The samples were heated by submerging the tubes in a hot oil bath at the desired temperature.[23] Elemental analyses were performed by Midwest Microlab LLC.

3-Hydroxy-3-methylbutyl 4-(trifluoromethyl)benzenesulfonate (3HA). To a solution of 3-methyl-1,3-butane diol (1.9 g, 18.2 mmol) in pyridine (15 mL) was added *p*-(trifluorormethyl)- benzenesulfonyl chloride (3.67 g, 15 mmol). The solution was stirred at 0 °C for 2 h. The reaction mixture was diluted with ethyl acetate (40 mL) and washed with 1 M HCl (3 × 50 mL), saturated aqueous $NaHCO_3$ (50 mL) and saturated aqueous NaCl (50 mL). The organics were dried over Na_2SO_4 and concentrated to give a white, low-melting-point solid (3.33 g, 71%). ^{1}H NMR (400 MHz $CDCl_3$) δ 8.04 (d, 2 H, J = 8.0 Hz), 7.81 (d, 2 H, J = 8.0 Hz), 4.72 (t, 2 H, J = 7.0 Hz), 1.87 (t, 2 H, J = 7.0 Hz), 1.21 (s, 6 H). Anal. Calcd for $C_{12}H_{15}F_3O_4S$: C, 46.15; H 4.84. Found: C, 46.14; H, 4.90.

3-Hydroxy-3-methylbutyl 2-(trifluoromethyl)benzenesulfonate (3HB). To a solution of 3-methyl-1,3-butane diol (2.5 g, 21 mmol) and TEA (1.63 g, 16 mmol) in CH_2Cl_2 (15 mL) was added *o*-(trifluorormethyl)benzenesulfonyl chloride (2.03 g, 8.3 mmol) dissolved in CH_2Cl_2 (20 mL). The solution was stirred at room temperature (RT) for 7 h. The reaction mixture was diluted with CH_2Cl_2 (75 mL) and washed with 1 M HCl (2 × 25 mL), saturated aqueous $NaHCO_3$ (25 mL), and saturated aqueous NaCl (25 mL). The organics were dried over Na_2SO_4 and concentrated to give a

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crude mixture. Silica gel chromatography with ethyl acetate in hexanes yielded the desired product (1.73 g, 66%). ^{1}H NMR (400 MHz $CDCl_3$) δ 8.23 (m, 1 H), 7.91 (m, 1 H), 7.75 (m, 2 H), 4.32 (t, 2 H, J = 7.0 Hz), 1.91 (t, 2 H, J = 7.0 Hz) 1.22 (s, 6 H). Anal. Calcd for $C_{12}H_{15}F_3O_4S$: C, 46.15; H 4.84. Found: C, 45.73; H, 4.88.

3-Hydroxy-3-methylbutyl 2,3,4,5,6-pentafluororbenzenesulfonate (3HC). To a solution of 3-methyl-1,3-butane diol (0.79 g, 7.5 mmol) and TEA (0.37 g, 3.6 mmol) in CH_2Cl_2 (7 mL) at 0 °C was added pentafluororbenzenesulfonyl chloride (0.80 g, 3.0 mmol). The solution was stirred at 0 °C for 1.5 h. Saturated aqueous $NaHCO_3$ (10 mL) was added to the solution and the mixture was stirred at RT for 15 min. The organics were extracted with CH_2Cl_2 and washed with 0.5 M HCl (20 mL) and saturated aqueous NaCl (20 mL). The organics were dried over Na_2SO_4 and concentrated to give a crude mixture. Silica gel chromatography with 30% ethyl acetate in hexanes yielded the desired product as a white, crystalline, low-melting-point solid (0.69 g, 66%). ^{1}H NMR (400 MHz $CDCl_3$) δ 4.49 (t, 2 H, J = 7.0 Hz), 1.97 (t, 2 H, J = 7.0 Hz) 1.27 (s, 6 H). Anal. Calcd for $C_{11}H_{11}F_5O_4S$: C, 39.53; H 3.32. Found: C, 39.54; H, 3.22.

3-Methoxy-3-methylbutyl 4-(trifluoromethyl)benzenesulfonate (3MA). To a solution of 3-methoxy-3-methylbutane-1-ol (0.58 g, 4.9 mmol) in pyridine (5 mL) was added *p*-(trifluorormethyl)-benzenesulfonyl chloride (0.98 g, 4 mmol). The solution was stirred at RT for 3.5 h. The reaction mixture was diluted with ethyl acetate (25 mL) and washed with 1 M HCl (6 × 25 mL), saturated aqueous $NaHCO_3$ (25 mL) and saturated aqueous NaCl (25 mL). The organics were dried over Na_2SO_4 and concentrated to give an oil (0.53 g, 40%). ^{1}H NMR (400 MHz $CDCl_3$) δ 8.03(d, 2 H, J = 8.0 Hz), 7.81 (d, 2 H, J = 8.0 Hz), 4.19 (t, 2 H, J = 7.3 Hz), 3.09 (s, 3 H), 1.88 (t, 2 H, J = 7.3 Hz), 1.12 (s, 6 H). Anal. Calcd for $C_{13}H_{17}F_3O_4S$: C, 47.85; H 5.25. Found: C, 47.72; H, 5.05.

