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Fluorinated Acid Amplifiers for EUV Lithography

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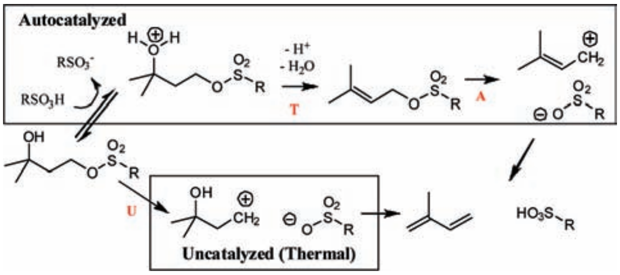
High resolution chemically amplified photoresists[1] are central to the manufacture of today's integrated circuits. These materials employ strong acids, generated during exposure to 248, 193, or 13.5 nm light, to catalyze the transformation of photoresist polymers from insoluble to soluble in alkaline developers. Critical to the microelectronics industry is the need to develop chemically amplified photoresists for use with extreme ultraviolet (EUV, 13.5 nm) light. 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 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]

Scheme 1. Proposed Reaction Mechanisms for the Autocatalytic (Acid Catalyzed) and Uncatalyzed Decomposition of Acid Amplifiers **1a** or **1b** (R_1 = *p*-$C_6H_4CF_3$ or *o*-$C_6H_4CF_3$, respectively)



To be successful in a modern photoresist, AAs must (1) be thermally stable in the absence of catalytic acid in phenolic polymer matrices at 70−120 °C; (2) rapidly decompose autocatalytically in the presence of the acids they produce; and (3) produce strong (fluorine-containing sulfonic) acids capable of participating in photoresist chemistry. To date, 26 AAs have been reported, but none of these would be appropriate for use in photoresist applications. Only two of the AAs produce fluorinated acids;[7] the others are either too difficult or expensive to synthesize,[8] do not decompose autocatalytically,[9] or are unstable under photoresist conditions.[10]

Here, we report on the design and kinetics of four AAs and one thermal AA (Figure 1).[11] We compare the relative rates of autocatalyzed and uncatalyzed reactions and show the unprecedented ability of **3b** to simultaneously improve resolution, sensitivity, and LER of EUV photoresists. Scheme 1 shows the proposed mechanism for the autocatalytic decomposition of **1a** and **1b**. Generically, these AAs consist of three parts, a body, an acid-sensitive trigger (**T**, either hydroxyl or acetate), and a sulfonic acid precursor (**A**). During autocatalysis, the trigger undergoes acidolysis[12] yielding an olefin. In successful AAs, this olefin forms an allylic sulfonic acid ester allowing the sulfonic ester to 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. Ideally, this autocatalytic pathway should occur 100−1000 times faster than the uncatalyzed thermal decomposition of the AA in the absence of acid.

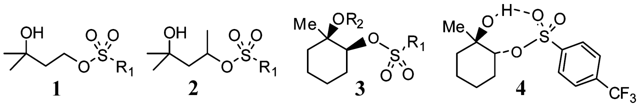


Figure 1. We report four acid amplifiers (**1a**, **1b**, **2**, **3b**) and one thermal acid generator (**3a**). **1a** = R_1 = *p*-$C_6H_4CF_3$; **1b** = R_1 = *o*-$C_6H_4CF_3$; **2** = R_1 = *p*-$C_6H_4CF_3$; **3a** = R_1 = *p*-$C_6H_4CF_3$, R_2 = H; **3b** = R_1 = *p*-$C_6H_4CF_3$, R_2 = Ac; **4** = Proposed transition state for the decomposition of **3a**.

We evaluated the thermal stability of the compounds in a positive photoresist matrix, by baking a blend of the AA in the resist matrix at 70 and 110 °C for 150 s, followed by development in a standard aqueous developer (Table 1).[13] Stable AAs retain most of their film thickness (losing <10 nm), while thermally unstable compounds decompose to create acid which converts the resist polymer to its soluble form allowing rapid dissolution in the aqueous developer. Table 1 shows that AAs **1a** and **3b** are stable to 110 °C anneal, AAs **1b** and **2** are stable to 70 °C anneal, and **3a** decomposes at 70 °C.

