Fluorinated acid amplifiers for extreme ultraviolet lithography

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FLUORINATED ACID AMPLIFIERS FOR EXTREME ULTRAVIOLET LITHOGRAPHY

By

Seth Kruger

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FLUORINATED ACID AMPLIFIERS FOR EXTREME ULTRAVIOLET LITHOGRAPHY

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I would like to express my utmost gratitude to my advisor, Prof. Robert Brainard. He has invested much time and effort in training and educating me. He has instilled in me the skills and desire to think critically and to solve problems. He has truly equipped me with the skills to succeed in life. I am also grateful that he has provided me the opportunity to travel around the world to utilize the most advanced lithography tools.

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ABSTRACT

Extreme ultraviolet lithography (EUV) is a promising candidate for next generation lithography. Although EUV has great potential there are still many challenges that must be solved before the technology can be implemented in the high volume manufacturing of semiconductor devices. The lithographic performance of EUV photoresists is one aspect that requires improvement. Particularly, EUV resists need simultaneous improvements in three properties: resolution, line-edge-roughness and sensitivity. The incorporation of acid amplifiers (AAs) in resists is one method to improve all three properties.

Acid amplifiers are compounds that decompose via acid-catalysis to generate more acid. Successful AAs must be thermally stable in resist films under normal resist process conditions and they must generate strong fluorinated sulfonic acids. To the best of our knowledge, there are only 29 AAs published in the literature prior to our work on this topic, none of which meet the requirements for use in EUV resists.

This thesis describes the synthesis and characterization of new AAs specifically designed for EUV resists. More than 40 new AAs were synthesized. The compounds were lithographically evaluated in EUV resists. Decomposition reaction kinetics were measured using $^{19}$F NMR spectroscopy. Investigations were done to measure AAs: thermal stabilities in resist films, acid generation in resist films, decomposition products, and species outgassed from resist films exposed to EUV light. A model was developed to predict AAs effects on acid gradients in resist films and on resists sensitivities. The last chapter shows some preliminary results of AAs that have record thermal stabilities and that generate triflic acid.
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CHAPTER 1

INTRODUCTION TO PHOTOLITHOGRAPHY AND ACID AMPLIFIERS

1.1 Introduction

Modern electronics are made possible by the integrated circuit (IC). IC’s were first developed in the 1950’s and popularized in the 1960’s. The first IC devices contained about a dozen transistors but the number soon increased as IC manufacturing matured [1]. In 1965, Gordon E. Moore made the observation that the number of components in the IC had doubled every year from 1958 until 1965 and predicted that this trend would continue for some time [2]. This observation was dubbed “Moore’s Law” and the trend of increasing the number of transistors per area has continued with unprecedented success.

Over the years, the number of transistors per device steadily increased. In the late 1960’s a single chip could contain several hundred transistors and in the 1970’s ICs’ could contain tens of thousands of transistors. Today’s microprocessors contain billions of transistors [3].

The ability to shrink IC components is made possible by advances in photolithography. Photolithography is the process used to make the circuitry in today’s microelectronics. The lithographic process transfers a template image onto a polymeric matrix known as a photoresist or resist. The pattern is etched into the underlying substrate, usually a single crystal silicon wafer [4].
1.2 Photoresist

Resists can be classified by their sensitivity toward the exposure radiation. Two types of resists are: optical and electron beam (E-beam). The smallest feature that an optical resist can resolve is limited by light diffraction and can be calculated using Rayleigh’s equation (Equation 1.1) [5]. The smallest resolution \( R \) is proportional to \( k_1 \) and the exposure wavelength \( \lambda \) and is inversely proportional to the numerical aperture (NA) of the lens. Traditionally, the easiest ways to improve resolution have been to reduce \( k_1 \) and to use smaller exposure wavelengths. The common wavelengths used to expose resist are 436 nm (g-line), 365 nm (i-line), 248 nm (KrF), and 193 nm (ArF). Focused electron beam (E-beam) gives some of the best resolution to date but the throughput is very low [6]. E-beam resists are generally used for fabricating photolithography masks or new device prototypes. The smallest features on today’s commercial ICs are printed using a 193 nm exposure source. Future devices might be fabricated using a 13.5 nm (EUV) exposure source [7,8].

\[
R = \frac{k_1 \lambda}{NA} = \frac{k_1 \lambda}{n \sin(\alpha)}
\]

**Equation 1.1** The minimum feature that optical lithography can print is determined by the Rayleigh equation, where \( k_1 \) is the resolution factor, \( \lambda \) is the wavelength of illuminating light, \( n \) is the index of refraction of the medium between the optics and resist and \( \alpha \) is the acceptance angle of the lens.

The work presented here describes the development of chemically amplified positive tone resists for EUV lithography. Figure 1.1 outlines the main process steps in traditional photolithography [9]. First, a resist film is applied onto a substrate using a technique
known as spin coating. Spin coating gives a uniform film thickness over the entire wafer. Generally, the film thickness is between 1-0.05 μm. Next, the coated wafer is baked on a hot plate to remove residual casting solvents. This bake step is referred to as a soft bake (SB) or post applied bake (PAB). The resist is then exposed to light through a mask. The incident light transforms a photo-active portion of the resist from soluble to insoluble or vice versa in a suitable developer. Next, the resist is developed with an appropriate developer. In the case of positive resists the exposed regions will dissolve in the developer leaving behind the unexposed regions. For negative resists the opposite occurs, exposed regions are insoluble in developer while the unexposed regions are washed away. The remaining photoresist protects the underlying substrate while the exposed regions are etched away during subsequent etching steps (not shown in the Figure). Lastly, the remaining resist is removed to leave behind a negative pattern etched into the substrate. This process is repeated many times to make an IC.

![Figure 1.1](image.png)

**Figure 1.1** Positive and negative resist process flow. 1. Spin coat and soft bake resist film. 2. Expose resist to radiation. 3. Develop resist in solvent.

Traditional resists require several photons to transform a photo-active unit in the resist [10,11] from soluble to insoluble. The concept of chemical amplification was proposed
in the 1980’s to improve resist photo sensitivity [12,13]. High-resolution, positive chemically-amplified photoresists (CAMPs) are central to the manufacture of today's integrated circuits [14,15]. These resist thin films are composed primarily of organic polymers and photoacid generators (PAGs) [16]. Figure 1.2 outlines the process flow of a positive tone resist. First, the resist is coated onto a substrate and post applied baked typically between 90-130 °C for 60-90 seconds. Next, the resist film is exposed to radiation. During exposure to 193 or 13.5 nm light, the PAGs produce strong acids. During a subsequent post exposure bake (PEB) step, these strong acids catalyze deprotection reactions on the organic polymer (Figure 1.3). These acid catalyzed deprotection reactions transform the resist from insoluble to soluble in aqueous alkaline. Development reveals a photoresist pattern where the exposed regions dissolved away and unexposed regions remain on the substrate. The use of catalytic acid in the resist improves the sensitivity over traditional resists by performing many functional group transformations per absorbed photon [17].

Figure 1.2 Positive CAMP resist process flow.

Figure 1.3 Acid catalyzed deprotection of a t-butyl ester group in a CAMP resist.
1.3 Photolithography at 193 nm

Current microelectronic manufacturing uses 193 nm lithography to print the smallest features of integrated circuits. The Rayleigh equation shows that the resolution is inversely proportional to the index of refraction of the medium between the last lens of the exposure optics and the photoresist. Originally, the space between the lens and resist was occupied by air but today’s chips are made using 193 nm immersion (193i) lithography [18]. This process incorporates a fluid between the lens and resist. The fluid has a refractive index greater than air and thus improves the resolution [19]. Higher refractive index fluids were investigated [20,21] to extend the capabilities of 193i lithography but this approach has been abandoned [22,23]. As integrated circuits continue to shrink down, the need for a next generation lithography technology continues.

1.4 Photolithography at 13.5 nm

Extreme ultraviolet lithography (EUV, 13.5 nm) is a promising candidate for the manufacturing of future microelectronics with features of 22 nm and smaller [24]. Because of the extremely small exposure wavelength, EUV lithography has several key distinctions from traditional optical lithography. The optics and wafer are contained in a vacuum chamber during EUV exposure because most materials including air absorb 13.5 nm light. The optics used in EUV exposure tools are reflective mirrors specially designed out of multiple layers of molybdenum and silicon [25,26]. Although the mirrors do reflect EUV light they are only ~70 % efficient [27]. Since the optical design of EUV steppers will require 8-12 reflective mirrors, \((0.7)^8 = 0.057\), and \((0.7)^{12} = 0.0138\), 94-99 % of the light will be lost. Highly sensitive photoresists [28] are needed for EUV
lithography because of the lack of a powerful EUV light source and much of the light will be lost before it gets projected onto the resists [29].

1.5 Research Motivation

Extreme ultraviolet lithography continues to be a strong candidate as a commercially viable solution for next generation lithography. However, the development of chemically amplified photoresists for use with EUV light is critical to meet the future photolithographic requirements of the microelectronics industry. These resists must simultaneously exhibit three properties: high resolution (below 22 nm), low line edge roughness (LER), [30] and high sensitivity [31]. 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 during exposure [32]. One method to improve the acid generation in resist films is to increase the film quantum yield by adding more PAG. This method only provides modest improvements in resist performance. Alternatively, we assert that acid amplifiers may be one of the best ways to achieve large simultaneous gains in resolution sensitivity and LER. This thesis focuses on the development and utilization of acid amplifiers for EUV resists. The goals of this work are to synthesize new AAs specifically for EUV resists, develop a fundamental understanding of their acid generation mechanism and evaluate resist films that contain AAs.

Acid amplifiers (AAs) are compounds that decompose via acid-catalyzed mechanisms to produce more acid [33]. When the product acid is strong enough to catalyze the decomposition of the AA, the decomposition occurs autocatalytically (Figure 1.4) [34].
Figure 1.4 Acid amplifier decomposition is a self-catalyzing reaction (autocatalytic).

1.5.1 Literature Examples of Acid Amplifiers

Previous work in the literature shows that to improve the imaging in a modern photoresist, AAs must meet the following requirements [35,36]: 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 catalyzing the polymer deprotection reaction. Prior to our first communication on this topic [37] there were twenty-nine acid amplifiers in the literature (Figure 1.5). The AAs previously reported consist of acetoacetate derivatives [35], cyclohexane-1,2-diol monosulfonates [38,39], a trioxane derivative [40], ketal sulfonates [41], pinane-1,2 diol monosulfonates [42,43], cyclohexane-1,4-disulfonates [44] and benzyl sulfonates [45]. Only two of the AA's described in the literature produce strong fluorinated acids [44]. In addition, only five of the AAs were evaluated for their additive effects on photoresist imaging. Non-fluorinated AAs were incorporated into acrylate based ArF resists [39,43] and phenolic KrF resists [46]. The AAs presented in the literature do not meet the requirements for use in EUV photoresists.
1.5.2 Design of Acid Amplifiers

Acid amplifiers are compounds that decompose in the presence of catalytic acid to generate more acid. Based on this definition, the chemical structure of AA molecules should contain an acid sensitive functional group and an acid precursor. Our synthetic efforts focus on designing thermally stable AAs that produce fluorinated sulfonic acids for use in phenolic EUV resists. In this work, we vary the chemical structures of our AAs to give a range of reactivities. These acid amplifiers consist of three parts (Figure 1.6), a body, an acid-sensitive trigger (T, either hydroxyl, methoxy, acetate or ketal), and a sulfonic acid precursor (A). Figure 1.7 shows two decomposition mechanisms that can occur to produce acid. The undesired decomposition pathway is uncatalyzed (U) thermal
decomposition which results in the formation of an olefin byproduct and acid. The desired acid generation pathway is via acid catalyzed decomposition. During autocatalysis, the trigger undergoes acidolysis yielding an allylic sulfonic ester. 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.

**Figure 1.6** Generic representation of AAs. These compounds consist of three parts: a trigger (T), an acid precursor (A) and a body.

**Figure 1.7** Proposed mechanism for acid catalyzed and uncatalyzed AA decomposition.
1.6 Summary

In summary, this thesis presents the use of acid amplifiers in EUV resists as a potential method to simultaneously improve resist resolution, sensitivity, and line-edge-roughness. Chapter 2 highlights key lithographic experiments. First, lithographic evaluation metrics are defined then the lithographic results are presented for control resists and resists with added AAs. Chapter 3 describes detailed decomposition kinetics of AAs using NMR spectroscopy. Chapter 4 covers several topics: 1) acid detection in resist films using acid sensitivity dyes. 2) Determination of AAs decomposition temperatures in resist films. 3) Identification of AA decomposition products in solution using $^1$H NMR. 4) Effects of AAs on resist outgassing. Chapter 5 discusses two mathematical models. The first model is designed to help understand how AAs affect the acid concentration gradient in a resist film by simulating AA reactivity and acid diffusion. The second model uses thermodynamic calculations to predict AA reactivity. The calculations are compared to the experimentally measured reaction kinetics. Chapter 6 gives detailed experimental procedures for the synthesis of all of the AAs that we synthesized. Lastly, chapter 7 shows the strategy for new AAs that have improved thermal stability and reactivity properties. Preliminary results confirm that these new AAs have very high thermal stabilities and they decompose autocatalytically with high decomposition rate constants.
References


CHAPTER 2

LITHOGRAPHIC EVALUATION OF PHOTORESISTS
WITH AND WITHOUT ACID AMPLIFIER

2.1 Objectives
In this chapter key lithographic experiments are highlighted to show the effects of incorporating acid amplifiers in EUV photoresists. The aim of these experiments is to show that AAs can simultaneously improve three resist properties, resolution, line-edge-roughness and sensitivity. Current methods can only improve two of these properties at one time and the benefits come at the expense of the third property. This is commonly referred to as the resolution, line-edge-roughness and sensitivity (RLS) trade-off [1,2]. Our hypothesis is that acid amplifiers will catalytically decompose in the exposed regions of resist films to generate strong acids. The increase in acid concentration will improve the photospeed (sensitivity) of the resist, similar to increasing the film quantum yield which has been shown to improve overall resist performance [3,4,5]. Additionally, we can design the resist and process conditions to limit the acid diffusion which will improve the resolution and line-edge-roughness (LER) [6,7,8,9].

2.2 Resist Evaluation Metrics
The purpose of this section is to define the parameters that are measured to evaluate resist lithographic performance. The overall goal is to simultaneously improve the resist resolution, LER and sensitivity.
Resolution is the smallest dimension of a desired feature that can be printed in the resist film. The resolution is determined by Rayleigh’s equation (Chapter 1, equation 1.1), and is a factor of the light aerial image and resist chemistry. Rayleigh’s equation accounts for resist chemistry by the $k_1$ factor which is always less than 1. Figure 2.1 shows the resolution limit for equal lines and spaces (L/S) of one of our common EUV resists. The resolution of this resist is 38 nm L/S. Although the resist has modulation below 38 nm, 36 nm L/S are not resolvable. Some factors that limit the resolution are pattern collapse and acid diffusion. Pattern collapse occurs when the resist thickness is much more than the width of the line, typically when this ratio (called the aspect ratio) is $>3$ [10]. The aspect ratio is lowered by simply reducing the film thickness. However, thinner films have worse LER than thicker films [11]. Acid diffusion can also limit the resolution [6,7,8,9,12]. Features are unattainable when acids diffuse on the same length scale as the feature dimension.