3-Methoxy-3-methylbutyl 2-(trifluoromethyl)benzenesulfonate (*3MB*). To a solution of 3-methoxy-3-methylbutane-1-ol (2.8 g, 24 mmol) and TEA (1.6 g, 16 mmol) in CH_2Cl_2 (15 mL) was added *o*-(trifluorormethyl)benzenesulfonyl chloride (1.9 g, 8 mmol) dissolved in CH_2Cl_2 (20 mL). The solution was stirred at RT for 4 h. Saturated aqueous $NaHCO_3$ (15 mL) was added to the solution and mixture was stirred at RT for 30 min. The organics were extracted with CH_2Cl_2 (75 mL) and washed with 1 M HCl (2 × 25 mL), saturated aqueous $NaHCO_3$ (25 mL), and saturated aqueous NaCl (25 mL). The organics were dried over Na_2SO_4 and concentrated to give a crude mixture. Silica gel chromatography with ethyl acetate in hexanes yielded the desired product (2.1 g, 81%). ^{1}H NMR (400 MHz $CDCl_3$) δ 8.23 (m, 1 H), 7.91 (m, 1 H), 7.74 (m, 2 H), 4.25 (t, 2 H, J = 7.5 Hz), 3.10 (s, 1 H), 1.92 (t, 2 H, J = 7.5 Hz) 1.13 (s, 6 H). Anal. Calcd. For $C_{13}H_{17}F_3O_4S$: C, 47.85; H 5.25. Found: C, 47.95; H, 5.11.

3-Methoxy-3-methylbutyl 2,3,4,5,6-pentafluororbenzenesulfonate (3MC). To a solution of 3-methoxy-3-methylbutane-1-ol (1.07 g, 9 mmol) and TEA (0.61 g, 6 mmol) in CH_2Cl_2 (12 mL) was added pentafluororbenzenesulfonyl chloride (0.99 g, 3.7 mmol). The solution was stirred at RT for 2 h. Saturated aqueous $NaHCO_3$ (12 mL) was added to the solution and the mixture was stirred at RT for 30 min. The organics were extracted with CH_2Cl_2 (50 mL) and washed with 0.5 M HCl (3 × 40 mL), saturated aqueous $NaHCO_3$ (40 mL), and saturated aqueous NaCl (40 mL). The organics were dried over Na_2SO_4 and concentrated to give a crude mixture. Silica gel chromatography with ethyl acetate in hexanes yielded the desired product (0.68 g, 51%). ^{1}H NMR (400 MHz $CDCl_3$) δ 4.42 (t, 2 H, J = 7.3 Hz), 3.13 (s, 3 H), 1.97 (t, 2 H, J = 7.4 Hz), 1.17 (s, 6 H). Anal. Calcd for $C_{12}H_{13}F_5O_4S$: C, 41.38; H 3.76. Found: C, 41.37; H, 3.77.

3-Hydroxybutyl 4-(trifluoromethyl)benzenesulfonate (2HA). To a solution of 1,3-butane diol (4.34 g, 48 mmol) and TEA (3.19 g, 31.5 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added *p*-(trifluorormethyl)benzenesulfonyl chloride (3.97 g, 16.2 mmol) dissolved in CH_2Cl_2 (20 mL). The solution was stirred at 0 °C for 2 h. Saturated aqueous $NaHCO_3$ (15 mL) was added to the solution and mixture was stirred at RT for 40 min. The organics were extracted with CH_2Cl_2 (50 mL) and washed with 1 M HCl (3 × 25 mL) and saturated aqueous NaCl (25 mL). The organics were dried over Na_2SO_4 and concentrated to give the desired product (3.28 g, 65%). ^{1}H NMR (400 MHz $CDCl_3$) δ 8.02 (d, 2 H, J = 8.2 Hz), 7.80 (d, 2 H, J = 8.3), 4.29 (m, 1 H), 4.17 (m, 1 H), 3.91 (m, 1 H), 1.83 (m, 1 H), 1.70 (m, 1 H), 1.17 (d, 3 H, J = 6.2 Hz). Anal. Calcd for $C_{11}H_{13}F_3O_4S$: C, 44.29; H 4.39. Found: C, 44.16; H, 4.17.

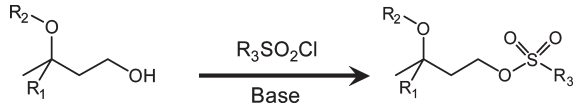
3-Hydroxybutyl 2-(trifluoromethyl)benzenesulfonate (2HB). To a solution of 1,3-butane diol (2.18 g, 24 mmol) and TEA (1.64 g, 16 mmol) in CH_2Cl_2 (15 mL) at 0 °C was added *o*-(trifluorormethyl)benzenesulfonyl chloride (2 g, 8 mmol) dissolved in CH_2Cl_2 (20 mL). The solution was stirred at 0 °C for 2 h. Saturated aqueous $NaHCO_3$ (15 mL) was added to the solution and mixture was stirred at RT for 45 min. The organics were extracted with CH_2Cl_2 (150 mL) and washed with 0.5 M HCl (2 × 80 mL) and saturated aqueous NaCl (50 mL). The organics were dried over Na_2SO_4 and concentrated to give a crude mixture. Silica gel chromatography (50% ethyl acetate in hexanes) yielded the desired product (2 g, 84%). ^{1}H NMR (400 MHz $CDCl_3$) δ 8.23 (m, 1 H), 7.92 (m, 1 H), 7.74 (m, 2 H), 4.34 (m, 1 H), 4.24 (m, 1 H), 3.95 (m, 1 H), 1.89 (m, 1 H), 1.73 (m, 1 H), 1.20 (d, 3 H, J = 6.3 Hz). Anal. Calcd for $C_{11}H_{13}F_3O_4S$: C, 44.29; H 4.39. Found: C, 44.29; H, 4.28.