Table 1. Film Stability and ^{19}F NMR Kinetics Results[14]

			$k \times 10^3$, 100 °C (s^{-1})		
AA	film stability	E_0 test/ control	1.2 equiv of base	no added base	k_{AUTO}/k_{BASE} 100 °C
1a	>110 °C	2.6/ 4.4	0.033	48	1425
1b	>70 °C	–	0.053	73	1359
2	>70 °C	5.0/ 6.0	4.3	105	25
3a	fail	–	1.1	0.98	0.9
3b	>110 °C	3.9/ 4.4	0.0050	2.50	490

The thermal decomposition kinetics in solution for the AAs were measured using ^{19}F NMR.[14] Solutions of AAs (18 m*M*) were monitored in 50/50 C_6D_6/ethylphenol (to simulate the environment of a phenolic polymer matrix) and in the presence and absence of 1.2 equiv of added tri-*tert*-butylpyridine. The sterically hindered base was added to consume acid as it formed, so that the uncatalyzed reactions could be studied independently.[15] All reactions evaluated in the presence of base showed first-order kinetics, typically with $R^2 > 0.98$ over two half-lives. In the absence of base, the kinetic data were consistent with the autocatalytic mechanism illustrated in Scheme 1. Rate constants were determined by fitting

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the data to second-order catalyzed kinetics.[16] Rate constants at 100 °C and k_{AUTO}/k_{BASE} ratios are shown in Table 1.

The film stability and kinetic data show that structural factors such as cyclic vs acyclic bodies, hydroxyl vs acetate triggers, and primary vs secondary sulfonic esters significantly influence the reactivity of the AAs. Compounds **1a**, **1b**, **3b** are useful AAs. They are relatively stable in polymeric films, have slow decomposition rates in the presence of base, yet have an excellent rate ratio between catalyzed and uncatalyzed decomposition. Preliminary lithographic evaluation shows that they can increase sensitivity (E_0) by 12−40%.[17] Compound **2** shows greatly reduced thermal stability, which we ascribe to the secondary attachment of the sulfonic acid to the acyclic chain.

Figure 2 shows thermal decomposition kinetics for compounds **3a** and **3b**. Remarkably, although these compounds only differ by the identity of the trigger group (OH or OAc, respectively), their thermal decomposition kinetics differ significantly. AA **3a** is thermally unstable, decomposing in the resist film <70 °C, and decomposing rapidly in solution independent of the presence of added base. Clearly, this compound does not decompose by an acid-catalyzed reaction mechanism. In contrast, AA **3b** is quite stable, as it passed the film stability test at 110 °C. Molecular modeling of the uncatalyzed thermolysis reactions for **3a** and **3b** provides some possible insight. The modeling predicts a transition state, **4** (Figure 1), where the proton on the hydroxyl moiety of AA **3a** protonates the sulfonyl oxygen during C−O bond breaking.

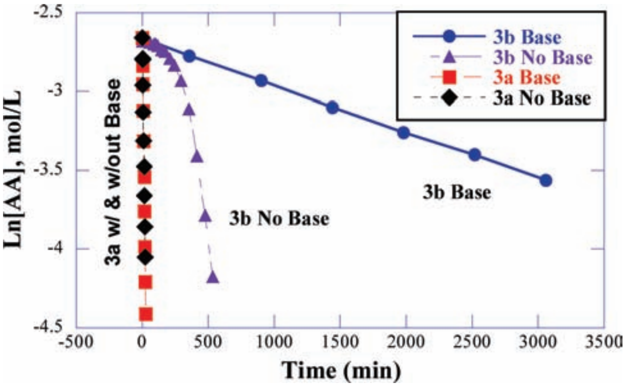

Figure 2. Kinetic plots for the thermal decomposition of **3a** and **3b** in the presence and absence of 2,4,6-tri-*tert*-butylpyridine.