![Figure 2.1](image)

**Figure 2.1** SEM images of equal lines and spaces for a typical resist formulation. This resist has a resolution limit of 36 nm.

Line-edge-roughness (LER) is a measure of the roughness of a photoresist line edge. There are many variables that contribute to LER, some of which are the aerial image profile, shot noise [15], acid diffusion and PAG distribution in the resist film [9,13,14].
We use SEM images of resist L/S patterns and the commercially available software, SUMMIT™ to determine LER. One common method to improve LER is to add base quencher to the resist formulation [16-20]. We optimized one of our resist formulations by varying the base quencher loading at a constant PAG loading. Figure 2.2 shows SEM images of 50 nm L/S patterns for 3 base loadings. At the lowest base loading (0.2 wt%) the dose to print 50 nm L/S is 3.7 mJ·cm\(^{-2}\) and the LER is 18.7 nm. As the amount of base is increased up to 0.5 wt% the LER is improved to 5.2 nm but the dose required to print 50 L/S is increased to 10.7 mJ·cm\(^{-2}\). Figure 2.3 shows the measured LER plotted as a function of \(1/\sqrt{E_{\text{size}}}\). This shows a trade-off between LER and dose. Our results agree with other resists reported in the literature [21].

Figure 2.2  SEM images of photoresist lines at 50 nm half pitch shows that LER improves with base loading.
Sensitivity is the dose in mJ·cm$^{-2}$ required to print a desired pattern in a photoresist. Sensitivity can be the dose to clear (Eo) or the dose to size (Esize). Eo is defined as the dose required to just clear the resist from the wafer using an open frame (no mask) exposure. Eo is quicker and easier to measure than Esize but it gives less information about the resist lithographic properties. Eo is often used to approximate Esize, usually $E_{size} \approx 2.5$ to $3 \times E_{o}$. Figure 2.4 shows the normalized film thickness plotted as a function of dose. The film thickness does not change significantly until a threshold dose is reached, then the film thickness is quickly reduced until it completely clears at a dose of 6.1 mJ·cm$^{-2}$.

Esize is the dose required to print the mask image in the resist. Figure 2.5 shows line width plotted as a function of dose for a mask pattern of 50 nm equal lines and spaces. The lines become thinner and the spaces get wider as dose increases. The dose reaches Esize at 5.2 mJ·cm$^{-2}$ because the lines and spaces are both 50 nm. The resist is under exposed below Esize and over exposed above Esize.
Figure 2.4  Film thickness vs. dose. $E_o$ is the dose to clear the resist in an open field exposure.

Figure 2.5  $E_{\text{size}}$ is the dose to print the mask image.

There are several mathematical equations that describe the relationship between resolution, LER and sensitivity [21-23]. These rigorous methods require experimentally determined resist properties such as blur, acid diffusion length, and exposure latitude, as well as exposure tool properties [23-27]. We use the simpler method of Z-Parameter to evaluate our resist performance [28]. Equation 2.1 shows the Z-Parameter equation. This approach allows us to compare the overall resist performance using easy to measure
properties. Simultaneous improvement in all three properties results in smaller Z-Parameters. In our work, we compare the Z-Parameter of control resists to resists with acid amplifiers.

\[(\text{Half Pitch})^3 \times (\text{LER})^2 \times \text{Esize} = \text{Z-Parameter}\]

**Equation 2.1** Z-Parameter is used to evaluate resist lithographic performance. Reducing Z-Parameter indicates improvements in lithographic performance.

### 2.3 Thermal Stability Testing

The thermal stability of new AAs are measured in a resist films before AAs are lithographically evaluated. Resist formulations are generally 2-5 wt% solids dissolved in solvent, so the solids are reported as wt% of the total solids. Our *OSI* control resist formulation is composed of di(4-t-butylphenyl)iodonium perfluoro-1-butanesulfonate (DTBP-I-PFBS, 7.5 wt%, 123 mM) PAG, tetrabutylammonium hydroxide (TBAH, 0.5 wt%) base quencher, and 4-hydroxystyrene / styrene / t-butyl acrylate (65/15/20) polymer. The solids are dissolved in a 50/50 mixture of ethyl lactate (EL) and propylene glycol methyl ether acetate (PGMEA). The thermal stability of AAs are measured by blending AAs (70 mM) into an *OSI* resist, a film is spin coated on silicon, baked at 70 or 110 °C for 150 seconds and developed in 0.26 N tetramethylammonium hydroxide (TMAH) for 45 seconds. The film thickness loss after development is < 10 nm for compounds that are deemed thermally stable at these bake temperatures. We chose these temperatures because they are in the range of PEB temperatures that we use when we lithographically evaluate our resists. Thermally unstable compounds decompose and produce acid throughout the entire film resulting in complete film loss after. Figure 2.6
shows the thermal stability results of fifteen compounds; symbols indicate their relative stability. These compounds encompass a variety of structural features. Comparisons can be made between primary and secondary sulfonates, between fluorinated and non-fluorinated acid precursors, and between acyclic and cyclic structures. In general, the most stable AAs are acyclic compounds with the acid precursor and trigger one carbon atom apart or cyclic compounds with the acid precursor and trigger on adjacent carbon atoms. However, the trigger type has a significant influence as seen by comparing 6AB and 6HB or 5AB and 5HB. This simple evaluation method helped to focus our synthetic efforts on 1,3-acyclic AAs. In chapter 5, we present a thermodynamic model to predict the reactivity of these compounds and compare the results with experimental measurements.

Figure 2.6 Symbols are assigned to compounds according to their response to the thermal stability test. Open and closed circles are assigned to compounds stable at 70 and 110 °C, respectively. Filled squares are assigned to compounds that decomposed at these temperatures.
2.4 AA Photosensitivity Experiment

To test the photosensitivity of acid amplifiers, resist films were prepared containing base quencher, the ESCAP polymer and one of four AAs (3HB, 3HA, 5AB, 7AB), but without PAG. These AAs were selected to test a range of structural features, cyclic vs. acyclic and aromatic vs. aliphatic containing bodies, as well as fluorinated vs. nonfluorinated acid precursors. The resist films were exposed up to 20 mJ/cm², baked at 110 °C for 90 s and developed in 0.13 N TMAH for 45 s. Dilute developer was used because resists without PAG are soluble in standard developer even without exposure. Figure 2.7 A) shows the results of these experiments [29]. No change in film thickness was measured under these conditions demonstrating that acid is not generated in the film. We therefore conclude that these AAs are not photoactive to EUV radiation. However, when PAG is added to the formulations the resist film is photoactive, with a clearing dose of 6.4 mJ·cm⁻² (Figure 2.7 B). The addition of 70 mM 3HB to the control resist improved the sensitivity to give an Eo of 1.6 mJ·cm⁻². This data shows that these AAs do not generate acid photolytically, at least not enough to change the resist solubility in developer. However, in combination with PAG they improve the sensitivity which we infer is the result of increased acid concentration in the resist film.
2.5 First Lithography Experiment Using AAs

The first AAs that we evaluated in a photoresist were compounds 1EA and 1EB (Figure 2.8). 1EA is a published AA [30,32,33] but it generates a weak acid and we desire AAs that generate strong fluorinated acids. We synthesized the fluorinated analogue 1EB and evaluated the sensitivity effects of both compounds when added to EUV resists. To our knowledge this is the first time that AAs were added to an EUV photoresist. The results of this experiment provided us with valuable information about how to formulate resist with AAs and allowed us to compare the effects between fluorinated and nonfluorinated AAs.

Two acid amplifiers were evaluated as a function of AA and base loadings. Equal molar concentrations of the AAs were added to resist formulations composed of: PAG (7.5 wt%, DTBP-I-PFBS) and ESCAP polymer. In this experiment the amount of TBAH
base quencher was varied from 0.2 to 0.8 wt%. Formulations were prepared at 5 wt% solids (vs. solvent), spin coated, and soft-baked (130 °C, 60 s) to a film thickness of 125 nm. Exposures were performed using an open field or using dense line/space patterns (annular illumination on the Berkeley EUV MET), followed by post-exposure bake (PEB, 130 °C, 90 s), and development (45 s) in 0.26 N TMAH.

Figure 2.8 shows Eo plotted against the molar ratio of TBAH:PAG. Eo improves (lower dose) at lower base loading as expected. Addition of 1EA or 1EB also improves the sensitivity compared to the control resist (no AA). At a base loading of 0.35 wt% the Eo of the control resist (2.0 mJ·cm⁻²) was improved 2X and 8X by the addition of 1EA and 1EB respectively. This comparison suggests AAs that generate fluorinated sulfonic acids give greater sensitivity improvement than nonfluorinated acids.

Another important observation that we made during this experiment is that resists containing AA clears outside of the exposed frame at a doses above Eo. Figure 2.9 illustrates this phenomenon that we refer to as “blooming.” This observation is also reported in the literature and is attributed to acid diffusion in the resist film and through the air [32]. We call the dose at which blooming begins the critical dose, Ec. The size of the blooming area increases as the dose increases above Ec. The lowest base loading resist had a blooming area that advanced over the entire wafer resulting in complete film loss. Blooming was more controlled for resists at higher base loadings. We also observed that the ratio of Ec/Eo was significantly bigger for resists with 1EB than resists with 1EA. Based on this ratio we conclude that the fluorinated acid does not diffuse as far as the nonfluorinated acid. In future experiments we control blooming by adding less AA to resist formulations.
Figure 2.8 AAs 1EA and 1EB can improve the sensitivity by $2 \times$ and $8 \times$ relative to the control resist.

<table>
<thead>
<tr>
<th>Acid Amplifier</th>
<th>Base wt %</th>
<th>$E_0$ (mJ·cm$^{-2}$)</th>
<th>$E_c$ (mJ·cm$^{-2}$)</th>
<th>$E_c/E_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>No AA</td>
<td>0.2</td>
<td>1.25</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>0.35</td>
<td>2.0</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>2.75</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>1EA</td>
<td>0.35</td>
<td>0.9</td>
<td>1</td>
<td>1.1</td>
</tr>
<tr>
<td>(7.5 wt % = 245 mM)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1.9</td>
<td>2.1</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>3.5</td>
<td>4.1</td>
<td>1.2</td>
</tr>
<tr>
<td>1EB</td>
<td>0.35</td>
<td>0.25</td>
<td>1.7</td>
<td>6.8</td>
</tr>
<tr>
<td>(8.6 wt % = 245 mM)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1.0</td>
<td>$&gt; 3.5$</td>
<td>$&gt; 3.5$</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>2.7</td>
<td>$&gt; 5.2$</td>
<td>$&gt; 1.9$</td>
</tr>
</tbody>
</table>

Figure 2.9 Blooming is more problematic in resists with 1EA than with 1EB.

2.6 Trigger and Acid Precursor Study

Figure 2.10 shows the imaging properties of OSI resist and OSI with 70 mM added AA [29]. We chose to evaluate four AAs that have the same body type, but they have two different triggers and two different acid precursors. These results suggest that AAs that generate fluorinated acids (3HB and 3AB) yield resists with higher sensitivity, better LER, and better exposure latitude relative to AAs that produce non-fluorinated toluene sulfonic acid. The trigger also influences the resist imaging properties. AAs with
hydroxyl triggers improve the resist sensitivity 1.5 to 2.6X more than AAs with acetate triggers. \(3HB\) improves the resist sensitivity by 4X, from 7.6 mJ·cm\(^{-2}\) (no AA) to 1.9 mJ·cm\(^{-2}\). However, with extreme improvements in sensitivity, LER and EL, performance is decreased. Nonetheless, it is clear that AAs with fluorinated sulfonic acid precursors give the best combination of sensitivity, LER, and exposure latitude. \(Z\)-Parameter analysis shows that \(3AB\) simultaneously improves sensitivity and LER, relative to \(OS1\).

Figure 2.10 SEM images at 60 nm lines/spaces of \(OS1\) control resist + 70 mM concentrations of \(3AA\), \(3AB\), \(3HA\) and \(3HB\). PAB 100 °C / 60 s, PEB 110 °C / 60 s. EUV exposures were performed on the BMET.
2.7 Resist Image Quality vs. 11HB Loading

Resist lithographic performance was evaluated as a function of AA 11HB loading [29] in our OS2 control resist formulation. OS2 (no AA) contains PAG (DTBP-I-PFBS, 7.5 wt%), TBAH (1.0 wt%) and ESCAP polymer. Resist films were spin coated, and soft-baked (110 °C, 60 s) to a film thickness of 125 nm. EUV exposures were performed using 50 nm dense line/space patterns (annular illumination on the Berkeley EUV MET), followed by post-exposure bake (PEB, 110 °C, 90 s), and 45 s development in 0.26 N TMAH.

Figure 2.11 shows the sensitivity (Esize) and LER as a function of AA loading. The Esize of OS2 improves from 15 to 6 mJ·cm⁻² as the concentration of 11HB increases from 0-280 mM. This three-fold increase in sensitivity occurs with only a minimal degradation in LER. Figure 2.12 A) shows the exposure latitude (EL) versus Esize. The EL decreases by about 30 % with increasing concentration of 11HB. Even with small losses in LER and EL, the Z-Parameter improves from 2.7 × 10⁻⁷ mJ·nm³ (OS2) 1.8 × 10⁻⁷ mJ·nm³ (OS2 + 280 mM 11BH). Further gains in Z-Parameter might be achieved with higher AA loadings and losses in EL could be prevented by developing AAs that generate acid with low diffusion lengths.
Figure 2.12  (A) Exposure latitude at 50 nm dense lines vs. Esiz.  (B) 11HB loading improves (lowers) Z-Parameter.

2.8 Z-Parameter as a Function of Temperature

Resist process conditions, particularly the PEB temperature can have large affects on resist sensitivity and LER.  For example, increasing the PEB temperature improves the sensitivity by increasing the acid catalytic activity and diffusion length.  However, this does not break the RLS trade off because LER and resolution are degraded when acids diffuse farther.  Therefore, the RLS trade off cannot be broken by changing process conditions so Z-Parameter should be constant independent of PEB temperature.

On the other hand, the effects of PEB temperature are not well studied for resists with AAs.  We investigated the effects of PEB temperature on resist performance because AA acid generation is a function of PEB temperature.  We expect AAs to generate more acid at higher PEB temperatures.  We evaluated OS1 resist and OS1 with 70 mM of 3HB or 6AB at three PEB temperatures, 90 °C, 110 °C and 130 °C [30].  Figure 2.13 shows that the Z-Parameter of OS1 does not change with PEB temperature but the Z-Parameter improves for resist with 3HB or 6AB.  The largest improvement in Z-Parameter occurs at
low PEB temperatures. At 90 °C PEB the Z-Parameter of OS1 improves from $7.4 \times 10^{-7}$ mJ·nm$^3$ to $5.4 \times 10^{-7}$ mJ·nm$^3$ and $2.5 \times 10^{-7}$ mJ·nm$^3$ for 3HB and 6AB respectively.

Figure 2.14 shows the image quality of OS1 with and without 6AB. The soft bake and PEB were 90 °C/60 s and 90 °C/90 s respectively for both resists. The resolution of OS1 is 38 nm lines/spaces but with 6AB, 32 nm lines/spaces are resolved. 6AB also improves the Esize of OS1 at 38 nm by 30 %, from 21.7 to 16.6 mJ/cm$^2$ and improves LER by 75 %, from 8.6 to 4.9 nm. The simultaneous improvements in sensitivity, LER and resolution are reflected by the Z-Parameter improvement.