3-Hydroxybutyl 2,3,4,5,6-pentafluororbenzenesulfonate (*2HC*). To a solution of 1,3-butane diol (0.9 g, 10 mmol) and TEA (0.61 g, 6 mmol) in CH_2Cl_2 (4 mL) at 0 °C was added pentafluororbenzenesulfonyl chloride (0.53 g, 2 mmol) dissolved in CH_2Cl_2 (4 mL). The solution was stirred for 6 h, during which time the solution slowly warmed to RT. Saturated aqueous $NaHCO_3$ (25 mL) was added to the solution and the mixture was stirred at RT for 30 min. The organics were extracted with CH_2Cl_2 (50 mL) and washed with 0.5 M HCl (3 × 20 mL), saturated aqueous $NaHCO_3$ (20 mL), and saturated aqueous NaCl (20 mL). The organics were dried over Na_2SO_4 and concentrated to give a crude mixture. Silica gel chromatography with ethyl acetate in hexanes yielded the desired product (0.26 g, 40%). ^{1}H NMR (400 MHz $CDCl_3$) δ 4.62 (m, 2 H), 4.13 (m, 1 H), 2.11 (m, 1 H), 1.94 (m, 1 H), 1.40 (d, 3 H, J = 6.2 Hz). Anal. Calcd for $C_{10}H_9F_5O_4S$: C, 37.51; H 2.83. Found: C, 37.70; H, 2.93.

3-Methoxybutyl 4-(trifluoromethyl)benzenesulfonate (2MA). To a solution of 3-methoxybutane-1-ol (0.58 g, 4.9 mmol) in pyridine (5 mL) was added *p*-(trifluorormethyl)benzenesulfonyl chloride (0.98 g, 4 mmol). The solution was stirred at RT for 3.5 h. The reaction mixture was diluted with ethyl acetate (25 mL) and washed with 1 M HCl (6 × 25 mL), saturated aqueous $NaHCO_3$ (25 mL), and saturated aqueous NaCl (25 mL). The organics were dried over Na_2SO_4 and concentrated to give an oil (0.53 g, 40%). ^{1}H NMR (400 MHz $CDCl_3$) δ 8.03 (d, 2 H, J = 8.1 Hz), 7.81 (d, 2 H, J = 8.3 Hz), 4.19 (m, 2 H), 3.35 (m, 1 H), 3.18 (s, 3 H), 1.78 (m, 2 H), 1.09 (d, 3 H, J = 6.0 Hz). Anal. Calcd for $C_{12}H_{15}F_3O_4S$: C, 46.15; H 4.84. Found: C, 45.99; H, 4.64.

3-Methoxybutyl 2-(trifluoromethyl)benzenesulfonate (2MB). To a solution of 3-methoxybutane-1-ol (0.63 g, 6.0 mmol) and TEA (0.42 g, 4.1 mmol), in CH_2Cl_2 (5 mL) was added *o*-(trifluorormethyl)benzenesulfonyl chloride (0.50 g, 2.0 mmol). The solution was stirred at RT for 2 h. The reaction mixture was

Scheme 2. Twelve AAs Were synthesized by Reacting Primary Alcohols with Sulfonyl Chlorides in the Presence of Base



diluted with CH_2Cl_2 (15 mL) and washed with 1 M HCl (3 × 15 mL), saturated aqueous $NaHCO_3$ (15 mL), and saturated aqueous NaCl (15 mL). The organics were dried over Na_2SO_4 and concentrated to give a crude mixture. Silica gel chromatography with ethyl acetate in hexanes yielded the desired product (0.34 g, 50%). ^{1}H NMR (400 MHz $CDCl_3$) δ 8.23 (m, 1 H), 7.91 (m, 1 H), 7.75 (m, 2 H), 4.24 (m, 2 H), 3.40 (m, 1 H), 3.21 (s, 3 H), 1.80 (m, 2 H), 1.10 (d, 3 H, J = 6.2 Hz). Anal. Calcd for $C_{12}H_{15}F_3O_4S$: C, 46.15; H 4.84. Found: C, 46.30; H, 4.88.

3-Methoxybutyl 2,3,4,5,6-pentafluororbenzenesulfonate (2MC). To a solution of 3-methoxybutane-1-ol (0.78 g, 7.5 mmol) and TEA (0.388 g, 3.8 mmol), in CH_2Cl_2 (15 mL) was added pentafluororbenzenesulfonyl chloride (0.79 g, 3.0 mmol). The solution was stirred at RT for 4 h. Saturated aqueous $NaHCO_3$ (10 mL) was added to the solution and the mixture was stirred at RT for 30 min. The organics were extracted with CH_2Cl_2 (30 mL) and washed with 0.5 M HCl (2 × 20 mL) and saturated aqueous NaCl (20 mL). The organics were dried over Na_2SO_4 and concentrated to give a crude mixture. Silica gel chromatography (15% ethyl acetate in hexanes) yielded the desired product (0.39 g, 36%). ^{1}H NMR (400 MHz $CDCl_3$) δ 4.40 (m, 2 H), 3.45 (m, 1 H), 3.26 (s, 3 H), 1.87 (m, 2 H), 1.15 (d, 3 H, J = 6.1 Hz). Anal. Calcd for $C_{11}H_{11}F_5O_4S$: C, 39.53; H 3.32. Found: C, 39.83; H, 3.45.

