Fluorine-Stabilized Acid Amplifiers for Use in EUV Lithography

Kenji Hosoi,^a Brian Cardineau,^b Seth Kruger,^b Koichi Miyauchi^a and Robert Brainard^b

a. Central Glass, Co. Ltd., Chiyoda-Ku, Tokyo, 101-0054 Japan

b. College of Nanoscale Science and Engineering, University at Albany, NY 12203

This paper presents two new concepts that together provide a 100,000X improvement in stability for AAs that produce highly-fluorinated, strong sulfonic acids. These two new design concepts are based on (1) an olefin-trigger structure and (2) a trifluoromethyl group *alpha* to the sulfonic ester. These approaches led to the synthesis of the first stable acid amplifier that generates triflic acid and for the synthesis of AAs that are stable enough to be used as monomers in free-radical polymerization reactions yet produce very strong, fluorinated acids. Lastly, we present preliminary results where one new AA is able to improve the LER of a control resist from 4.6 ± 0.5 nm to 2.1 ± 0.1 nm.

Keywords: Acid amplifier, EUV, photoresists

1. Introduction

Extreme ultraviolet (EUV) lithography continues to be a strong candidate for a commercially viable solution to next generation lithography. However, further development of chemically amplified photoresists for use with EUV is critical to meet the future photolithographic requirements of the microelectronics industry. EUV resists must simultaneously meet three requirements: high resolution, low line edge roughness (LER),¹ and high sensitivity.² We have proposed that the best way to simultaneously improve these three properties in EUV resists is to increase the number of strong acids generated per photon absorbed during exposure³ and we assert that acid amplifiers may be one of the best ways to achieve decompose in the presence of acid to generate more acid *via* acid-catalyzed mechanisms.⁴ When the product acid is strong enough to catalyze the decomposition of the AA, the decomposition occurs autocatalytically (Figure 1).⁵

Typically, acid amplifiers consist of three parts (Figure 1), a body, an acid-sensitive trigger (T, either hydroxyl, methoxy, acetate or ketal), and a sulfonic acid precursor

Figure 1. Generic representation of acid amplifiers (AAs). These compounds consist of three parts: a trigger (T), an acid precursor (A) and a body.

(A). The desired acid generation pathway is *via* acid-catalyzed decomposition. During autocatalysis, the trigger undergoes acidolysis yielding an allylic sulfonic ester (Figure 2). This olefin intermediate allows the sulfonic ester to thermally decompose *via* an E₁ or E₂ elimination reaction more rapidly than the starting AA, yielding a second double bond alkene fragment and a sulfonic acid. The undesirable decomposition pathway is uncatalyzed thermal decomposition which results in the formation of an olefin byproduct and an acid.

Figure 2. Proposed acid-catalyzed decomposition pathway for **AA1** in which a tertiary alcohol trigger is removed to generate intermediate **14** containing a sulfonic ester with an allylic C-O bond ($R = -C_6H_4CF_3$).

Several acid amplifiers (20-30) were reported in the literature⁶⁻¹³ prior to the beginning of our research in 2005. For the most part, these AAs generate weak sulfonic acids such as toluene sulfonic acid. Only two of these acid amplifiers produce fluorinated sulfonic acids.¹³ Since our interest has been to create AAs that are useful to chemically amplified photoresists, our focus has always been to create AAs that generate strong, fluorinated acids, since these acids are better catalysts and ultimately provide better lithographic performance than do weaker acids.¹⁴ Unfortunately, however, acid amplifiers that produce the strongest acids are the least stable (in the absence of catalytic acid) and typically are unable to withstand the temperatures required for synthesis or lithography.¹⁵

Here, we present two new concepts that together provide a 100,000X improvement in stability for AAs that produce highly-fluorinated, strong sulfonic acids. These two new design concepts are based on (1) an olefin-trigger structure and (2) a trifluoromethyl group *alpha* to the sulfonic ester.

2. Results and Discussion

2.1 Olefin-Trigger Acid Amplifiers

All of the acid amplifiers previously reported by us¹⁴⁻¹⁸ and others⁴⁻¹³ have triggers that are leaving groups. In general, the acid activates the trigger; the trigger then leaves creating a double bond (**14** in Figure 2). Since the double bond in **14** is allylic to the acid, the compound decomposes thermally thereby producing an acid.

We have considered that the mechanism for the development of AAs could include the generation of an olefin intermediate for which the C-O sulfonic ester bond **was not** allylic (**15**) and, therefore, **would not** produce acid. Yet, we also considered the additional possibility that the non-allylic **15** could be isomerized by catalytic acid to the allylic **14** as a potential pathway for producing acid. This mechanistic analysis led to the idea of using non-allylic double bonds as triggers. For example, the olefin can be positioned three carbons away from the sulfonic ester (acid precursor). In this state, there is no allylic stabilization to the acid precursor and the compound is thermally stable. The trigger is effectively in the “off” position. Isomerization of the initial olefin can occur to produce the more highly-substituted olefin which is also allylic to the sulfonic ester. In the presence of a catalytic acid, the double bond can isomerize toward the acid precursor and then thermally decompose releasing the acid.