![AA Improves Z-Parameter at 90°C PEB](image)

**Figure 2.13** Z-Parameter for resist without and with 70 mM of 3HB or 6AB. $Z = Z$-Parameter $\times 10^7$ (mJ·nm$^3$).
2.9 1,3-Acyclic AAs: 12 Compound Array

To assess the impact of AAs on improving EUV patterning performance, Z-Parameter was calculated for the control resist, OS1 (no AA) along with resists containing 70 mM AA [34]. 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 PEB (90 °C, 90 s), and 45 s development in 0.26 N TMAH.

Z-Parameter was compared 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. Figure 2.15 shows lithographic results for the control resist without AA and twelve resists with 70 mM AA. The sizing dose, LER and Z-Parameter
are reported for each resist. All resists prepared with 70 mM concentration of AAs showed sensitivity improvements (except \textit{11HF}). The best overall resists contained AAs \textbf{3MB, 3MF, 3HF} or \textbf{11MB}. 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 mJ·nm$^3$). Addition of \textit{3HB, 11HB} or \textit{11HG} improves the Z-Parameter from 13 mJ·nm$^3$ (control) to 7 mJ·nm$^3$ but AAs \textit{11MF} and \textit{11HF} do not improve Z-Parameter. Figure 2.16 shows representative scanning electron micrographs of 50 nm lines and spaces for the control resist (no AA) and resists with 70 mM of added tertiary AAs (\textit{3HB} or \textit{3MB}) and secondary AAs (\textit{11HB, 11MB}). Both secondary and tertiary AAs are capable of yielding lithographic improvements in 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. High concentrations of acid would improve sensitivity, and allow the domain of each acid to be smaller (see Chapter 5 for more explanation), resulting in better LER.

Three of the four resists prepared with perfluorobenzenesulfonate ester AAs (\textit{3HG, 3MG} or \textit{11MG}) gave poor lithographic performance \textit{vs.} the control, so they were evaluated at 60 or 80 nm L/S. Thermal stability analysis showed that these AAs decompose between 70 and 110 °C so their poor lithographic performance may be associated with their poor thermal stability. Interestingly, the only AA with a perfluorobenzenesulfonate ester that gave good lithographic performance is \textit{11HG} which has a secondary hydroxyl trigger. This AA resulted in the greatest improvement in resist sensitivity with only a modest degradation in LER.
Control, No AA

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{size}}$ (mJ/cm²)</th>
<th>LER (nm)</th>
<th>$Z \times 10^7$ (mJ·nm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11HB</td>
<td>18.4</td>
<td>5.6 ± 0.3</td>
<td>7</td>
</tr>
<tr>
<td>11MB</td>
<td>19.2</td>
<td>5.0 ± 0.1</td>
<td>6</td>
</tr>
<tr>
<td>3HB</td>
<td>16.7</td>
<td>5.9 ± 0.3</td>
<td>7</td>
</tr>
<tr>
<td>3MB</td>
<td>15.4</td>
<td>4.6 ± 0.2</td>
<td>4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{size}}$ (mJ/cm²)</th>
<th>LER (nm)</th>
<th>$Z \times 10^7$ (mJ·nm³)</th>
</tr>
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<tbody>
<tr>
<td>11HF</td>
<td>23.1</td>
<td>10.4 ± 0.3</td>
<td>31</td>
</tr>
<tr>
<td>11MF</td>
<td>19.3</td>
<td>7.3 ± 0.2</td>
<td>13</td>
</tr>
<tr>
<td>3HF</td>
<td>16.1</td>
<td>4.8 ± 0.2</td>
<td>5</td>
</tr>
<tr>
<td>3MF</td>
<td>18.6</td>
<td>4.6 ± 0.2</td>
<td>5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{size}}$ (mJ/cm²)</th>
<th>LER (nm)</th>
<th>$Z \times 10^7$ (mJ·nm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11HG</td>
<td>9.3</td>
<td>7.5 ± 0.3</td>
<td>7</td>
</tr>
<tr>
<td>11MG</td>
<td>9.8</td>
<td>7.0 ± 0.2</td>
<td>13</td>
</tr>
<tr>
<td>3HG</td>
<td>6.9</td>
<td>7.7 ± 0.4</td>
<td>5</td>
</tr>
<tr>
<td>3MG</td>
<td>7.0</td>
<td>7.0 ± 0.4</td>
<td>5</td>
</tr>
</tbody>
</table>

**Figure 2.15** We exposed one control resist without AA and twelve resist with 70 mM AA to EUV light. The sensitivity ($E_{\text{size}}$), LER and Z-Parameter of these resists are reported for 50 nm equal lines and spaces (L/S) or at best resolution.

**Figure 2.16** Scanning electron micrographs showing 50 nm dense lines of the control resist (no AA) and resists with 70 mM of added 11HB, 11MB, 3HB or 3MB.
Figure 2.17 compares AA decomposition kinetics (experimental details are described in chapter 3) with resist lithographic performance. In general, we found that the AAs that are the most stable toward uncatalyzed thermal decomposition yet decompose autocatalytically, give the best lithographic improvements. We think that AAs improve the sensitivity of EUV resists by generating additional acid during the PEB. The relative diffusion rates of the acids generated by PAGs and AAs are 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 improvement; however, more diffusion can also degrade resolution and LER. Therefore, the interpretation of imaging results is complicated by a trade-off between higher sensitivity arising from more total acid being generated in the exposed regions vs. the detrimental effects of increased overall acid diffusion.

Seven of the AAs were capable of showing improved lithographic performance (lower Z-Parameter) vs. the control resist. The Z-Parameter improved 3-fold with the addition of 3MB, the best improvement for the twelve AAs presented here. We speculate that 3MB gives the best lithographic improvements because of the combination of the three attributes; it decomposes autocatalytically, generates the slowest diffusing acid and releases methanol as a byproduct.
Table 2.17 Lithographic properties at 50 nm resolution (unless noted) and rate ratios at 100 °C are compared for hydroxyl and methoxy trigger AAs.  

<table>
<thead>
<tr>
<th>Name</th>
<th>$k_{\text{tol}}$ / $k_{\text{base}}$</th>
<th>$E_{\text{size}}$ (mJ/cm²)</th>
<th>LER (nm)</th>
<th>$cZ \times 10^7$ (mJ·nm³)</th>
<th>Name</th>
<th>$k_{\text{tol}}$ / $k_{\text{base}}$</th>
<th>$E_{\text{size}}$ (mJ/cm²)</th>
<th>LER (nm)</th>
<th>$cZ \times 10^7$ (mJ·nm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me $\cdot$-CF₃C₆H₄</td>
<td>3HB</td>
<td>1210</td>
<td>16.7</td>
<td>5.9 ± 0.3</td>
<td>7</td>
<td>Me $\cdot$-CF₃C₆H₄</td>
<td>3MB</td>
<td>230</td>
<td>15.4</td>
</tr>
<tr>
<td>Me $\cdot$-CF₃C₆H₄</td>
<td>3HF</td>
<td>1390</td>
<td>16.1</td>
<td>4.8 ± 0.2</td>
<td>5</td>
<td>Me $\cdot$-CF₃C₆H₄</td>
<td>3MF</td>
<td>270</td>
<td>18.6</td>
</tr>
<tr>
<td>Me</td>
<td>C₂F₅</td>
<td>3HG</td>
<td>300</td>
<td>6.9</td>
<td>7.7 ± 0.4</td>
<td>9</td>
<td>Me</td>
<td>3MG</td>
<td>80</td>
</tr>
<tr>
<td>H $\cdot$-CF₃C₆H₄</td>
<td>11HB</td>
<td>1</td>
<td>18.4</td>
<td>5.6 ± 0.3</td>
<td>7</td>
<td>H $\cdot$-CF₃C₆H₄</td>
<td>11MB</td>
<td>1</td>
<td>19.2</td>
</tr>
<tr>
<td>H $\cdot$-CF₃C₆H₄</td>
<td>11HF</td>
<td>1</td>
<td>23.1</td>
<td>10.4 ± 0.3</td>
<td>31</td>
<td>H $\cdot$-CF₃C₆H₄</td>
<td>11MF</td>
<td>1</td>
<td>19.3</td>
</tr>
<tr>
<td>H C₂F₅</td>
<td>11HG</td>
<td>1</td>
<td>9.3</td>
<td>7.5 ± 0.3</td>
<td>7</td>
<td>H C₂F₅</td>
<td>11MG</td>
<td>1</td>
<td>9.8</td>
</tr>
</tbody>
</table>

Figure 2.17 Lithographic data are reported for 60 nm lines and spaces.  $^a$ Lithographic data are reported for 80 nm lines and spaces.  $^c$ Z = Z-Parameter.

2.10 Exposure Latitude as a Function of PAG and AA Acid Combination

Acid diffusion is an important factor in resist performance.  In the previous section we showed that some AAs can help beat the RLS trade off but other AAs only improve the sensitivity, they make the resolution and LER worse.  One hypothesis is that some AAs degrade the resolution and LER because the acids they generate have high diffusion in the resist film.  To test this, a set of resists were prepared to study the sensitivity and exposure latitude effects as a function of PAG and AA acid combinations.

Four acid amplifiers that generate a nonfluorinated or fluorinated sulfonic acid ($p$-CH₃C₆H₅SO₃H or $o$-CF₃C₆H₅SO₃H) were evaluated by adding equal molar concentrations (70 mM) of AA to control resist formulations composed of: TBAH (1.0 wt%) and ESCAP polymer.  Three different iodonium PAGs were used so that the PAG acids would have different diffusion lengths in the resist films.  The control resists had DTBP-I-PFBS, (7.5 wt%, 123 mM), di(4-tert-butylphenyl) iodonium o-(trifluoromethyl)-
benzene-sulfonate (DTBP-I-OTFMB, 6.6 wt%, 123 mM) or di(4-tert-butylphenyl) iodonium \( p \)-methylbenzene-sulfonate (DTBP-I-PMBS, 6.1 wt% 123 mM). Formulations were prepared at 5 wt% solids (vs. solvent), spin coated to a film thickness of 125 nm and soft-baked (110 °C / 60 s). Exposures were performed using annular illumination on Berkeley EUV MET, followed by post-exposure bake (110 °C / 90 s) and 45 s development in 0.26 N TMAH.

Figure 2.18 shows the design of the experiment. Our aim is to compare the resolution, LER and sensitivity of these resists as a function of PAG and AA acid combinations. The PAGs generate a photo acid (acid 1) and the AAs generate a second type of acid (acid 2) during the PEB. We predict that some AA acids diffuse more than, some diffuse less than and some diffuse the same as the acids produced by the PAG.

\[
\begin{array}{c|c|c}
\text{PAG Acid} & \text{Low} & \text{High} \\
\hline
\text{Low} & \text{No AA} & \text{Acid 1 = Acid 2} \\
\text{Medium} & \text{Acid 1 = Acid 2} & \\
\text{High} & \\
\end{array}
\]

**Figure 2.18** Exposure latitude was measured for various combinations of PAG and AA. The AA acids diffuses more than, less than or equal to the PAG acid.

Our first attempt at this experiment we tried to resolve dense lines and spaces so that we could measure the resolution, LER and sensitivity. We processed the resist with a
110 °C PAB (60 s) and 110 °C PEB (90 s). All of the resist prepared with either the DTBP-I-PFBS or DTBP-I-OTFMBS PAGs resolved down to 50 nm L/S. These PAGs both generate a strong fluorinate sulfonic acid. Addition of AAs to the control resists improved the sensitivity, even AAs that generate the weak nonfluorinated toluenesulfonic acid. Unfortunately, resists prepared with the DTBP-I-PMBS PAG could not resolve the patterns. This PAG generates the weak nonfluorinated toluenesulfonic acid. Figure 2.19 shows SEM images of resist films at 60 nm L/S. Comparisons between resist performance and acid diffusion could not be made with this data set because not all of the resists resolved the intended features.

**Representative SEMs for 60 nm 1:1 L/S**

<table>
<thead>
<tr>
<th>PAG Acid</th>
<th>SEM Images</th>
</tr>
</thead>
<tbody>
<tr>
<td>No AA</td>
<td><img src="image1.jpg" alt="SEM Images" /></td>
</tr>
</tbody>
</table>

**Figure 2.19** SEM images show that DTBP-I-PMBS PAG could not resolve 60 nm L/S.
To study the effects of PAG and AA acid combinations using these resists we exposed them a second time but with the aim of printing contact holes (2:1 pitch). To give the acids more catalytic activity we increased the PAB and PEB temperatures to 110 °C. One benefit of evaluating contact holes is that we can measure exposure latitude data over a wider dose range than by measuring dense lines.

Figure 2.20 shows the printed diameter as function of relative dose for three control resists; each generates a different photo acid. The dose is normalized to Esize for 60 nm diameter contact holes so that the slopes of the lines correlate to exposure latitude. A steep slope indicates poor exposure latitude which is attributed to high acid diffusion [34]. The two resists with PAGs that generate either nonaflate acid (NF) or o-(trifluoromethyl)benzenesulfonic acid (o-CF₃Ts) have essentially the same exposure latitude and their Esize is 24 mJ·cm⁻² and 17 mJ·cm⁻² respectively. The third resist contains PAG that makes toluenesulfonic acid (Ts). This resist has a worse exposure latitude and sensitivity (Esizel 46 mJ·cm⁻²) than the two resists with fluorinated sulfonic acid PAGs. We speculate the reason toluenesulfonic acid results in worse sensitivity and exposure latitude than the fluorinated acids is because toluenesulfonic acid is weaker and has higher diffusion.
Figure 2.20  This plot show the resist with toluenesulfonic acid has a poorer exposure latitude and sensitivity than resists with nonaflate and o-CF$_3$Ts acids.

Figure 2.21 shows the exposure latitude and sensitivity of the control resists are affected by AAs 3HF and 3HA. Resists in plot-A have PAGs that generate nonaflate acid, in plot-B PAGs generate o-(trifluoromethyl)benzenesulfonic acid and in plot-C PAGs generate toluenesulfonic acid.

Figure 2.21 A shows the impact on sensitivity and exposure latitude when AAs generate weaker acids than the PAG acid. 3HF and 3HA both improve the sensitivity (Esize) of the control resist (no AA) from 24 mJ·cm$^{-2}$ to 14 mJ·cm$^{-2}$ and 19 mJ·cm$^{-2}$, respectively. Although both AAs improve the sensitivity, the steeper slopes of the plot show that the exposure latitude is negatively affected. This data suggests that the AAs produce acid in the resists film but the acids diffuse more than the PAG acid.
Figure 2.21 Plots of printed diameter vs. relative dose show that AAs which generate toluenesulfonic acid degrade the exposure latitude.

Figure 2.21 B compares a control resist (no AA) to resists with AAs that generate the same acid (3HF) as the PAG or a weaker acid (3HA) than the PAG. 3HF improves the resist sensitivity from 17 mJ·cm⁻² (no AA) to 8 mJ·cm⁻² without adversely effecting the
exposure latitude. On the other hand, $3HA$ makes the sensitivity ($28 \text{ mJ} \cdot \text{cm}^{-2}$) and exposure latitude worse than the control resist. These results show that AAs that make the same acid as the PAG can improve the sensitivity without degrading the exposure latitude but AAs that make a weaker acid than the PAG can make the sensitivity and exposure latitude worse.