Lithographic Evaluation. We evaluated acid amplifiers by adding equal molar concentrations of the AAs (70 mM except where noted) to a control ESCAP resist formulation composed of: 7.5 wt % of solids of Di(4-tert-butylphenyl) iodonium perfluoro-1-butane-sulfonate (DTBI-PFBS) PAG, 1.0 wt % of tetrabutylammonium hydroxide base (TBAH), 4-hydroxystyrene/styrene/t-butyl acrylate (65/15/20) polymer and a 50/50 mixture solvent of ethyl lactate and propylene glycol methyl ether acetate. Formulations were prepared at 5 wt % solids (vs solvent), spin coated to a film thickness of 125 nm and soft-baked (90 °C, 60 s). Exposures were performed using dense line/space patterns (annular illumination on Berkeley EUV MET), followed by postexposure bake (PEB, 90 °C, 90 s), and 45 s development in 0.26 N $Me_4N^+OH^-$ (TMAH).

Results and Discussion

Synthesis of Twelve Fluorinated Acid Amplifiers. Twelve acid amplifiers were synthesized to give a range of reactivities by reacting primary alcohols with sulfonyl chlorides in the presence of pyridine or triethylamine (TEA). Pyridine and TEA give similar yields when *p*-$(CF_3)C_6H_4SO_2Cl$ or *o*-$(CF_3)C_6H_4SO_2Cl$ are reacted with a 1,3-diol. Most of the other reactions give better yields when TEA is used, especially reactions with perfluorobenzenesulfonyl chloride. The acid sensitive triggers are secondary (2°) or tertiary (3°) hydroxyl or methoxy groups and the acids generated upon AA decomposition are *p*-$(CF_3)C_6H_4SO_3H$, *o*-$(CF_3)C_6H_4SO_3H$ or $C_6F_5SO_3H$. Scheme 2 shows the general synthetic strategy and Table 1 lists the 12 AAs that were synthesized using this method.

Decomposition Kinetics of Acid Amplifiers in Solution. The thermal decomposition kinetics of the AAs in solution (in sealed NMR tubes) were measured using ^{19}F NMR. Solutions of AAs (70 m*M*) in 50/50 wt % C_6D_6/*m*-ethylphenol (to simulate the environment of a phenolic polymer matrix) in the presence and absence of 1.2 eq of added 2,4,6-tri-*t*-butylpyridine (TBP) were monitored. The sterically hindered base was added to consume acid as it formed, so that the uncatalyzed reactions could be studied independently.[9] All rate constants[24] at 100 °C and kinetic parameters are reported in Table 2. We chose to compare rate constants at 100 °C because they can be measured accurately at this temperature for all 12 compounds in the presence and absence of added base. Additional rate constants were measured at temperatures chosen on the basis of the boiling points of readily available, nonflammable solvents that are used to heat an oil bath at a constant temperature.[23]

Table 1. Unique Names for Twelve AAs Synthesized for This Study Based on Their Body, Trigger, and Acid Precursor Combination[a]

compd	R_1	R_2	R_3
3HA	Me	H	*p*-$CF_3C_6H_4$
3HB	Me	H	*o*-$CF_3C_6H_4$
3HC	Me	H	C_6F_5
3MA	Me	Me	*p*-$CF_3C_6H_4$
3MB	Me	Me	*o*-$CF_3C_6H_4$
3MC	Me	Me	C_6F_5
2HA	H	H	*p*-$CF_3C_6H_4$
2HB	H	H	*o*-$CF_3C_6H_4$
2HC	H	H	C_6F_5
2MA	H	Me	*p*-$CF_3C_6H_4$
2MB	H	Me	*o*-$CF_3C_6H_4$
2MC	H	Me	C_6H_5

[a] The Names of AAs start with either a 3 or a 2 indicating bodies with tertiary or secondary triggers, respectively.

Uncatalyzed Thermal Decomposition of Acid Amplifiers in the Presence of Base. All decomposition reactions conducted in the presence of excess base showed first-order reaction kinetics. As expected, the decomposition rate increases as the number of fluorine atoms increase or when they are located closer to the sulfonate ester, because increasing the electronegativity of sulfonates increases their leaving ability. In particular, the AAs having perfluorobenzenesulfonate (PFBS) esters decompose at 100 °C in the presence of base 11−27 times faster than do the AAs prepared with either of the *p*- or *o*-trifluoromethyl benzenesulfonate (TMBS) esters.

The trigger also has a significant effect on the first-order rate of decomposition. Comparisons of decomposition rates in the presence of base made between AAs with the same body and acid precursors show that AAs prepared with methoxy triggers decompose faster than AAs prepared with hydroxyl triggers (Body-3, 3−4× faster; Body-2, 1.1−1.3× faster).

Uncatalyzed first-order reaction rates (k_{Base}) were measured at three temperatures in the presence of excess base. Eyring plots of these rate constants yielded $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ for each reaction (Table 2). Interestingly, the enthalpy of activation ($\Delta H^{\ddagger}$) values are constrained within a fairly narrow range of values (16.6−19.1 kcal/mol), whereas the entropy of activation ($\Delta S^{\ddagger}$) seems to give the largest range of values (0 to

(24) Second-order catalyzed reaction kinetics was evaluated by fitting data to Capellos, C.; Bielski, B. *Kinetic Systems: Mathematical Description of Chemical Kinetics in Solution*; Wiley-Interscience: New York, 1972.