To assess the impact of our AAs on improving EUV patterning performance, we calculated the *Z*-parameter[18] of the control resist along with resists prepared using 70 mM AAs **1a** and **3b** to be 74, 54, and 25 mJ*nm^3, respectively (smaller is desired). These results demonstrate simultaneous improvements in resolution, LER, and sensitivity for **1a** and **3b** and as illustrated in the SEM images shown in Figure 3 for **3b**.[19]

1,3-Acyclic and 1,2-cyclic AAs expand the scope of available methods for introducing strong fluorine-containing sulfonic acids in chemically amplified photoresists enabling us to achieve simultaneous improvements in resolution, LER, and sensitivity and realize a 3-fold gain in the *Z*-parameter. These studies demonstrate that small structural changes dramatically affect AA activity. Further studies of this type will allow us to design even more effective acid amplifiers.

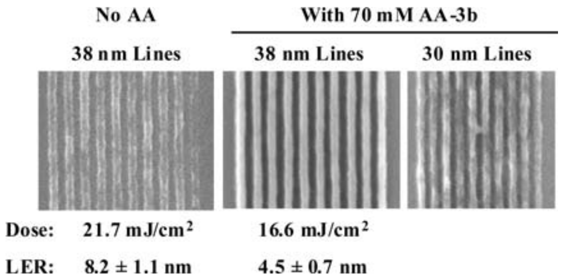

Figure 3. Scanning electron micrographs of dense line images printed using a control resist formulation with and without 70 mM **3b**.[12]

Acknowledgment. This work was supported by Intel Corporation.

Supporting Information Available: Experimental procedures and spectroscopic data for starting materials and products. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) We selected *p*- and *o*-$CF_3(C_6H_4)SO_3$−acid precursors because they yield AAs with good thermal stability and give simple ^{19}F spectra.
(12) Arimitsu, K.; Kudo, K.; Ichimura, K. *J. Am. Chem. Soc.* **1998**, *120*, 37–45.
(13) Photoresist films were prepared containing 70 mM of an AA, 7.5% of the photoacid generator bis(4-*tert*-butylphenyl)iodonium nonaflate and phenolic terpolymer [poly(hydroxystyrene)-(styrene)(*tert*-buylacrylate) 65/20/15 mol %] and 0.5 wt % of tetrabutyl ammonium hydroxide in 125 nm film on a Si wafer. The film was then baked at 110 or 70 °C for 150 s and developed in 0.26 N Me_4N^+ OH^- for 45 s.
(14) Reaction rates (with and without 1.2 equiv of 2,4,6-tri-*tert*-butylpyridine) were followed by integration of the CF_3 peaks for the starting AA and the product $CF_3C_6H_4SO_3H$ (or its pyridine salt). Estimated error for rate constants with and without base is 2.5% and 5%, respectively.
(15) Compound **1a** was decomposed in the presence of 2,4,6-trimethylpyridine, 2,6-di-*tert*-butyl-4-methylpyridine, and 2,4,6-tri-*tert*-butylpyridine giving first-order decomposition rate constants of $k = 9.7 \times 10^{-5}$, 1.0×10^{-4}, and 1.0×10^{-4} s^{-1}, respectively. This result is consistent with the interpretation that the base removes the acid from the reaction mechanism, but the base does not actively participate in the reaction by extracting protons from the AA bodies.
(16) 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.
(17) E_0's were determined by exposing the resist film described in ref 15 to stepwise doses of EUV light, baking at 110 or 70 °C for 90 s and then developing for 45 s. The lowest dose to give zero thickness is E_0.
(18) *Z*-parameters simultaneously evaluate the resolution, LER, and sensitivity of a resist. Wallow, T.; Higgins, C.; Brainard, R.; Petrillo K.; Montgomery W.; Koay C.-S.; Denbeaux G.; Wood O.; Wei Y. Proc. SPIE 2008,6921, 69211F/1−69211F/11.
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