Figure 2.21 C compares a control resist (no AA) to resists with AAs that generate a stronger acid ($3HF$) than the PAG or the same acid ($3HA$) as the PAG. $3HF$ improves the resist sensitivity from $42 \text{ mJ} \cdot \text{cm}^{-2}$ (no AA) to $22 \text{ mJ} \cdot \text{cm}^{-2}$ with a slight improvement in exposure latitude. However, $3HA$ has essentially no impact on the sensitivity and degrades the exposure latitude, despite the fact that $3HA$ makes the same acid as the PAG. These results show that AAs can improve the sensitivity and exposure latitude when they generate an acid that is stronger and diffuses less than the PAG acid. On the other hand, AAs that make a weak acid with high diffusion only make the resist performance worse.

Figure 2.22 compares the exposure latitudes of the control resist and resist with AAs that have a methoxy trigger or a hydroxyl trigger. Methoxy trigger AAs have the same effects on exposure latitude and sensitivity as their hydroxyl trigger counterparts. This is expected because they generate the same types of acid and the exposure latitude is mostly impacted by the acid diffusion.


**Figure 2.22** The best EL and Esize are achieved when the PAG and AA both generate o-CF$_3$C$_6$H$_5$SO$_3$H acid. Values in the table are percent exposure latitude (%EL).

### 2.11 Polymer-Bound Acid Amplifier

One method to control acid diffusion is to covalently attach the acid to the polymer [35,36,37]. To test this theory we synthesized and lithographically evaluated a polymer-bound acid amplifier where the generated acid is linked to the polymer side chain. The first step was to synthesize a co-polymer of 4-hydroxystyrene/t-butyl acrylate (PHS/TBA) (65/35) and a linkable AA. Using readily available starting materials, we chose to make an AA similar to 3HA but with a benzylbromide on the acid precursor. The second step was to react the benzyl bromide with a phenol on the polymer. One benefit to evaluating AAs that make toluenesulfonic acid is that this acid has a high diffusion so attaching it to a polymer should result in a significant reduction in diffusion. If we used an AA that generates a low diffusing acid then gains in lowering the diffusion by attaching it to a polymer might not be significant and harder to measure.

Three resists were lithographically evaluated: a control (no AA), the control resist with 70 mM 3HA and a polymer-bound AA (240 mM AA) resist. The AA attached to the
polymer has the same trigger and body type as 3HA. We intentionally added 3X as much polymer-bound AA as the blended AA resist to help compensate for sensitivity losses due to lower acid diffusion. The resist formulations composed of: DTBP-I-PFBS, (7.5 wt%) TBAH (1.0 wt%) and polymer, 4-hydroxystyrene/t-butyl acrylate (65/35) or polymer-bound AA. Formulations were prepared at 3 wt% solids (vs. solvent), spin coated to a film thickness of 60 nm and soft-baked at 130 °C / 60s. Exposures were performed using annular illumination on the Berkeley EUV MET, followed by post-exposure bake 130 °C / 90s and 45 s development in 0.16 N TMAH.

Figure 2.23 shows the line width as a function of dose for 80 nm L/S. The control resist (no AA) has a sizing dose of 12.6 mJ·cm⁻². 3HA improves the sensitivity of the control resist to 7.3 mJ·cm⁻² and the polymer-bound AA improves the sensitivity to 8.9 mJ·cm⁻². Although unbound 3HA improves the sensitivity, the exposure latitude is severely degraded from 35 % to 8 % (Figure 2.24). On the other hand, the polymer bound AA improves the sensitivity and has no adverse affects on the exposure latitude. Figure 2.25 shows SEM images (near Esize) of 80 nm L/S for the three resists. We compare the imaging at 80 nm because the polymer-bound AA resist did not resolve smaller features. The control resist (no AA) gives the best imaging performance because the AAs generate weak nonfluorinated acids which we know degrade the imaging quality. Despite poor imaging, the exposure latitudes show that attaching the acid to the polymer does limit acid diffusion.
Figure 2.23  Line width (at 80 nm CD) vs. dose for three resist: ♦ without AA, ● with 70 mM 3HA and ■ with 240 mM polymer-bound AA.

<table>
<thead>
<tr>
<th>Relative Acid Diffusion</th>
<th>Polymer (PHS/TBA)</th>
<th>[AA] (mM)</th>
<th>Es (mJ / cm²)</th>
<th>EL (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No AA</td>
<td>Low</td>
<td>65/35</td>
<td>0</td>
<td>12.6</td>
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<td></td>
<td>High</td>
<td>65/35</td>
<td>70</td>
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<tr>
<td></td>
<td>Low</td>
<td>62/3/35</td>
<td>~240</td>
<td>8.9</td>
</tr>
</tbody>
</table>

Figure 2.24  Exposure latitude and Esize at 80 nm CD for three resist: without AA, with 70 mM blended 3HA and with 240 mM polymer-bound AA. The polymer-bound AA polymer has monomer molar ratios of PHS/AA/TBA, 62/3/35.
Figure 2.25 SEM micrographs at 80 nm CD for three resist: without AA, with 70 mM 3HA and with 240 mM polymer-bound AA.

2.12 Summary

In this chapter, we evaluated the lithographic performance of EUV resists by measuring their resolution, line-edge-roughness, and sensitivity. The interdependence between these three properties is referred to as the RLS trade-off. The lithographic results of resists with added acid amplifiers showed simultaneous improvements in resolution, LER, and sensitivity. These results show that AAs provide a route to beating the RLS trade-off. The benefits of using AAs can furthered be improved by developing new AAs that have high thermal stability, decompose quickly in the presence of catalytic acid and generate strong fluorinated sulfonic acids that have short diffusion lengths.
References


CHAPTER 3

REACTION KINETICS OF ACID AMPLIFIERS

3.1 Objectives

This chapter describes the development of an NMR-based technique for measuring the uncatalyzed and autocatalytic decomposition kinetics of acid amplifiers. Some NMR-based kinetics experiments have been reported in the literature, but they have several disadvantages compared to our method. AA decomposition experiments reported in the literature [1-10] showed that AAs decomposed faster in the presence of acid than in the absence of acid. Reaction rates are not reported, so it is difficult to compare the reactivity of different AAs. Also, the experiments are conducted at various temperatures and in different solvents which also makes it difficult to compare the reactivity of AAs.

Our hypothesis is that successful AAs must be thermally stable, but decompose quickly in the presence of catalytic acid. AAs that have the same decomposition rate regardless of the presence of catalytic acid will not be suitable for photoresist applications. We test our hypothesis by independently measuring the uncatalyzed and autocatalytic decomposition rates. From the decomposition rates we also extract thermodynamic parameters for the rate limiting transition states. We expect a fast decomposition reaction will have a low activation energy barrier for the rate limiting transition state.

Figure 3.1 illustrates the two different reactions pathways that we measured. The y-axis of the curve represents energy and the x-axis represents reaction coordinate. We expect uncatalyzed (U) reactions will have higher activation energies than the acid
catalyzed reactions. The acid catalyzed reaction is separated into two steps, the trigger pull (T) and the acid formation (A). We arbitrarily show the trigger pull as having a higher energy barrier than the acid formation. We do not know if this is accurate for all AAs but we expect both of these steps to have a lower energy barrier than the uncatalyzed reaction.

**Figure 3.1** Reaction coordinate diagram illustrates two decomposition pathways, Uncatalyzed (U) and a two step acid catalyzed pathway, trigger pull (T) and acid formation (A).
3.2 Experimental Setup

Acid amplifier decomposition kinetics were measured using $^{19}$F NMR. Acid amplifier solutions were prepared in vacuum sealed NMR-tubes so that solvent or volatile byproducts are not lost during heating. Figure 3.2 shows the heating apparatus. The reactions were carried out at multiple temperatures by submerging the tubes into a custom made oil bath that was designed so that the full length of the tubes is uniformly heated. The oil bath was heated to a constant temperature by refluxing non-flammable solvents with known boiling temperatures and allowing the vapors to condense on the oil bath. The oil temperature was monitored with a thermometer.

Figure 3.2 Picture (left) and schematic (right) of our custom made oil bath for heating NMR tubes.
3.3 Solvent System Optimization

The first few decomposition experiments were designed to find suitable reaction conditions. Initially, we needed to identify a good reaction solvent and to determine a method for independently measuring the rates of uncatalyzed and acid catalyzed decomposition pathways.

In the literature, these experiments are usually done in non-polar solvents or mixtures of solvents such as toluene [1,2,3,5] chloroform [4,6,7,8,10] or 1,4-dioxane [9]. One of our objectives was to find a solvent system that would keep our starting materials and decomposition products in solution over the course of the reaction. We were particularly concerned that the polar sulfonic acids might fall out of solution if we used non-polar solvents. The starting AAs are soluble in non-polar organic solvents but the generated acids are more soluble in polar solvents. Phase separation during the decomposition reactions can cause two problems: 1) it can help drive the reactions forward and 2) it can result in inaccurate concentration measurements. Several solvents were tested for AA and decomposition product solubility. Acid amplifier 3HB (70 mM) was decomposed in solutions of d₆-benzene, 50/50 wt% d₆-benzene/d₄-methanol, 50/50 wt% d₆-benzene/d₃-acetonitrile and 50/50 wt% d₆-benzene/m-ethylphenol. The only solution that dissolved 3HB and all of the decomposition products was 50/50 wt% mixture of d₆-benzene/m-ethylphenol. The limitation of using d₆-benzene/m-ethylphenol is that m-ethylphenol is not deuterated so that ¹H NMR is not practical. However, a benefit to this solvent mixture is that it mimics the photoresist polymer because the polymer mostly contains styrene and phenol. As a result of this study, a 50/50 wt% mixture of d₆-benzene/m-ethylphenol was chosen and concentrations of AA and acid were measured using ¹⁹F NMR. This limited the analysis to AAs that have a fluorinated acid precursor.
Uncatalyzed decomposition reactions were monitored by adding molar excesses of base to neutralize the acid as it was generated so that the acid could not catalyze the AA decomposition. A concern about adding base is that it could react with the AA. To address this concern, we measured the decomposition rates of $3HB$ (70 mM) at 120 °C in the presence of three different sterically hindered bases, 2,4,6-tri-methylpyridine, 2,6-tri-$t$-butyl-4-methyl-pyridine and 2,4,6-tri-$t$-butylpyridine. Figure 2.3 shows $^{19}$F NMR spectra for the decomposition of $3HB$ at 120 °C in the presence of 2,4,6-tri-$t$-butylpyridine. The concentrations of AA and acid were measured by integrating the NMR signals. Initially, at time 0 the only signal peak was from the AA but as heating time progressed a second peak appeared which corresponds to the acid. After 225 minutes the AA was almost completely decomposed. Figure 2.4 shows the natural-log of AA concentration vs. time. The reactions follow first-order reaction kinetics and the rate constants are calculated from the slopes. The rate constants were found to be unaffected by the different bases. We chose to use the most sterically hindered base, 2,4,6-tri-$t$-butylpyridine, to measure uncatalyzed AA decomposition kinetics.
Figure 2.3 $^{19}$F NMR spectra showing the decomposition of $3HB$ as a function of heating time. Concentrations are proportional to the integrated signal peak.

Figure 2.4 Decomposition rate of $3HB$ in the presence of three different bases.
3.4 Experimental Conditions for Decomposition Kinetics

The thermal decomposition kinetics of the AAs in solution (in sealed NMR tubes) were measured using $^{19}$F NMR. Solutions of AAs (70 mM) in 50/50 wt% C$_6$D$_6$/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 were monitored [11,12]. The sterically-hindered base was added to consume acid as it formed, so that the uncatalyzed reactions could be studied independently. We chose to compare rate constants at 100 °C because they can be measured accurately at this temperature for all AA that were investigated in the presence and absence of added base. Additional rate constants were measured at temperatures chosen based on the boiling points of readily available, non-flammable solvents that are used to heat an oil bath at a constant temperature.

3.5 Analysis of First Set of Compounds

Figure 3.5 shows the chemical structures of the first five compounds that we studied [11-13]. We chose these compounds because they encompass a variety of structural features. We can compare the AAs decomposition rates versus the type of trigger, acid precursor and body. Compounds 3HB and 3HF compare acid precursor type ($p$-CF$_3$C$_6$H$_5$SO$_3$- vs. $o$-CF$_3$C$_6$H$_5$SO$_3$-), 3HB and 8HB compare acid precursor substitution (primary vs. secondary) and 6HB and 6AB compare trigger type (HO- vs. AcO-).

Figure 3.5 Chemical structures of the first 5 compounds whose decomposition kinetics were measured.
Figure 3.6 shows the rate equations that are used to calculate the decomposition reaction rate constants. All reactions evaluated in the presence of base showed first-order kinetics. In the absence of base, the kinetic data was consistent with an autocatalytic reaction mechanism (except $6HB$). First-order rate constants ($k_{Base}$) were determined using the first-order rate equation and second-order autocatalytic rate constants ($k_{No\ Base}$) were determined by fitting the data to the autocatalytic rate equation [14]. Table 3.1 tabulates the rate constants and $k_{No\ Base}/k_{Base}$ ratios at 100 °C.

\[
\text{First Order Reaction} \quad \rightarrow \\
\text{(Uncatalyzed)} \quad \quad \quad \quad A + B \\
\text{Rate Law} \quad \nu = k[A] \\
\ln[A]_t = \ln[A]_0 - kt \\
\]

\[
\text{Second Order Autocatalytic Reaction} \quad \rightarrow \\
\text{(Catalyzed)} \quad \quad \quad \quad A + B ightarrow 2B \\
\text{Rate Law} \quad \nu = k[A][B] \\

P_0 + x = \frac{A_0 + P_0}{1 + \frac{A_0}{P_0} \exp[-(A_0 + P_0)kt]} \\
\]

\[
\text{Figure 3.6} \quad \text{First order and second order autocatalytic rate equations are used to determine the rate constants, } k_{Base} \text{ and } k_{No\ Base}, \text{ respectively.}
\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k_{Base} \times 10^5$ (s$^{-1}$)</th>
<th>$k_{NoBase} \times 10^5$ (M$^{-1}$·s$^{-1}$)</th>
<th>$k_{NoBase}/k_{Base}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3HB$</td>
<td>$3.3 \pm 0.1$</td>
<td>$4,800 \pm 230$</td>
<td>1455</td>
</tr>
<tr>
<td>$3HF$</td>
<td>$5.3 \pm 0.1$</td>
<td>$7,300 \pm 350$</td>
<td>1377</td>
</tr>
<tr>
<td>$8HB$</td>
<td>$430 \pm 20$</td>
<td>$10,500 \pm 500$</td>
<td>24</td>
</tr>
<tr>
<td>$6HB$</td>
<td>$110 \pm 3$</td>
<td>$98 \pm 5$</td>
<td>0.9</td>
</tr>
<tr>
<td>$6AB$</td>
<td>$0.50 \pm 0.01$</td>
<td>$245 \pm 10$</td>
<td>490</td>
</tr>
</tbody>
</table>

\[
\text{Table 3.1 Decomposition rate constants at 100 °C with and without added base.}
\]
The 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 3HB, 3HF and 6AB are useful AAs for lithographic applications because they have slow decomposition rates in the presence of base, yet decompose quickly in the absence of base. The rate $k_{\text{No Base}}/k_{\text{Base}}$ ratios of these compound are 1455, 1377, and 490 respectively. In contrast, 8HB and 6HB would not be useful in a photoresist because they decompose quickly in the presence of base and have small ratios between catalyzed and uncatalyzed decomposition rates.