Table 2. Rate Constants and Activation Parameters for the Thermal Decomposition of Acid Amplifiers Vary with Chemical Structure

compd	$k_{Base} \times 10^5$ (s^{-1})[a]	$k_{NoBase} \times 10^5$ ($M\ s)^{-1}$[a]	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/(mol K))	$\Delta G^{\ddagger}$ (kcal/mol)[a]
3HA	3.6 ± 0.1	4400 ± 800	18.0 ± 0.4	−7.7 ± 0.9	20.9 ± 0.4
3HB	5.1 ± 0.1	7100 ± 1300	17.3 ± 0.1	−8.9 ± 0.3	20.6 ± 0.1
3HC	73 ± 2	22 000 ± 3000	18.6 ± 0.9	−0.1 ± 2.5	18.6 ± 0.9
3MA	16 ± 1	3700 ± 200	19.1 ± 1.0	−2.1 ± 2.7	19.9 ± 1.0
3MB	21 ± 1	5700 ± 300	18.6 ± 0.8	−2.7 ± 2.2	19.6 ± 0.8
3MC	240 ± 10	20 000 ± 2000	17.6 ± 1.3	−0.3 ± 3.8	17.7 ± 1.3
2HA	1.2 ± 0.1	1.1 ± 0.1	17.2 ± 1.5	−12.0 ± 3.7	21.6 ± 1.5
2HB	1.7 ± 0.1	1.7 ± 0.1	17.7 ± 0.3	−9.8 ± 0.6	21.4 ± 0.3
2HC	33 ± 3	27 ± 3	16.8 ± 1.5	−6.9 ± 4.1	19.4 ± 1.5
2MA	1.6 ± 0.1	1.7 ± 0.1	18.7 ± 1.6	−7.3 ± 4.0	21.4 ± 1.6
2MB	2.4 ± 0.1	2.6 ± 0.1	18.9 ± 0.3	−6.1 ± 0.7	21.2 ± 0.3
2MC	37 ± 1	42 ± 2	16.6 ± 0.1	−6.9 ± 0.2	19.2 ± 0.1

[a] Temperature = 100 °C. The AAs were decomposed in 50/50 wt % d_6-benzene/*m*-ethylphenol in sealed NMR tubes. The activation parameters were calculated using Erying plots.

−12 cal/(mol K)). Not surprisingly, therefore, the entropy of activation seems to be the strongest predictor of rate and $\Delta G^{\ddagger}$, with the most negative values of $\Delta S^{\ddagger}$ giving the slowest first-order rate constants and the highest values of $\Delta G^{\ddagger}$.

The most significant pattern that emerges from these kinetic parameters is the differences between the $\Delta S^{\ddagger}$ values of AAs prepared with hydroxyl vs methoxy triggers. A pairwise comparison of the eight AAs prepared with either *p*- or *o*-TMBS esters, shows that the AAs with hydroxyl triggers have considerably lower $\Delta S^{\ddagger}$ values. This pattern does not exist for the AAs prepared with the PFBS esters, presumably because of a change in mechanism of the first-order decomposition for these highly fluorinated compounds.

Thermal Decomposition of Acid Amplifiers without Added Base. In order for a resist containing an AA to properly distinguish between exposed and unexposed regions, the acid-catalyzed decomposition rate of the AA must be significantly faster than the uncatalyzed decomposition rate. To study the interactions between acid amplifiers and the acid generated by them during their decomposition, we studied the thermal decomposition kinetics of the 12 AAs without any added base at 100 °C. The six acid amplifiers with tertiary triggers (Body-3) decompose according to the autocatalytic mechanism illustrated in Scheme 1. For example, in the presence of added base, AA-**3HA** decomposes according to first-order kinetics so that the plot of ln [**3HA**] vs time is linear (R^2 = 0.998, Figure 2A). Without base, the plot of ln [**3HA**] vs time is initially first-order, but once a small amount of acid is generated, the reaction proceeds autocatalytically, giving the observed curvature. Conversely, the six acid amplifiers with secondary triggers (Body-2) give first-order kinetics independent of the presence or absence of added base as illustrated by AA-**2HA** (Figure 2B), indicating that the build-up of the sulfonic acid product has no effect on reaction rate.

One important criterion we use for evaluating the performance of an acid amplifier is the ratio of rate constants evaluated in the absence and presence of added base (k_{NoBase}/k_{Base}). Table 3 shows the ratios of all compounds at 100 °C. Body-3 AAs have rate ratios in the range of 80−1400. Unexpectedly, all six Body-2 AAs with secondary triggers have rate ratios of 1.0. This means that the decomposition rates of Body-2 AAs are independent of the presence or absence of the buildup of sulfonic acid generated during their decomposition. Yet, as described

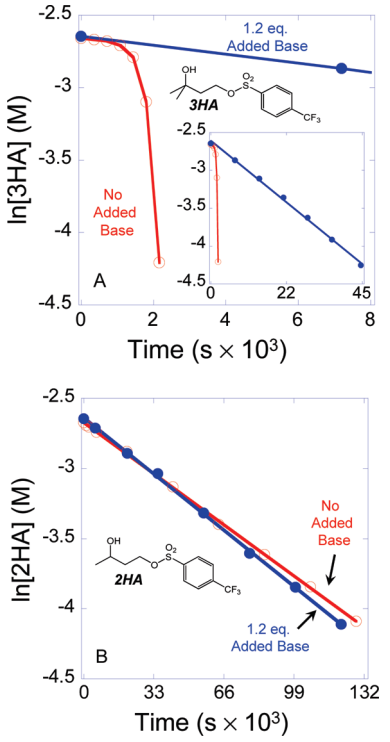


Figure 2. (A) Decomposition rate of ● **3HA** with base is first-order and ○ **3HA** without base is autocatalytic. (B) Decomposition rates of ● **2HA** with base and ○ **2HA** without base are both first order, regardless of the build up of acid generated by AA decomposition.