The lithographic performance of two olefin-trigger AAs was evaluated as a function of PEB temperature (Figure 3).¹⁹ **AA2** increases the sensitivity of the control by 0.1 to 2X and **AA3** increases the sensitivity of the control by 2 to 10X, depending upon post exposure bake (PEB) temperature.

2.2 Fluorine-Stabilized Acid Amplifiers

One of the biggest challenges in designing and preparing acid amplifiers for use in chemically amplified

Figure 3. Clearing doses (E_0) of a control resist¹⁹ and resists prepared with 70 mM of **AA2** and **AA3**.

resists is that the AAs that generate fluorinated acids tend to be unstable. Product analysis experiments¹⁴ showed

that the pathways for the unwanted, noncatalytic decomposition reactions involved either S_N2 or S_N1 reactions between phenolic nucleophiles in polymer films or in solution and the primary sulfonic ester bonds (Figure 4). We, therefore, devised a strategy for blocking both decomposition pathways by preparing acid amplifiers with a trifluoromethyl ($-CF_3$) group alpha to the sulfonic ester. We proposed that the CF_3 would reduce the rate of S_N2 pathway by increasing steric hindrance; and would reduce the rate of the S_N1 pathway by preventing the buildup of positive charge.

Combining both the olefin trigger and the fluorine-stabilized capacity into one trigger-body design, we produced acid amplifiers **AA4** and **AA5** (Figure 5), which are designed to produce pentafluorobenzene-sulfonic acid ($C_6F_5SO_3H$, PFBS) and triflic acid (CF_3SO_3H , TfOH), respectively. Using some of our original body-trigger designs,¹⁴⁻¹⁸ we have been able to prepare AAs that generate PFBS, but, until now, we have never been able to prepare stable AAs that make acids any stronger than PFBS acid. Using the olefin/ α - CF_3 design, not only have we been able to prepare AAs that generate PFBS, but for the first time, we are able to prepare an AA that generates TfOH

2.2.1 Film Stability Studies

One convenient method to assess the stability of a resist film is to measure its thickness as a function of temperature using temperature-programmed spectroscopic ellipsometry.^{20,21} We compared the thermal

Figure 4. CF_3 alpha to the sulfonic ester inhibits S_N2 and S_N1 reactions.

Figure 5. Chemical structures of fluorine stabilized AAs **AA4** and **AA5**.

stability of a control resist,¹⁹ vs. the analogous resists to which 70 mM concentrations of **AA4**, **AA5**, and **AA6** had been added. The thickness curves (Figure 6) show that **AA6** that produces $C_6F_5SO_3H$ decomposes with peak decomposition rate of 125 °C, whereas the resists prepared with **AA4** and **AA5** decompose at about the same temperature as the control resist (195 °C).

2.2.2 ^{19}F NMR Kinetics

The rate of decomposition of **AA4** and **AA5** was determined using ^{19}F NMR in the presence and absence of 1.2 eq. of base using previously described procedures (Figure 7).¹⁵ These experiments determine the uncatalyzed and catalytic rate constants (k_{BASE} and k_{CAT} , respectively). These new AAs show dramatic stabilities at a temperature that is much higher than is typically used (145 vs. 100 °C, respectively). For example, the AA that produces ($C_6F_5SO_3H$) only decomposes 10% after 29 days at 145 °C. The kinetics conducted in the absence of base provide catalytic rate constants.²² We typically use the rate ratios of catalytic vs. noncatalytic acids as one criteria for judging the usefulness of an AA. This k_{CAT}/k_{BASE} ratio should be as large as possible. The best rate ratio that we had observed previously for an AA that produced $C_6F_5SO_3H$ was 300, and the best ever observed was 1425.¹⁶ However, these new AAs based on olefin/ α - CF_3 design have rate ratios of 1,000,000 and 28,000 for the AAs that produce $C_6F_5SO_3H$ and CF_3SO_3H , respectively.

2.2.3 Tuning the Reactivity of Stable Acid Amplifiers

After demonstrating the remarkable stabilizing effect of placing a CF_3 group alpha to the sulfonic acid, we

Figure 6. Thermally-programmed spectroscopic ellipsometry shows that AAs **AA4** and **AA5** are as thermally stable as the control resist without AA.

Figure 7. Thermal decomposition of **AA4** and **AA5**: A) With added base B) In the absence of base.

considered the possibility that the new body/trigger design might be too stable to be useful within the temperature range typically used during PEBs (90–130 °C). We, therefore, produced new AAs that combined the alpha-CF₃ body with the more reactive ketal triggers (Figure 8) and evaluated their effect of sensitivity (clearing dose, Eo) as a function of PEB bake (100–130 °C). The new acid amplifiers provide 0–4X improvement in photosensitivity. Clearly, these new AAs are capable of participating in photoresist reactions within a useful range of PEB temperatures.

2.2.4 Stability vs. pKa of Product Acid

Figure 9 shows the first-order rate constants for 14 AAs arranged according to body/trigger type and the pKa calculated²⁶ for the sulfonic acid generated by the AA.