Figure 3.7 shows the thermal decomposition kinetics for compounds 6HB and 6AB. Interestingly, these compounds only differ by the identity of the trigger group (HO- or AcO-) yet their decomposition kinetics differs significantly. 6AB is quite stable in the presence of base (♦) and the decomposition is catalyzed by acid (▲) whereas 6HB decomposes rapidly in solution independent of the presence of added base (● and ■). Molecular modeling (details are in Chapter 5) of the uncatalyzed thermolysis reaction for 6HB and 6AB provides one possible explanation for the unexpected reactivities. The model predicts that 6HB goes through a transition state where the hydroxyl trigger protonates the sulfonyle oxygen during C-O bond breaking. This self protonation could lower the decomposition energy compared to 6AB. 6AB has a higher thermal stability because it has an acetate trigger that is unable to protonate the sulfonic ester.
Figure 3.7  Decomposition kinetics of: 6HB in the presence ● and absence ■ of added base and 6AB in the presence ♦ and absence ▲ of added base.

3.6 Analysis of Second Set of Compounds

Figure 3.8 shows the chemical structures of 12 AAs that we evaluated in our second round of kinetic measurements [15,16]. The trigger, acid precursor and body of these AAs are systematically varied to give a range of reactivities. This array of compounds allows us to study AA reactivity as a function of trigger (HO- or MeO-), acid precursor (p-CF₃C₆H₅SO₃-, o-CF₃C₆H₅SO₃-, or C₆H₅SO₃-), and body types (secondary or tertiary trigger).
3.6.1 Thermal Decomposition of Acid Amplifiers with Added Base

All decomposition reactions of AAs in the presence of excess base showed first-order reaction kinetics. As expected, the decomposition rate increased as the number of fluorine atoms increased or when they were located closer to the sulfonate ester, since increasing the electronegativity of sulfonates increases their leaving ability (Table 3.2). In particular, the AAs \((11HG, 11MG, 3HG\) and \(3MG)\) with perfluorobenzenesulfonate (PFBS) esters decomposed 11-27 times faster than the AAs with \(para-\) or \(ortho-\) trifluoromethyl benzenesulfonate (TMBS) esters at 100 °C in the presence of base. Triggers also had a significant effect on the first-order rates of decomposition. Acid amplifiers with the same body and acid precursor decomposed faster with a methoxy trigger than AAs with a hydroxyl trigger (body-3: 3-4X faster; body-11: 1.1-1.3X faster).
Table 3.2  Decomposition rate constants and activation parameters for the thermal decomposition of acid amplifiers vary with chemical structure.  

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k_{\text{Base}} \times 10^5$ (s$^{-1}$)</th>
<th>$k_{\text{NoBase}} \times 10^5$ (M·s$^{-1}$)</th>
<th>$k_{\text{NoBase}} / k_{\text{Base}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3HB</td>
<td>3.6 ± 0.1</td>
<td>4,400 ± 800</td>
<td>1210</td>
</tr>
<tr>
<td>3HF</td>
<td>5.1 ± 0.1</td>
<td>7,100 ± 1300</td>
<td>1390</td>
</tr>
<tr>
<td>3HG</td>
<td>73 ± 2</td>
<td>22,000 ± 3000</td>
<td>300</td>
</tr>
<tr>
<td>3MB</td>
<td>16 ± 1</td>
<td>3,700 ± 200</td>
<td>230</td>
</tr>
<tr>
<td>3MF</td>
<td>21 ± 1</td>
<td>5,700 ± 300</td>
<td>270</td>
</tr>
<tr>
<td>3MG</td>
<td>240 ± 10</td>
<td>20,000 ± 2,000</td>
<td>80</td>
</tr>
<tr>
<td>11HB</td>
<td>1.2 ± 0.1</td>
<td>1.1 ± 0.1</td>
<td>1</td>
</tr>
<tr>
<td>11HF</td>
<td>1.7 ± 0.1</td>
<td>1.7 ± 0.1</td>
<td>1</td>
</tr>
<tr>
<td>11HG</td>
<td>33 ± 3</td>
<td>27 ± 3</td>
<td>1</td>
</tr>
<tr>
<td>11MB</td>
<td>1.6 ± 0.1</td>
<td>1.7 ± 0.1</td>
<td>1</td>
</tr>
<tr>
<td>11MF</td>
<td>2.4 ± 0.1</td>
<td>2.6 ± 0.1</td>
<td>1</td>
</tr>
<tr>
<td>11MG</td>
<td>37 ± 1</td>
<td>42 ± 2</td>
<td>1</td>
</tr>
</tbody>
</table>

Uncatalyzed first-order reaction rates ($k_{\text{Base}}$) were measured at 100 °C and two other temperatures (above or below 100 °C) such that AA decomposition is slow enough to measure using our experimental method. The data is analyzed using the Eyring equation. We chose to use Eyring analysis because it is based on transition state theory and is applicable to solution phase reactions as opposed to the Arrhenius analysis which is empirically derived and better suited for gas phase reactions. Eyring plots ($\ln(k/T)$ vs. $1/T$) of AA decomposition rate constants yielded the activation parameters $\Delta H^\ddagger$, $\Delta S^\ddagger$ and $\Delta G^\ddagger$ for each reaction [17,18]. Table 3.3 shows the activation parameters for each compound. Interestingly, the enthalpy of activation ($\Delta H^\ddagger$) values are constrained within a fairly narrow range of values (15.9 to 18.4 kcal/mol), while the entropy of activation
($\Delta S^\ddagger$) seems to give the largest range of values (-25.1 to -37.4 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 thermodynamic parameters is the differences between the $\Delta S^\ddagger$ values of AAs prepared with hydroxyl vs. methoxy triggers. A pair-wise comparison of the eight AAs prepared with either para- or ortho-trifluoromethylbenzene sulfonate (TFMBS 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.

<table>
<thead>
<tr>
<th>$R_1$</th>
<th>$R_3$</th>
<th>Name</th>
<th>$\Delta H^\ddagger$ (kcal/mol)</th>
<th>$\Delta S^\ddagger$ (cal/(mol·K))</th>
<th>$\Delta G^\ddagger$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>-CF$_3$C$_6$H$_4$</td>
<td>3HB</td>
<td>17.2 ± 0.4</td>
<td>-33.0 ± 1.0</td>
<td>29.5 ± 0.4</td>
</tr>
<tr>
<td>Me</td>
<td>o-CF$_3$C$_6$H$_4$</td>
<td>3HF</td>
<td>16.6 ± 0.1</td>
<td>-34.2 ± 0.3</td>
<td>29.3 ± 0.1</td>
</tr>
<tr>
<td>Me</td>
<td>C$_6$F$_5$</td>
<td>3HG</td>
<td>17.9 ± 0.9</td>
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</tr>
<tr>
<td>H</td>
<td>p-CF$_3$C$_6$H$_4$</td>
<td>11HB</td>
<td>16.4 ± 1.4</td>
<td>-37.4 ± 3.5</td>
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<td>o-CF$_3$C$_6$H$_4$</td>
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<tr>
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<tr>
<td></td>
<td></td>
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<tr>
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<td></td>
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<td>28.3 ± 0.8</td>
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<tr>
<td></td>
<td></td>
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<td>-31.9 ± 0.2</td>
<td>27.8 ± 0.1</td>
</tr>
</tbody>
</table>

Table 3.3 The activation parameters for 12 AAs were calculated using Erying plots.

### 3.6.2 Thermal Decomposition of Acid Amplifiers without Added Base

In order for resists containing AAs to distinguish between exposed and unexposed regions, the acid-catalyzed decomposition rates of the AAs must be significantly faster than the uncatalyzed decomposition rates. To study the interactions between acid amplifiers and the acid generated by them during their decomposition, we studied the
thermal decomposition kinetics of the twelve AAs without added base at 100 °C. The six acid amplifiers with tertiary triggers (body-3) decomposed autocatalytically. For example, in the presence of added base, $3\text{HB}$ decomposed according to first-order kinetics so that the plot of $\ln[3\text{HB}]$ vs. time is linear ($R^2 = 0.998$, Figure 3.9 A. Without base, the plot of $\ln[3\text{HB}]$ vs. time is initially first-order, but once a small amount of acid was generated, the reaction proceeded autocatalytically, giving the observed abrupt downward curvature. Conversely, the six acid amplifiers with secondary triggers (Body-11) gave first-order kinetics independent of the presence or absence of added base as illustrated by $11\text{HB}$ (Figure 3.9 B), indicating that the build-up of the sulfonic acid products had no effect on reaction rates.

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 ($k_{\text{NoBase}}/k_{\text{Base}}$). Table 3.2 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-11 AAs with secondary triggers have rate ratios of 1.0. This means that the decomposition rates of body-11 AAs are independent of the presence or absence of the buildup of sulfonic acid generated during their decomposition. However, in Chapter 2, we showed that body-11 AAs gave good lithographic imaging and improved resist sensitivities, indicating that they increased the acid concentrations in resist films. These observations led us to study the rate of decomposition of $11\text{HB}$ in the presence of added nonaflate acid. This acid, $\text{C}_4\text{F}_9\text{SO}_3\text{H}$, 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 twelve AAs studied here. We measured the decomposition rate of $11\text{HB}$ at 100 °C in
the presence of 0, 0.25, 0.5 and 0.75 equivalents of nonaflate acid. Figure 3.10 shows that the rate increases linearly with increasing nonaflate acid concentration. This means that \textit{11HB} does not decompose autocatalytically, but instead, its decomposition is catalyzed by nonaflate acid. Figure 3.11 compares the reaction energy profiles for body-3 and body-11 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-11 AAs (solid curve) but nonaflate acid does (dashed curve).

**Figure 3.9** A. The decomposition rate of $\bullet$ \textit{3HB} with base is first-order and $\circ$ \textit{3HB} without base is autocatalytic. B. The decomposition rates of $\bullet$ \textit{11HB} with base and $\circ$ \textit{11HB} without base are both first-order, regardless of the build up of acid generated by AA decomposition.
**Figure 3.10** The decomposition rate constant of 11HB at 100 °C increases linearly with respect to the concentration of added nonaflate acid, the same acid generated photochemically in resist formulations.

**Figure 3.11** Body-3 AAs have a lower activation energy barrier for acid catalyzed decomposition than uncatalyzed decomposition. Body-11 AAs have a lower activation energy barrier for uncatalyzed decomposition than acid catalyzed decomposition, except when the acid is sufficiently strong as in the case of nonaflate.
3.7 Summary

In this chapter $^{19}$F NMR spectroscopy was used to measure the decomposition rates of AAs in solution. This method successfully identified AAs that decompose autocatalytically and AAs that do not decompose autocatalytically. Although not all AAs decompose autocatalytically, we showed that nonaflate acid is strong enough to catalyze AA decomposition. This is a significant result because nonaflate acid is typically generated by PAGs in a photoresist. The AAs $k_{\text{NoBase}}$ rate constants are a good indicator of thermal stability and are strongly dependent on the chemical structures of AAs. The data showed that a tertiary trigger lowers AA stability versus a secondary trigger, and a methoxy trigger lowers AA stability versus a hydroxyl trigger. This information will be used to design new AAs with improved thermal stabilities.
References


CHAPTER 4

FUNDAMENTALS: ACID DETECTION, THERMAL STABILITY, PRODUCT IDENTIFICATION, AND RESIST OUTGASSING

4.1 Introduction
In Chapter 2 we showed that acid amplifiers can simultaneously improve the resolution, LER and sensitivity of imaged EUV resist films. Demonstrating that AAs are capable of improving resist imaging quality is only one step toward encouraging industry to use AAs in commercial applications. To improve the success of AAs as a commercially viable option to beat the RLS trade off we attempted to answer several fundamental questions that industry might have. The questions that we attempt to answer in this chapter are: (1) How much acid do AAs generate in resist films? (2) How does the resist polymer affect the thermal stability of AAs? (3) What are the by products of AA decomposition? (4) What effect do AAs have on resist outgassing?

4.2 Three Unsuccessful Attempts to Detect Acid in Resist Films
This section describes three unsuccessful attempts to measure AA acid generation in resist films. Although the reasons why these methods were unsuccessful are complex and not fully understood, the main reason is thought to be acid quenching by base contamination.

Lithographic results in Chapter 2 showed that AAs improved the sensitivity of a resists. The sensitivity improvement is attributed to increased acid generation during the PEB
step. To test this theory, we attempted to quantify the amount of acid that AAs generate in a resist films. In the literature, there are many examples that quantify PAG acid generation in resist films using spectrophotometric techniques [1]. In these published experiments, an acid sensitive dye was added to resist films, the films were exposed to 248 nm [2], 193 nm [3], electron beam [4,5] or EUV [6,11] radiation causing PAG photolysis, and the absorbance of the films are measured. The amount of generated acid was determined by comparing the film absorbance with a calibration curve that was made by adding known amounts of acid to the resist films.

We used a similar approach to quantify AA acid generation in resist films but with some modifications to the experimental procedure. Because the dyes are basic in nature they quench the autocatalytic AA reaction. Under these conditions the AAs generate less acid than they would under standard lithographic conditions. In order to circumvent this problem the dye was added to the resist after it was exposed and baked. This method allowed the AAs to undergo autocatalysis.

Figure 4.1 shows an overview of our experimental approach. First, resists are formulated and spin coated onto silicon wafer. Second, wafers are exposed to EUV light and baked. During exposure the PAGs are converted to photo-acids then during the PEB the acids catalyze the AA decomposition. Next, the resist films are extracted with a known amount of THF. A known amount of acid sensitive dye is added to an aliquot of the resist extract and the absorbance is recorded. The amount of acid is determined by comparing the measured absorbance to a calibration curve.
In the literature, the most commonly used dyes for this experiment are coumarin-6 (C6) [12] and tetrabromophenol blue (TBPB) [13,14]. All examples in the literature that used C6, added the dye to the resist film before exposure, which we cannot do. The literature procedures that used TBPB, added the dye to solutions of the resist after exposure, similar to our procedure. In our experiments we investigated both C6 and TBPB dyes. Tetrahydrofuran (THF) was chosen as the solvent because it is transparent and it dissolved both dyes and the resists.

**Figure 4.2** Protonated and nonprotonated structures of: (A) coumarin-6 and (B) tetrabromophenol blue acid sensitive dyes.
4.2.1 Experimental Conditions

To test the acid generation of acid amplifiers in resist films, we prepared five resists containing di(4-tert-butylphenyl) iodonium perfluoro-1-butane-sulfonate PAG (3 wt%, 49 mM) the ESCAP polymer and AA 3HB or 11HB, but without base. Our control resist contains no AA. We prepared resists with 35, 70 and 140 mM 3HB, and a resist with 70 mM 11HB. The resist films were coated to 200 nm thickness on 200 mm wafers. The films were exposed uniformly to 10 mJ/cm² of EUV radiation using the EUV-ROX tool at Albany followed by PEB at 110 °C for 60 s. The wafers were then processed according to the description outlined in Figure 4.1.