below, Body-2 AAs show reasonably good lithographic performance and improved resist sensitivity, indicating that acids are being generated. These observations led us to study the rate of decomposition of AA-**2HA** in the presence of added nonaflate acid. This acid, $C_4F_9SO_3H$, is produced during photodecomposition of the photoacid generator (PAG) in the polymeric resist film during imaging. Nonaflate acid is stronger than any of the acids generated by the 12 AAs studied here. We measured the decomposition rate of **2HA** at 100 °C in the presence of 0, 0.25, 0.5, and 0.75 equiv. of nonaflate acid. Figure 3 shows that the rate increases linearly with increasing nonaflate acid concentration. This means that although **2HA** does not decompose autocatalytically, the decomposition is catalyzed by nonaflate acid (Figure 3). Figure 4 compares the reaction energy profiles for Body-3 and

Body-2 AAs. The trigger-pull (T) reaction for Body-3 AAs is catalyzed by the acid generated from the AA decomposition resulting in a lower energy pathway than the uncatalyzed decomposition (U). On the other hand, these acids do not catalyze the trigger-pull for Body-2 AAs (solid curve) but nonaflate acid does (dashed curve).

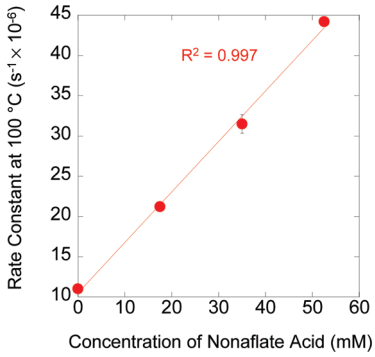
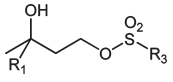
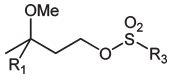


Figure 3. Decomposition rate constant of **2HA** at 100 °C increases linearly with respect to the concentration of added nonaflate acid, the acid generated photochemically in the resist formulations.

Lithographic Evaluation of Acid Amplifiers. To assess the impact of our AAs on improving EUV patterning performance, we calculated the *Z*-Parameter of the control resist (no AA) along with resists containing 70 mM AA. We compare the *Z*-Parameter at 50 nm equal lines and spaces because most of the resists resolved these features. A smaller *Z*-Parameter reflects overall improvement in lithographic performance.[21] Figure 5 shows lithographic results for the control resist without AA and 12 resists with 70 mM AA. For the most part, resist performance was evaluated by printing 50 nm equal lines and spaces. The sizing dose, LER and *Z*-Parameter are reported for each resist. All resists prepared with 70 mM concentration of AAs show sensitivity improvements (except **2HB**). The best overall resists contain AA **3MA**, **3MB**, **3HF**, or **2MA**. The Z-Parameter of resists that contain 70 mM of either of these AAs improves by factors of two or three relative to the control resist (control *Z*-Parameter = 13). Addition of AA **3HA**, **2HA**, or **2HC** improves the *Z*-Parameter from 13 (control) to 7. The AAs **2MB** and **2HB** do not improve Z-Parameter of the control resist. Figure 6 shows representative scanning electron micrographs

Table 3. We Compare Lithographic Properties at 50 nm Resolution (unless noted) and rate ratios at 100 °C for Hydroxyl and Methoxy Trigger AAs





R_1	R_3	name	k_{NoBase}/k_{Base}	E_{size} (mJ/cm^2)	LER (nm)	$Z \times 10^7$ (mJ nm^3)[c]	name	k_{NoBase}/k_{Base}	E_{size} (mJ/cm^2)	LER (nm)	$Z \times 10^7$ (mJ nm^3)[c]
Me	*p*-$CF_3C_6H_4$	**3HA**	1210	16.7	5.9 ± 0.3	7	**3MA**	230	15.4	4.6 ± 0.2	4
Me	*o*-$CF_3C_6H_4$	**3HB**	1390	16.1	4.8 ± 0.2	5	**3MB**	270	18.6	4.6 ± 0.2	5
Me	C_6F_5	**3HC**[a]	300	6.9	7.7 ± 0.4	9	**3MC**[b]	80	7.0	7.0 ± 0.4	18
H	*p*-$CF_3C_6H_4$	**2HA**	1	18.4	5.6 ± 0.3	7	**2MA**	1	19.2	5.0 ± 0.1	6
H	*o*-$CF_3C_6H_4$	**2HB**	1	23.1	10.4 ± 0.3	31	**2MB**	1	19.3	7.3 ± 0.2	13
H	C_6F_5	**2HC**	1	9.3	7.5 ± 0.3	7	**2MC**[b]	1	9.8	7.0 ± 0.2	25

[a] Lithographic data are reported for 60 nm lines and spaces. [b] Lithographic data are reported for 80 nm lines and spaces. [c] *Z* = *Z*-Parameter.