Figure 8. Clearing doses (Eo) of a control resist¹⁹ and resists prepared with 70 mM of **AA7**, **AA8**, and **AA9**.

Interestingly, our new strategy for attaching AAs to polymers generate an acid with an amide linkage (PhNHCOCF₂SO₃H) which is predicted to be slightly stronger than triflic acid (CF₃SO₃H). Indeed, decomposition rate of an AA that generates our amide-based sulfonic acid is 3.5x faster than an AA that generates triflic acid. A plot of the log of the acid amplifier and first-order uncatalyzed rate constant (k_{BASE}) is shown vs. pKa (Figure 10). Clearly, the new olefin/ α -CF₃-type AAs demonstrate remarkable stability despite producing highly-fluorinated sulfonic acids. In fact, when comparing AAs that produce C₆F₅SO₃H, the new design

Sulfonic Acid Predicted pKa (± 0.5)	OMe	OH	OH	CF ₃	CF ₃	CF ₃
	OSO ₂ R	OSO ₂ R	OSO ₂ R	OSO ₂ R	OSO ₂ R	OSO ₂ R
CF ₃ SO ₃ H -1.1	16	3.6	1.2			Most Stable
CF ₃ SO ₃ H -1.2	21	5.1	1.7			
C ₆ F ₅ SO ₃ H -2.2	240	73	33			0.009*
CF ₃ SO ₃ H -3.9						0.43*
PhNHCOCF ₂ SO ₃ H -4.1	Least Stable			0.82 54*	0.036 3.8*	0.028 1.5*

Figure 9. First-order rate constants ($\times 10^{-5} \text{ s}^{-1}$) vs. calculated pKas of product acids at 100 °C or if marked with *, at 145 °C.

Figure 10. Log(decomposition rate) in the presence of excess base vs. calculated pKa of acids produced by AAs.

provides a 100,000X improvement in stability over the most stable AAs previously evaluated. Interestingly, AA14 may have the right balance between stability and reactivity, by combining the strongly acidic amide acid precursors with the spiro-ketal trigger design.

2.3 Synthesis and Preliminary Lithographic Performance of Fluorine-Stabilized Polymers

We prepared three monomers based on the *alpha*-CF₃ stabilization and ketal triggers that have a *para*-amide-styrene functionality capable of participating in polymerization reactions as described elsewhere²⁴ and shown in Figure 11.

Preliminary lithographic performance of resists prepared with blend and polymer-bound fluorine-stabilized AA against AA-free controls were evaluated at the Paul Sherrer Institut (PSI) using EUV interference lithography.²⁵ Resists were prepared with 10% DTBPI-Nf PAG and either 1 or 2% base (Figure 12 and 13, respectively) and were used to print 50-nm dense lines.

The control resist prepared with 1% base produced an LER of 5.6 ± 0.4 nm (Figure 12). Blending 70 mM of AA10 provided an improvement in LER to 3.1 ± 0.1 nm. The polymer bound AA (PBAA11) also showed an improvement in LER to 3.8 ± 0.4 nm.

The control resist prepared with 2% base produced an LER of 4.6 ± 0.5 nm (Figure 13). Blending 70 mM of

AA12 showed no significant improvement in LER, yet blends of AA10 produced an LER of 2.1 ± 0.2 nm. The polymer-bound AA, PBAA13, provided a modest improvement in LER of 3.8 ± 0.1 nm.

Figure 11. Synthesis of polymers starting with a monomer that generated a polymer-bound AA.

Figure 12. Lithographic properties of new acid amplifiers. Base loading = 1.0%

Figure 13. Lithographic properties of new acid amplifiers. Base loading = 2.0%

3. Conclusions

Two new AA design strategies have been presented based on olefin triggers and trifluoromethyl groups

positioned alpha to sulfonic ester groups. Comparison between previous body-trigger design strategies show:

- A 100,000X improvement in thermal decomposition stability for AAs that produce $C_6F_5SO_3H$.
- The first stable AA capable of producing the very strong triflic acid (CF_3SO_3H).
- Dramatic improvement in the k_{CAT}/k_{BASE} reactivity ratio from the previous high of 1425 to 38,000 and 1,000,000 for **AA5** and **AA4**, respectively.

New ketal-triggered AAs were presented that provide good sensitivity enhancement of the fluorine-stabilized AAs within useful PEB temperature range. Additionally, these new AAs are sufficiently stable enabling them to be converted to styrene-based monomers capable of being incorporated into polymers via overnight free radical polymerization reactions.

Although the lithographic results are very preliminary, and lack information about sensitivity,²⁵ the significant improvements in LER provide strong evidence that fluorine-stabilized acid amplifiers have a promising future for use in chemically amplified resists.

4. Acknowledgements

The authors of this paper would like to thank Central Glass, Co. Ltd. for financial support of this research and would like to thank Intel Corporation for the original funding. We thank Dow Electronic Materials for supplying us with monomers. We also thank the staff at PSI (Yasin Ekinici, Michaela Vockenhuber) for assistance in conducting lithographic evaluations, and thank Alain Diebold for help with Ellipsometry. Lastly, we thank Patrick Naulleau and Summit Corporation for providing an academic license to Summit

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