4.2.2 Acid Detection Using C6 Dye

The first step to measure acid in a resist film was to make a calibration curve. This was accomplished by preparing solutions with known concentrations of C6 dye and nonaflate acid (NF) acid. Figure 4.3A shows the absorbance measurements of these solutions. The absorbance peak at 518 nm increases as the concentration of NF acid increases. The calibration curve was made by plotting the absorbance at 518 nm versus the concentration of NF acid (Figure 4.3B). The lowest detectable amount of acid is $2.8 \times 10^{-8}$ moles at a concentration of $1.0 \times 10^{-5}$ M. If 20 % of the PAG in the resist films were converted to acid during exposure then the amount of photo-acid in the resist film would be $9.3 \times 10^{-8}$ moles, which is more than the lowest detectable limit. Based on this assumption the acid in resist with only PAG should detectable. We expect resist films with AAs to have 2-10 times as much acid as the PAG only resist. Therefore, resist with AAs should give a large increase in absorbance at 518 nm.
Figure 4.3 (A) UV-Vis absorbance spectra of C6 and nonaflate acid mixtures  (B) Acid Absorbance at 518 nm increases linearly with nonaflate acid concentrations.

The first resist tested contained 70 mM of 11HB. Assuming 30 % PAG conversion and 100 % AA conversion the total amount of acid in the resist film is $5.3 \times 10^{-7}$ moles. The resist was extracted, 2 equivalents of C6 dye were added to the extract and the solution was diluted with THF to a final volume of 27 mL. The estimated acid concentration is $1.7 \times 10^{-5}$ M which should give a measured absorbance around 0.3 at 518 nm. Unfortunately, the measured absorbance was 0, no acid was detected in the resist. Because we did not detect any acid in the resist, we assumed that we overestimated the amount of PAG and AA that gets converted. We try to correct for this by making the sample more concentrated.

The second resist that was tested contained 140 mM of 3HB. This resist is more likely to give an acid signal than the first resist because it has the highest AA loading and 3HB decomposes autocatalytically giving a higher turnover than 11HB. The resist was exposed and baked in the same way as the first resist. The film was extracted with THF into a beaker and dye was added to the extract. The THF was evaporated until only 4.5 mL remained. The absorbance of the solution was measured to be 0. Again, no acid was
detected in the resist. This leads us to conclude that something is quenching the dye because we know that at least the PAG generates acid but we are unable to measure it.

4.2.3 Acid Detection Using TBPB Dye

Tetrabromophenyl blue (TBPB) is a common acid sensitive dye that has also been used to measure the concentration of acid generated by various PAGs in resist films [13,14]. The experimental procedure reported in the literature is similar to our method.

We attempted to reproduce the published [13] calibration curve using our slightly modified experimental procedure to make sure we can obtain accurate results. We prepared solutions of TBPB with various concentrations of camphorsulfonic acid as described by the published procedure, but we omitted adding resist to the solutions. The absorbencies of our solutions were significantly lower than what was previously reported. We also noticed that the color of the solution in the absence of acid was green when it should be blue. Based on these observations we conclude that the dye is already in the acidified form. To correct this we convert the dye into the basic sodium salt by adding sodium hydroxide dissolved in water. Figure 4.4 demonstrates that the absorbance of a dye solution increases with increasing concentrations of sodium hydroxide. It is also reported in the literature that the purity of TBPB varies from batch to batch [15].
Figure 4.4 Absorbance of TBPB at 620 nm increases with sodium hydroxide concentration.

A stock solution of TBPB was prepared with added sodium hydroxide to convert the dye into the sodium salt. Calibration solutions were made by adding known amounts of nonaflate acid to 1 mL of the dye stock solution and diluting with THF to a final volume of 5 mL. Figure 4.5 shows the absorbance at 620 nm for each solution plotted as a function of acid concentration. As expected, the absorbance decreased with increasing acid concentration.
Two sets of resists were analyzed using the TBPB dye, six month old resists and freshly formulated resists. Table 4.1 compares the moles of acid that were measured in the two sets of resist films under two different process conditions, exposed to EUV radiation and baked, or baked only. Most notable is the large difference in measured acid between the six month old resists and the freshly prepared resists. For example, the amount of acid measured in the six month old resist with 140 mM of $3HB$ was $7.5 \times 10^{-7}$ moles/wafer but only $0.01 \times 10^{-7}$ moles/wafer in the freshly prepared resist. We also found that the amount of acid is essentially the same between resists that are exposed and baked and resist that are baked only (not exposed). This was not expected because we know that the AAs are thermally stable in resist films. However, these films do not have base quencher and we have not tested the AA thermal stability in films without base quencher. Therefore, it is possible that the AAs were not thermally stable in these formulations. If this is correct then the AAs could have decomposed thermally to
generate acid. Despite our ability to quantitatively measure the amount of acid in the resist films, we did measure increasing amounts of acid with increasing amounts of AA loading.

Our inability to reproducibly generate a calibration curve and measure the amount of acid in resist films suggests that there is a source of experimental error that we have not identified. Possible sources of error are oxygen quenching or base contamination from the borosilicate glassware that is use to prepare the dye-acid solutions. Based on our measurements we conclude that TBPB can be use to qualitatively detect acid in resist films but we are unable to quantify the amount of acid.

<table>
<thead>
<tr>
<th>AA (mM)</th>
<th>6 Month Old Resists</th>
<th>Freshly Prepared Resists</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated</td>
<td>Exposed + PEB</td>
</tr>
<tr>
<td>AA (mM)</td>
<td>Total acid</td>
<td>Measured acid</td>
</tr>
<tr>
<td>0</td>
<td>3.1</td>
<td>0.6</td>
</tr>
<tr>
<td>3HB</td>
<td>5.3</td>
<td>2.9</td>
</tr>
<tr>
<td>3HB</td>
<td>7.5</td>
<td>4.7</td>
</tr>
<tr>
<td>11HB</td>
<td>11.9</td>
<td>7.5</td>
</tr>
<tr>
<td>70</td>
<td>7.5</td>
<td>3.1</td>
</tr>
</tbody>
</table>

**Table 4.1** Acid was measured in 6 month old and freshly prepared resist films. Moles of acid are reported as moles × 10⁻⁷ and the measurement error is ±15 %.

### 4.3 AA Thermal Stability in Resist Films

In Chapter 2 a simple qualitative screening test to measure AA stability in resist films was described. In this section, a quantitative method to measure AA thermal decomposition temperature in resist films is described. Thermally-programmed spectroscopic ellipsometry [16] was used to measure the film thickness as a function of
temperature. When AAs thermal decomposed they released acid which deprotected the polymer causing isobutene to outgas. The outgassing resulted in a sudden decrease in film thickness which was measured by the ellipsometer. We assume changes to film optical properties are the result of changes in film thickness. This assumption does not account for changes to the film chemistry such as polymer deprotection and AA decomposition. As a result the film thickness has some uncertainty and in the future the film thickness should be measured by an independent method. For these experiments the film thickness is normalized to the starting thickness. Acid amplifier relative decomposition temperatures (Td) in resist films were quantified using this method. In this section we report AA decomposition temperatures as a function of temperature ramp rate, AA type and resist platform.

4.3.1 AA Thermal Stability as a Function of Temperature Ramp Rate

We expect that AA decomposition temperature is dependent on the heating ramp rate. We prepared OSI resist with 3HB (70 mM). Resist films were cast onto silicon without further processing. We measured the decomposition temperature at 5 temperature ramp rates, 5, 10, 20 30 and 40 °C/min. Figure 4.6 shows the results of this experiment. Figure 4.6A shows the normalized film thickness (initial film thickness is 143 ± 3 nm) as a function of temperature for the five different temperature ramp rates. The initial gradual film loss is due to solvent evaporation but the rapid decrease in film thickness is the result of isobutene outgassing (final film thickness is 123 ± 3 nm). At these relatively low temperatures, the formation of isobutene requires an acid catalyst, which comes from AA decomposition. We define the decomposition temperature as the
The steepest part of the curve in Figure 4.6A. We determine the decomposition temperature by plotting the derivative of film thickness \textit{versus} temperature (Figure 4.6B). Figure 4.6C shows the AA decomposition temperatures as a function of temperature ramp rate. Interestingly, the decomposition temperature increases linearly with increasing ramp rate. We chose to compare AA decomposition temperatures at a ramp rate of 10 °C/min. This is also consistent with other methods that monitor isobutene outgassing to measure polymer decomposition [17].

\textbf{Figure 4.6} (A) Isobutene outgassing causes a sudden decrease in film thickness. (B) AA decomposition temperature is defined as the steepest part of the film thickness curve. (C) Decomposition temperature increases linearly with temperature ramp rate.

\textbf{4.3.2 Dependence of AA Thermal Stability on Chemical Structure}  
Thermally-programmed spectroscopic ellipsometry was used to measure the decomposition temperatures of \textit{OSI} resist (no AA) and \textit{OSI} with 70 mM added \textit{3HB}, \textit{3HF}, \textit{3MB} and \textit{3HG} at a temperature ramp rate of 10 °C/min. Resist films were spin coated onto silicon substrates and soft baked at 90 °C for 60s. Figure 4.7 shows the results of this experiment. Figure 4.7A shows the normalized film thickness (initial film thickness is 70 ± 3 nm, final film thickness is 60 ± 3) as a function of temperature and Figure 4.7B shows the derivative of film thickness \textit{versus} temperature. The
decomposition temperatures of \textbf{OS1}, \textbf{3HB}, \textbf{3HF}, \textbf{3MB} and \textbf{3HG} are 195, 152, 139, 128 and 112 °C, respectively. Surprisingly, the decomposition temperature of \textbf{3HB} is 9 °C higher than previously measure (Figure 4.6B). There are two differences between this experiment and the experiment described above that might explain this discrepancy. In the first experiment the initial film thicknesses were 143 nm and the samples were not soft baked prior to ellipsometry measurements. In this experiment the initial film thicknesses were only 70 nm and the samples were soft baked before ellipsometry measurements. Thin films that are soft baked to remove residual casting solvent have a higher density than thicker non soft baked films. Higher density films could slow acid diffusion resulting in an apparent higher AA decomposition temperature than would have been measure in a less dense film.

Despite the difference in decomposition temperature of \textbf{3HB} between the two different sets of experiments, the trend in decomposition temperatures of the AAs agree with the thermal decomposition rates presented in Chapter 3. These decomposition temperature results show that the trigger and acid precursor contribute significantly to the thermal stability of AAs. Compounds \textbf{3HB} and \textbf{3MB} differ only by their trigger, yet \textbf{3HB} (Td = 152 °C) is 24 °C more stable than \textbf{3MB} (Td = 128 °C). This suggests that the methoxy trigger is more thermally labile than the hydroxyl trigger. Compounds \textbf{3HB}, \textbf{3HF} and \textbf{3HG} all have the same trigger but differ by their acid precursor type. The results suggest that the acidity of the liberated AA acid correlates with the AA thermal stability. The AA decomposition temperature decreases as the acid strength increases. This is a major challenge for designing new AAs because our goal is to make AAs that have high thermal stabilities and generate highly fluorinated super acids.
**Thermal Decomposition of Acid Amplifiers In EUV Resist Films**

![Diagram showing normalized film thickness over temperature for different acids.](image)

**Figure 4.7** (A) Isobutene outgassing causes a sudden decrease in film thickness. (B) AA chemical structure affects the decomposition temperature.

### 4.3.3 Acid Amplifier Stability in High Activation Energy, Low Activation Energy and 193-nm Resist Platforms

To increase the usefulness of AAs in photoresists, it is important to know how resist polymers affect the thermal stability of AAs. To this aim, we studied the decomposition temperatures of 3HB and 11HB in three resist platforms: a high activation energy (Ea) EUV resist, a low activation energy EUV resist, and a 193 nm resist. The high Ea resist is our standard OSI formulation and the low Ea and 193 resists were provided by a commercial supplier. We know the composition of the high Ea resist but the compositions of the low Ea and 193 nm resists are unknown. The only compositional information we have is that the 193 nm resist does not have phenol in the polymer. We blended equal molar concentrations of 3HB or 11HB into the three resist platforms, spin coated resist films onto a silicon substrate and measured the decomposition temperatures.
Figure 4.8 shows the normalized film thickness as a function of temperature for three resist platforms: (A) high Ea resist, (B) low Ea resist and (C) 193 nm resist. In each plot the curves composed of the red ♦ corresponds to resist films without AA, the blue ● corresponds to resist films with 3HB and the green ■ corresponds to resist films with 11HB. Figure 4.8A shows the results for high Ea resists. The high Ea resist decomposes at 185 °C in the absence of AA. With added 3HB or 11HB the high Ea resist decomposes at 145 and 155 °C respectively. The lower decomposition temperatures are the result of AA decomposition. Figure 4.8B shows the results for low Ea resists. The low Ea resist polymer decomposes at 160 °C. Both resist with added 3HB or 11HB decomposes at 140 °C. This data suggests that the polymer does not affect the AAs decomposition temperatures. Figure 4.8C shows the results for 193 nm resists. Both 193 nm resists with 3HB or 11HB decompose at the same temperature, 183 °C. We cannot be certain if the AAs or the polymer is decomposing because we did not measure the resist decomposition without AA.

We conclude from this experiment that the resist polymer can affect the thermal stability of AAs. We found that this method works best for our high Ea resist because there is a large decrease in film thickness due to isobutene outgassing. The other two resist platforms did not give as large of a film loss, particularly the low Ea resist. We hypothesize that the AAs are more stable in the 193 nm resist than the high Ea resist because the phenol in the high Ea resist displaces the AA sulfonate ester via an SN2 reaction but 193 nm resist do not have phenol. We cannot speculate further on reaction mechanisms because we do not know the compositions of the low Ea and 193 nm resists.
Figure 4.8 Resist formulation: ♦ without AA, ● with 70 mM $3HB$, and ■ with 70 mM $11HB$. (A) OS1 high Ea resist. (B) Low Ea resists. (C) 193 nm resists.

4.4 AA Decomposition Products

Identification of key AA decomposition products can help us better understand AA decomposition mechanisms. Figure 4.9 shows two possible decomposition mechanisms for $3HB$. We hypothesize that during acid catalyzed decomposition, $3HB$ goes through a carbocation intermediate to give sulfonic acid, water and isoprene. However, in the presence of phenol the carbocation can be trapped [18]. The two different decomposition pathways could have detrimental effects on the imaging quality of photoresists. For instance, high concentrations of isoprene in the presence of acid can polymerize to polyisoprene. Polyisoprene is insoluble in TMAH developer and therefore it could increase the LER. Similarly, if a phenol traps the carbocation intermediate and a second phenol on a neighboring polymer chain displaces the sulfonate ester then cross linking occurs which could increased LER and worsen sensitivity. We used $^1$H-NMR to identify the key decomposition products of $3HB$ and show that both mechanism are possible to some extent.
Figure 4.9 3HB decomposition byproducts are dependent on the reaction pathway.