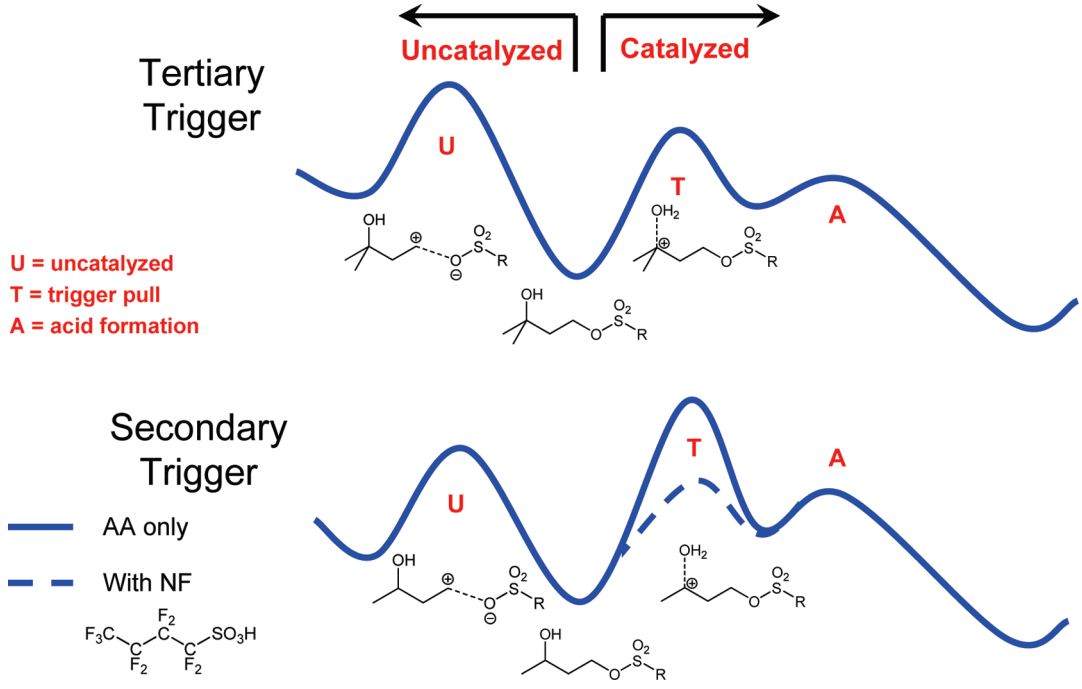


Figure 4. Acids generated by these AAs are strong enough to catalyze the trigger pull reaction of Body-3 AAs but not Body-2 AAs. However, nonaflate acid is strong enough to catalyze the trigger pull reaction of Body-2 AAs.

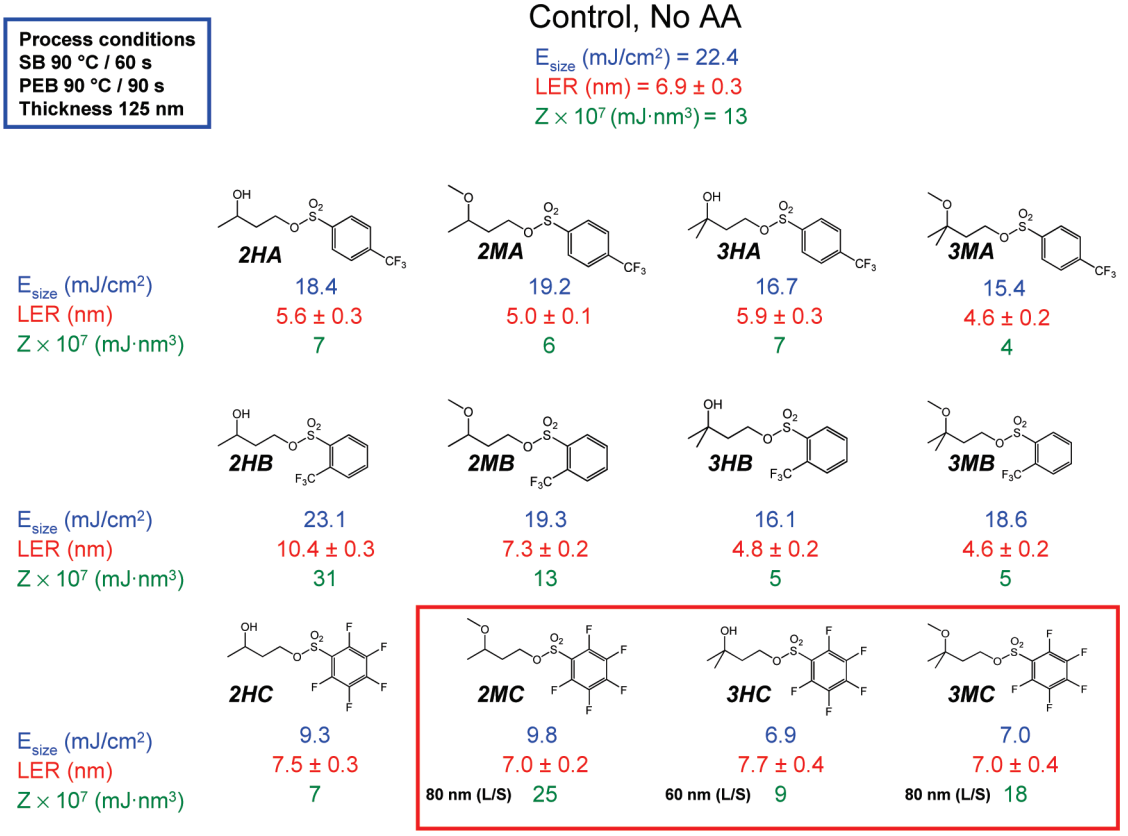


Figure 5. We exposed one control resist without AA and 12 resist with 70 mM AA to EUV light. The sensitivity (E_{size}), LER, and Z-Parameter of these resists are reported for 50 nm equal lines and spaces (L/S) or at best resolution.