We prepared four solution in d$_6$-benzene consisting of 70 mM 3HB with and without added base (2,4,6-tri-$t$-butylpyridine) and or m-ethylphenol (1.1 equivalents relative to 3HB) in sealed NMR tubes. Figure 4.10 shows the compositions of the four samples: A, B, C and D. Sample A has no additives so we expect to detect isoprene and or polyisoprene after AA decomposition. If isoprene is generated and it polymerizes then the addition of base to the solution (samples B and D) will trap the acid so that it cannot catalyze isoprene polymerization. Therefore, we expect samples B and D will not contain poly-isoprene after AA decomposition. Samples C and D both contain phenol so there is the possibility to detect phenol products byproducts. As with samples A and B, samples C and D can also produce isoprene and or poly-isoprene. However, if phenol traps a significant amount of the carbocation intermediate then the amount of isoprene/poly-isoprene should be significantly reduced compared to samples A and B and we should detect phenol byproducts.
Figure 4.10 Four AA samples were prepared (A AA only, B with base, C with phenol and D with base and phenol) and their decomposition products were monitored by NMR.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[\text{AA only}]</th>
<th>[\text{with base}]</th>
<th>[\text{with phenol}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>No</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Yes</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>No</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.11 compares the proton NMR spectra of samples A and B after complete decomposition of $3HB$. The spectrum of sample A has broad peaks near 1.0 and 6.25 ppm. These peaks are attributed to poly-isoprene. The spectrum of sample B has sharp peaks near 5.0 and 6.5 ppm consistent with isoprene. The results from these two samples show that $3HB$ does decompose to isoprene and that the isoprene polymerizes in the presence of acid. However, this does not necessarily mean that isoprene polymerizes in resist films. Sample A required more than 16 hours at 100 °C for $3HB$ to completely decompose and make poly-isoprene, but a resist is only subjected to elevated temperatures for 60-90 seconds. This short baking time might not be long enough for polymerization to occur. Also, sample A is in a sealed tube so the isoprene cannot escape but in a resist film the isoprene will volatilize. We conclude from this data that $3HB$ does decompose to give isoprene as a byproduct.
Figure 4.11  Proton NMR spectra of samples A (no base) and B (with base) after complete AA decomposition.

Figure 4.12 compares the proton NMR spectra of samples C and D after complete decomposition of 3HB. The spectrum of sample C has broad peaks near 1.25 and 4.5 ppm. These peaks are attributed to poly-isoprene. There are two possible explanations for the differences in poly-isoprene chemical shifts between samples A and C. One factor that influences chemical shifts is the solvent polarity. Samples A and C both contain benzene but sample C also has some phenol which makes the solvent slightly more polar than sample A. Another explanation for the differences in chemical shifts is that different isomers of poly-isoprene were formed. Isoprene can polymerize by 1,4-, 1,2-, and 1,3- addition. 1,4- addition can also have cis- and trans- isomers for a total of four different poly-isoprene structures. The spectrum of sample D has sharp peaks near 5.0 and 6.5 ppm which are assigned to isoprene. These results also show that 3HB does
decompose to isoprene and that isoprene polymerizes in the presence of acid. In addition to generating isoprene, the phenolic methylene peak at 2.5 ppm also shifts suggesting that phenol participates in the decomposition of 3HB to form byproducts. Figure 4.13 highlights the methylene peak at 2.5 ppm for samples C and D. The spectrum of sample D before decomposition is also shown as a reference. By comparing the peak heights of the starting phenol and phenol products, ~50 % of the phenol in sample C was converted to a new product but only a small fraction of the phenol in sample D was converted to new products. This suggests that that 3HB is more likely to go through a tertiary carbocation intermediate and be trapped by phenol under acid catalyzed conditions (sample C, no base) than in the absence of acid (sample D, with base). We conclude from samples C and D that phenol does react with the carbocation intermediate.

**Figure 4.12** Proton NMR spectra of samples C (no base) and D (with base) after complete AA decomposition.
**Figure 4.13** Proton NMR spectra shows more phenol byproducts in sample C than D after complete AA decomposition.

### 4.5 AAs Effect on Resist Outgassing

One challenge for the commercialization of EUV lithography is to improve the lifetime of the expensive molybdenum-silicon multilayer optics and mask [19,20]. The lifetime of these components is significantly reduced by carbon contamination on the surfaces of the reflective optics [21,22]. Carbon containing compounds in the EUV vacuum chamber adhere to the optics, form thin films when exposed to EUV radiation and lower the reflectivity of the multilayer optics. One major source of the carbon containing compounds is resist outgassing [23-25]. We investigated the outgassing properties of photoresists with and without added AAs because AAs decomposed into volatile hydrocarbons. We compare the outgassing of *OS1* control resist (no AA) with the outgassing of *OS1* with 70 mM added AA. We studied five different combinations of
AAs and OSI resist. We exposed the resist to 2.5X the clearing dose (Eo). Figure 4.14 shows the outgassing measurements. Compared to the control resist, 6AB increased the clearing dose and had a higher amount of outgassing species. Resist with 3HF and 3HB improved the sensitivity by ~30 % and had no significant impact on the outgassing. The biggest change in outgassing came from the addition of 6HB or 8HB to the control resist. Both 6HB and 8HB improved the sensitivity by ~50 % and lowered the amount of outgassing 50 % and 75 %, respectively. In general, outgassing increases as a function of dose so AAs that improve the sensitivity of a resist will likely lower the amount of outgassed species. However, all new AAs should have their outgassing measured before using them in EUV production tools.

\[ \text{Figure 4.14} \quad \text{AAs that improve the resist sensitivity also improve (reduce) the number of outgassing species.} \]
4.6 Summary

Four fundamental questions were addressed in this chapter: (1) How much acid do AAs generate in resist films? (2) How does the resist polymer affect the thermal stability of AAs? (3) What are the by products of AA decomposition? (4) What effect do AAs have on resist outgassing? An acid sensitive dye was use to measure the amount of acid generated in resist films by AAs. This approach was unsuccessful at quantifying the amount of acid but it did qualitative show that AAs increase the amount of acid generated in resist films. The thermal decomposition temperatures of AAs in resist films were measured using spectroscopic ellipsometry. The results show that AAs are more stable in resists that do not have phenol groups in the polymer than resists with phenolic polymers. Identification of AA decomposition products in solution revealed that phenol can participate in the decomposition mechanism. Lastly, resist outgassing measurements showed that AAs do not increase the amount of outgassed species.
References


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CHAPTER 5

MODELING RESIST PERFORMANCE AND ACID AMPLIFIER REACTIVITY

5.1 Acid Diffusion Model

5.1.1 Introduction

The purpose of this section is to develop a mathematical model to predict how acid amplifiers affect the lithographic performance of EUV photoresists. In the absence of AAs, increasing the amount of base quencher in a resist improves the LER (Chapter 2, Figure 2.2). One explanation for this improvement is that the base increases the chemical contrast (acid gradient) at the line edge. We developed a model that simulates PAG and AA acid and allows the acids and base quencher to diffuse as a function of time. Figure 5.1 shows an overview of how the model is divided into four calculable components: PAG photolysis, base quenching, acid and base diffusion and AA decomposition. Using this simple model, we can compare the acid gradient at a line edge for various resist formulations. We can explore the acid gradient as a function of quantum yield (QY), AA and base loadings, acid and base diffusion lengths and AA reactivity. Our aim is to determine which conditions give the most gains in sensitivity and acid gradient.
Figure 5.1 The model is composed of 4 interdependent components, (1) photo acid generation (2) base quenching (3) diffusion (4) AA decomposition.

5.1.2 Model Assumptions
We made several simplifying assumptions to build this model. We think these assumptions will not affect any trends that the model predicts and the benefits of simplicity outweigh the accuracy of a more sophisticated model [1-4]. Simplifying the model allows us to apply the calculations to any resist formulation and process conditions. The assumptions are: (1) acid from the PAG and AA are the same, (2) AAs are homogenously dispersed and do not diffuse, (3) acid does not outgas, (4) base quenching reaction is instantaneous, (5) diffusion is the same in exposed and unexposed regions, (6) concentration gradients are only in the x-direction (7) quantum yield does not change as PAG is consumed.
5.1.3 Correlating Model Results to Resist Formulations

One caveat about acid, base and AA concentrations must be addressed in order to compare simulation results with experimental resist formulations. This model is not intended to make direct comparisons with experimental resist formulations but it is designed to predict trends. With this in mind, we can make some approximations in order to relate the model results to actual resist formulations.

We chose to have quantum yield as an input variable because it contributes significantly to a resist's performance [5]. However, many variables affect the QY, such as resist composition and PAG loading, for this reason the PAG loading is not an input variable. As a reference point, the quantum yields for our resist with di(4-tert-butylphenyl) iodonium perfluoro-1-butanesulfonate PAG loadings of 7.5 wt% (123 mM), 15 wt% (247 mM) and 30 wt% (494 mM) are 2.6, 3.8 and 5 respectively. The base loadings that we use in our resist formulations range from 0.5 wt% to 2 wt% (22 to 88 mM) and the AA loadings range from 0 to 280 mM. The concentrations of acid, base and AA used in the model are scaled down by approximately 0.1 versus our resist formulation (for example 1 base in the model $\approx 10$ mM). The model does not use the exact concentrations of PAG, base and AA as our resist formulations but the relative amounts of each component agree reasonably well with actual resist formulations. Therefore, concentrations in the model are considered relative values and will be unitless.

5.1.4 Model Equations

The first step in building this model is to determine the initial acid concentration profile from PAG photolysis. We assume that the aerial image intensity will have a sinusoidal shape with the peak intensity at the center of the transparent regions of the mask and zero
intensity at the center of the opaque regions. Figure 5.2 illustrates the aerial image profile relative to the mask pattern. The amplitude of the aerial image is a function of exposure dose (mJ/cm²) and the acid concentration is calculated by multiplying the aerial image intensity with film quantum yield (moles of acid generated / moles of photons absorbed). Figure 7.3 shows the equation used to calculate the initial acid concentration profile. After PAG photolysis, the acid concentration is reduced by the amount of base quencher [6].

Figure 5.2 Aerial image for equal L/S mask pattern has a sinusoidal shape due to light diffraction.

\[
C_{x,t=0} = \left(\frac{QY \times Dose}{10}\right) \times \left(\cos\left(\frac{\pi x}{l}\right) + 1\right)
\]

- \(C\) = acid concentration (M)
- \(x\) = position (nm)
- \(l\) = feature size (nm)
- \(t\) = time (s)
- \(QY\) = quantum yield
- \(Dose\) = amount of photons (mJ/cm²)
- \(Base\) = concentration of base quencher (M)

Figure 5.3 Acid concentration profile from PAG photolysis is correlated to the aerial image intensity.
The next step in the model is to calculate the concentrations of acid and base as they diffuse. The main driving force for diffusion is the concentration gradients. The acid and base diffuse from high concentrations toward low concentrations at a rate proportional to the acid diffusion length ($\sqrt{2Dt}$). The concentration, $(C)$ at any position $(x)$ and time $(t)$ is calculated by subtracting the concentration that diffused during a time interval $(\Delta t)$, from the starting concentration. Figure 5.4 shows the equation used to calculate the acid and base concentrations at $t > 0$.

The acid concentration is increased by the amount of acid from AA decomposition $(P)$ if acid amplifier is present. Figure 5.5 shows the equation used to calculate AA decomposition. Acid amplifier decomposes autocatalytically with rate constant $k$, and can only decompose when there is initial catalytic acid $(C_{x,t-\Delta t} > 0)$. Acid from AA decomposition is added to the total acid concentration $(C_{x,t})$ and diffuses the same as the PAG acid.

The last step is to subtract the base from the acid concentration; this completes one time interval. The process of diffusion, AA decomposition and base quenching is repeated 1000 times for a total simulation time of 100 s.

\[ C_{x,t} = C_{x,t-\Delta t} - D\Delta t \times \left( \frac{2C_{x,t-\Delta t} - C_{x-\Delta x,t-\Delta t} - C_{x+\Delta x,t-\Delta t}}{\Delta x^2} \right) \]

**Figure 5.4.** Acid and base diffusion is driven by concentration gradients.
\[ P_{x,t} = \frac{AA_{x,t-M} + C_{x,t-M}}{1 + \frac{AA_{x,t-M}}{C_{x,t-M}} \exp[-(AA_{x,t-M} + C_{x,t-M}) k \Delta t]} \]

\( P \) = acid concentration from AA decomposition (M)
\( C \) = initial acid concentration (M)
\( AA \) = acid amplifier concentration (M)
\( k \) = AA decomposition rate constant (Ms\(^{-1}\))
\( x \) = position (nm)
\( t \) = time (s)

**Figure 5.5** AAs decompose according to the autocatalytic rate equation.

Figure 5.6 helps illustrate acid diffusion by showing the acid concentration as a function of position at 0, 30, 60 and 90 s. For simplicity, this simulation does not contain base or AA. The left plot shows the acid concentration over the full range of the 60 nm L/S mask pattern and the right plot focuses in from the center of the exposed region (\( x = 0 \) nm) to the center of the unexposed region (\( x = 66 \) nm) with the line edge between \( x = 30 \) and \( x = 36 \) nm. At time 0, the initial acid concentration profile (green curve) has a maximum of 3.9 (at \( x = 0 \)) and a minimum of 0 (at \( x = 66 \)). As time progress the acid diffuses from high concentration to low concentrations and after 90 s the acid concentrations at \( x = 0 \) nm and \( x = 66 \) nm are 3.5 and 0.3 respectively.

**Figure 5.6** Simulation example without added base or AA showing the acid concentration profile at 0, 30, 60, and 90 s.
Figure 5.7 illustrates key parameters that remain constant between simulated results. Experimental lithographic results are typically compared at a sizing dose under constant process conditions. The sizing dose is determined by the level of polymer deprotection, which is a function of acid concentration and reaction time [8]. Likewise, our simulation results are compared at a sizing dose and at a constant amount of diffusion time. We define the sizing dose as the dose required to reach an accumulated acid concentration of 200 at the line edge at 90 s. Resist LER is influenced by the chemical contrast at the line edge [7], so the analogous figure of merit that we compare between simulations is the accumulated acid concentration gradient at the line edge (red dashed line); a steeper gradient indicates a better performing resist.

Figure 5.7 For consistency, model results are compared at a threshold accumulated acid concentration of 200 at the line edge at 90 s
5.1.5 Acid and Base Diffusion Study

Acid and base diffusion impacts the resist sensitivity and LER [9,10]. To model this, we calculated the sensitivities and acid gradients as a function of acid and base diffusion lengths. We did this by varying the acid and base diffusivities at a constant base loading of 3. We chose the range of diffusivities to be 0.1-100 nm²/s based on values reported in the literature [11-14]. Figure 5.8 shows the acid gradient as a function of dose. The red data set shows the effects of changing the acid diffusivity from 0.1-100 nm²/s at a constant base diffusivity of 1.0 nm²/s. In contrast, the blue data set shows the effects of changing the base diffusivity from 0.1-100 nm²/s at a constant acid diffusivity of 1.0 nm²/s.