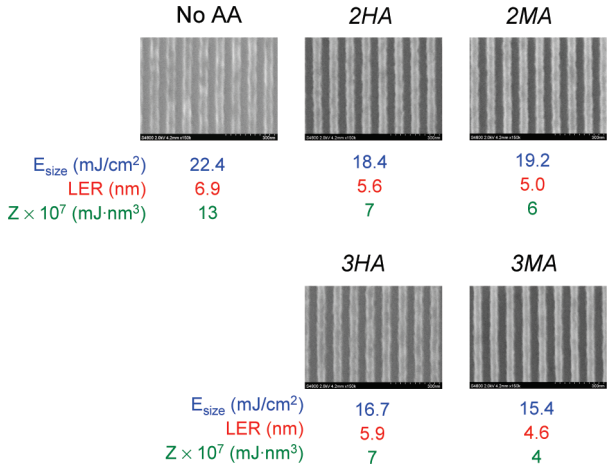


Figure 6. Scanning electron micrographs showing 50 nm dense lines of the control resist (no AA) and resists with 70 mM of added **2HA**, **2MA**, **3HA**, or **3MA**.

of 50 nm lines and spaces for the control resist (no AA) and resists with 70 mM of added tertiary AAs (**3HA** or **3MA**) and secondary AAs (**2HA**, **2MA**). All four AAs improve both sensitivity and LER. Our working hypothesis is that the performance of the resist is improved because more acid is generated in the exposed regions of the resist resulting in more efficient catalytic transformation of the polymer, resulting in better sensitivity, and the higher concentrations of acid allow the domain of each acid to be smaller, resulting in better LER. Both secondary and tertiary AAs are capable of yielding lithographic improvements.

For the most part, resists prepared with perfluorobenzenesulfonate esters (**3HC**, **3MC**, or **2MC**) gave poor lithographic performance versus the control, so they were only evaluated lithographically using 60−80 nm dense lines and space patterns. ^{19}F NMR kinetics showed that these three AAs gave the fastest thermal decomposition rates, so their poor lithographic performance may have been due to poor thermal stability in the resist. Interestingly, the only AA with a perfluorobenzenesulfonate ester that gave good lithographic performance is **2HC**, which has a secondary hydroxyl trigger. This AA resulted in the greatest improvement in resist sensitivity with only a modest degradation in LER.

In general, we found that the AAs that are the most stable toward uncatalyzed thermal decomposition give the best lithographic improvements. We think that AAs improve the sensitivity of EUV resists by generating acid during acid catalyzed decomposition. However, the relative diffusion rates of the acids generated by PAGs and AAs are certainly important factors in determining lithographic performance. We suspect that the acids generated by AAs in our experiments tend to diffuse further than the nonaflate acid generated by the PAG. Increasing acid diffusion rates generally results in sensitivity improvements, however, more diffusion can also degrade resolution and LER.[25] Therefore, the interpretation of imaging results is complicated by a trade-off between higher

(25) Mack, C. *Fundamental Principles of Optical Lithography*; Wiley: London, 2007.

sensitivity arising from more total acid being generated in the exposed regions vs the detrimental effects of increased overall acid diffusion.

Conclusions

We systematically varied the chemical structure of 12 acid amplifiers and studied their reaction kinetics. We found that decomposition rates of AAs in the presence of base follow first-order kinetics regardless of body, trigger or acid precursor type. Entropy of activation ($\Delta S^{\ddagger}$) appears to be the primary criteria for determining decomposition rate at 100 °C. Acid amplifiers with methoxy triggers all have higher entropies of activation than their corresponding hydroxyl analogues. In the absence of base, AAs with tertiary triggers decompose according to second-order autocatalytic kinetics, but AAs with secondary triggers decompose by first-order kinetics. We find that tertiary AAs have no-base/base rate ratios at 100 °C between 80 and 1400, whereas secondary AAs all have no-base/base rate ratios of 1.0. Although secondary AAs do not decompose autocatalytically, their decomposition can be catalyzed by nonaflate acid as shown by **2HA** in Figure 3. This is important for photoresist applications because nonaflate acid or similar super acids are produced in modern resist formulations. In a resist, Body-2 AAs are catalytically decomposed by the photo acid. Indeed, five of the six AAs with secondary triggers gave photoresists with improved sensitivity.

We used the *Z*-Parameter to compare the lithographic performance of EUV resists prepared with and without 70 mM concentration of acid amplifier. Resists that contain AAs that generate perfluorobenzensulfonic acid have the best sensitivity but poorest resolution. Seven of the AAs were capable of showing improved lithographic performance (lower *Z*-Parameter) versus the control resist. The *Z*-Parameter improved 3-fold with the addition of **3MA**, the best improvement for the 12 AAs presented here. We speculate that **3MA** gives the best lithographic improvement on the basis of the combination of the three attributes; it decomposes autocatalytically, generates the slowest diffusing acid, and releases methanol as a byproduct.

Acknowledgment. This work was supported by Intel Corporation. We also thank DuPont for supplying polymers.