The result of these calculations predicts a trade-off between sensitivity and acid gradient. Reducing the acid diffusivity from 100 nm²/s to 0.1 nm²/s improved the acid gradient from 3.8 to 22.2, over 5.5X improvement. This benefit in acid gradient is achieved with only a slight loss in sensitivity, from 18.2 mJ/cm² to 18.6 mJ/cm². Base diffusion is also predicted to affect the acid gradient and sensitivity. Reducing the base diffusivity from 100 nm²/s to 0.1 nm²/s degrades the acid gradient from 18.0 to 15.2 but improves the sensitivity from 20.5 mJ/cm² to 18.0 mJ/cm². The effects of varying base diffusion are less than acid diffusion because the concentration of base is always lower than the concentration of acid. Reports in the literature [15] show that the optimum acid diffusion length depends on the base concentration and diffusion length. We concluded from our calculations that simultaneous gains in acid gradient and sensitivity cannot be achieved by changing acid and base diffusion lengths.
5.1.6 Acid Gradient vs. Quantum Yield and Base Loading

This set of calculations was designed to determine the effects of quantum yield (QY) on sensitivity and acid gradient at a constant base loading of 0.5. The acid and base diffusivities (D) are both 1 nm²/s. We chose to vary the QY from 1.99 to 5.09 because we can compare our model results with experimental data at these QYs. Table 5.1 compares the experimental and calculated doses, LERs and acid gradients at various QYs. Figure 5.9 shows the acid gradient and LER plotted as a function of QY. Experimentally, increasing QY improves the sensitivity but has no effect on LER. The model also shows the same trend, increasing QY improves sensitivity but has not effect on the chemical gradient.

![Acid Gradient vs. Acid and Base Diffusion Length](image)

Figure 5.8 Acid gradient as a function of: ▲ acid and ♦ base diffusivities.
<table>
<thead>
<tr>
<th>YQ</th>
<th>Experimental Dose (mJ/cm²)</th>
<th>Experimental LER (nm)</th>
<th>Model Dose (mJ/cm²)</th>
<th>Model Gradient (ΔH⁺/Δnm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.99</td>
<td>16.9</td>
<td>4.5</td>
<td>12.0</td>
<td>9.3</td>
</tr>
<tr>
<td>2.61</td>
<td>10.3</td>
<td>4.6</td>
<td>9.2</td>
<td>9.3</td>
</tr>
<tr>
<td>3.84</td>
<td>5.9</td>
<td>4.6</td>
<td>6.2</td>
<td>9.3</td>
</tr>
<tr>
<td>4.39</td>
<td>5.1</td>
<td>4.2</td>
<td>5.4</td>
<td>9.3</td>
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<tr>
<td>5.09</td>
<td>4.3</td>
<td>4.5</td>
<td>4.7</td>
<td>9.3</td>
</tr>
</tbody>
</table>

**Figure 5.1** Experimental and calculated sensitivities improve as quantum yield increases.

**Figure 5.9** Experimental LER (♦) and calculated acid gradient (▲) are constant as a function of quantum yield.
The next set of calculations compares the affects of base loading on the sensitivity and acid gradient for various QYs. Figure 5.10 shows the accumulated acid concentration gradient plotted as a function of dose. Each set (same color) of data points represents a different QY ranging from 2 to 5. Each point within a set corresponds to a different base loading from 0 to 3 in increments of 0.5. As expected, the dose increases as base loading increases but the dose decreases as the QY increases (at a constant base loading). An interesting comparison to make is with the acid gradient at a constant dose. For example, at 10 mJ/cm², the acid gradient improves as QY increases; however the base loading is also increased to maintain a constant dose. This result predicts that a resists LER performance can be improved by increasing the QY and base loading without penalty to sensitivity and has been confirmed experimentally [5].

**Figure 5.10** Acid gradient as a function of quantum yield and base loading.
5.1.7 Acid Gradient vs. AA and Base Loading

This set of calculations was designed to determine the effects of acid amplifier and base loadings on sensitivity and acid gradient at a constant QY of 2.5. The acid and base diffusivities (D) are both 1 nm²/s and the AA decomposition rate constant (k) is 0.02 (Ms)⁻¹. Figure 5.11 shows the acid gradient plotted as a function of dose. Each set of data (same color) corresponds to a different base loading, 0, 0.5, 1.0, 1.5, 2.0, and 3.0. Each data point within a set is a different AA loading. At 0 base loading, the AA loadings are 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 4.0; for all other base loadings the AA loadings are 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 4.0, 5.0, 6.0 and 7.0. As expected, the dose increases with increasing base loading. At all base loadings the addition of AA improves the sensitivity but does not always improve the acid gradient. In the absence of base, AA only makes the acid gradient worse. At base loadings of 0.5, 1.0 and 1.5, low AA loading degrades the acid gradient but high AA loading improves the gradient. The addition of AA when the base loading is 2.0 and higher improves the acid gradient. This result predicts that AAs can simultaneously improve the sensitivity and acid gradient at the proper base and AA loadings.
Figure 5.11 Acid gradient as a function of acid amplifier and base loading.

The model predicts that QY and AA both have the potential to improve the sensitivity and acid gradient. We calculated an analogous Z-Parameter value using the model results to compare the overall benefits of increasing QY with the benefits of using AAs. Equation 5.1 is used to calculate the model Z-Parameter. The model Z-Parameter equation uses $1/(\text{acid gradient})^2$ as opposed to $(\text{LER})^2$ because the acid gradient is inversely correlated to LER. The model Z-Parameter is calculated for three resists, one with AA (C) and two without (A and B). Table 5.2 shows the model Z-Parameter results for the three resists. Resist A has a QY of 2.5 and Z-Parameter of 23.6. Increasing the QY to 5.0 (resist B) and adding base to maintain a nearly constant dose improves the Z-Parameter by 3.8X. We chose a QY of 5.0 because that is the maximum QY
experimentally achieved (for a usable resist) with our resist formulation. Resist C has the same QY as resist A, but contains acid amplifier and a higher base loading to keep the dose nearly constant. Resist C improves the Z-Parameter by 4.5X (*versus* resist A). Higher AA loadings can further improve the sensitivity and acid gradient as previously shown in Figure 5.11. This result suggests that the overall resist performance can be increased more by using AAs than by increasing the quantum yield.

\[
(Half \ Pitch)^3 \times (Acid \ Gradient)^{-2} \times Esize = Z-Parameter
\]

**Equation 5.1** Model Z-Parameter is used to calculate the overall resist performance.

<table>
<thead>
<tr>
<th>Resist</th>
<th>QY</th>
<th>Base</th>
<th>AA</th>
<th>Dose (mJ/cm²)</th>
<th>Gradient (ΔH⁺/Δnm)</th>
<th>Model Z-Parameter (mJ·nm⁻¹ · 10³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.5</td>
<td>0.5</td>
<td>0</td>
<td>9.6</td>
<td>9.3</td>
<td>23.6</td>
</tr>
<tr>
<td>B</td>
<td>5</td>
<td>3.0</td>
<td>0</td>
<td>9.2</td>
<td>18.0</td>
<td>6.1</td>
</tr>
<tr>
<td>C</td>
<td>2.5</td>
<td>3.0</td>
<td>5</td>
<td>9.8</td>
<td>20.0</td>
<td>5.3</td>
</tr>
</tbody>
</table>

**Table 5.2** Acid amplifiers improve the Z-Parameter more than increasing QY.

**5.1.8 Acid Gradient vs. AA Loading and Decomposition Rate Constant**

We synthesized many AAs that have a range of decomposition rates. Here, we calculate the acid gradient as a function of AA decomposition rate constant to help us understand the effects of AA decomposition kinetics on the acid gradient and sensitivity. Figure 5.12 shows acid gradient as a function of AA rate constant for two base loadings (0.5 and 3.0) and eight AA loadings (0 to 10). The calculations were done using autocatalytic rate constants of 0.007 (▲) 0.02 (♦) and 0.04 (Ms)⁻¹ (■). The results show that AAs improve the sensitivity regardless of AA rate constant or base loading. However, AAs with high rate constants improve the sensitivity more than AAs with small
rate constants. An unexpected finding from these calculations is that AAs with smaller rate constants give better acid gradients when all other variables are constant. This is most apparent at the higher base loading. Data for the AA decomposition rate constant of 0.04 (■) shows the acid gradient is only improved from 18.0 to 18.5 (3 %) as the AA loading is increased from 0-10. On the other hand, the AA rate constant of 0.007 (▲) shows an acid gradient improvement from 18.0 to 25.5 (41 %) over the same AA loading. We conclude from these calculations that slow decomposing AAs will give the most gains in acid gradient but less sensitivity improvement than a fast decomposing AAs at the same loading. The most benefit is achieved by using high concentrations of AAs that have a slow decomposition rate.

**Figure 5.12** Acid gradient as a function of AA and base loading for three AAs with different decomposition rate constants
5.1.9 Diffusion Model Conclusions

In general, the calculations show that optimizing the performance of a resist is complicated by the many variables, such as diffusion lengths, formulation composition and reaction rates. This model gives insight about how each variable affects the resist performance but requires more refinement to calibrate the calculated results with experimental results. The most important conclusion that we draw from the model results is that AAs simultaneously improve the acid gradient and sensitivity at high base loadings, which is critical to beat the RLS-tradeoff. We hypothesize that these improvements are the result of two factors. First, AAs improve the sensitivity because they generate acid in the resist without increasing the dose. Second, AAs gradually release acid during the entire PEB time allowing younger acids to have smaller diffusion domains which improves the acid gradient at the line edge.

5.2 Model to Predict AA Reactivity

5.2.1 Thermodynamic Analysis of ESCAP Debloking Reactions

The purpose of this section is to develop a thermodynamic model to predict AA reactivity. We begin by validating our assumptions by comparing the model results with known chemistries. ESCAP polymers with \( t \)-butyl esters undergo acid catalyzed deprotection reactions to give carboxylic acids and isobutylene as shown in Figure 5.13. It is important that the ester deprotection only occurs in the presence of catalytic acid and not thermally in the absence of acid otherwise the system will not function as a photoresist.
Figure 5.13 Thermal and acid catalyzed ESCAP polymer deprotection reaction.

We calculated the thermodynamics of this reaction using the PM3 potential function in Chem3D™ (Cambridge Software) using t-butyl acetate as a model for the t-butyl ester in the polymer. The heats of formation were calculated for each compound, the starting material, intermediates, and products. We use a dielectric constant of 7.0 to approximate the phenolic polymer environment. We chose this value because it is intermediate between the dielectric constant of phenol (ε = 10) and the value favored by Tagawa (ε = 4) [16,17]. We subtracted the heat of formation of the starting material from each compound so that the starting material has an enthalpy of zero. We show the relative heat of formation (ΔΔH) of each molecule in Figure 5.14. The acid catalyzed pathway (28 kcal/mol) is clearly more favorable than the thermal reaction pathway (45 kcal/mol). As a side note, the homolytic C-O bond cleavage reaction is even less favored than the heterolytic bond cleavage. The enthalpies of these two reactions are +44 and +66 kcal/mole respectively. This thermodynamic analysis is consistent with the known technology so it gives us some support that we can use this method to predict the relative reactivity of AAs.
Figure 5.14 Thermodynamic comparison of acid catalyzed and thermal pathways for \( t \)-butylacetate decomposition.

The thermodynamic analysis shown here relies on an important assumption. We assumed that the Hammond Postulate [18] is true, or that thermodynamic properties of reactants and intermediates can be used to predict the relative reaction rates or kinetics. We will use this analysis as a guide to identify target compounds for our initial synthesis. As experimental data becomes available we can modify the model as needed.

5.2.2 Target Acid Amplifiers

Based on the thermodynamic calculations, the AAs that we selected to investigate have three main features. (1) They have a fluorinated sulfonate ester groups capable of producing strong sulfonic acids. (2) The trigger (alcohol, ether, or ester) is located on a carbon that is \( \beta \) to the sulfonic acid carbon. (3) The trigger reacts to generate a double bond that is allylic to the sulfonate ester.

Figure 5.18 shows the thermodynamic analysis of how compound \( 1A \) might function as an acid amplifier. The tertiary alcohol could be protonated (13 kcal/mol endothermic),
then elimination of water leaving the tertiary carbocation (Trigger Pull, 29 kcal/mol). Elimination of the catalytic acid generates the olefin (Trigger Reaction 2) thereby activating the sulfonate group towards heterolytic cleavage. Further elimination of triflic acid generates a diolefin (not shown). Figure 5.15 also shows the direct thermal (uncatalyzed) pathway in which triflate is eliminated directly from the starting acid amplifier, 1A. This analysis shows that compound 1A may not be a very good AA as the thermal pathway appears to be more favorable than the catalyzed pathway (21 Kcal/mol vs. 29 Kcal/mol). Compound 1A can therefore be modified by adding phenyl and methyl groups to the β and α positions (vs. the sulfonate group) leading to compound 2A (Figure 5.16). The trigger pull reaction (dehydration) has now been stabilized by 10 kcal/mol so that it is now slightly more favored than the undesired thermal reaction.

**Figure 5.15** Comparison between acid catalyzed and thermal (uncatalyzed) decomposition pathways for compound 1A.
Figure 5.16  Comparison between acid catalyzed and thermal (uncatalyzed) decomposition pathways for compound 2A.

Table 5.3 shows the chemical structures of sixteen possible acid amplifiers and their relative heats of formation. Based on the thermodynamic analysis, the best amplifiers will have a low energy pathway for acid catalysis (Trigger Pull and subsequent steps) and a high energy pathway for thermal decomposition. An option to improve the acid catalyzed reactivity of AAs is to convert the alcohol groups into esters. This makes the protonation and trigger reactions more favorable as shown by comparison of 1A with 1C. The table includes the ratio of Therm/Cat, and the best AAs will have high ratios. We selected eight compounds with the highest ratios as our first target compounds to synthesize.
<table>
<thead>
<tr>
<th>#</th>
<th>Structures</th>
<th>Protonation</th>
<th>Trigger Pull</th>
<th>Trigger 2 Ron</th>
<th>Catalyzed Acid Formation</th>
<th>Thermal Acid Formation</th>
<th>Therm / Cat</th>
</tr>
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<td>1A</td>
<td><img src="image1.png" alt="Structure" /></td>
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<td>29</td>
<td>10</td>
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<td>-2</td>
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<td>19</td>
<td>16</td>
<td>19</td>
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<td>22</td>
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<td>18</td>
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<td>21</td>
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<td>2</td>
<td>20</td>
<td>30</td>
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<td>-1</td>
<td>7</td>
<td>22</td>
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</tr>
</tbody>
</table>

**Table 5.3** Chemical structures and model results for 16 acid amplifiers. We identified 8 target compounds as potential AAs based on their Therm/Cat values greater than 1.0.
5.2.3 Comparing Model and Experimental Results

The first compound that we attempted to synthesize from Table 5.3 was 9A. This acid amplifier is predicted to have one of the best Therm/Cat ratios but unfortunately we were unable to synthesize the compound. In fact, our initial attempts to synthesize any triflate containing AA were unsuccessful because triflate is one of the best leaving groups. Unable to synthesize our initial target compounds, we began using weaker acid precursors such as toluenesulfonate and p-trifluoromethylbenzene sulfonate. Using these acid precursors we were able to synthesize a variety of AAs with different reactivities.

The thermal stability’s of successful AAs were tested using the method described in Chapter 2. Figure 5.17 shows the chemical structure and thermal stability results for 25 AAs. Using these experimental results, we improved the model’s ability to predict AA reactivity by changing how we interpret the calculations. Figure 5.18 shows the calculated uncatalyzed activation energy of acid formation versus the difference of activation energies between the uncatalyzed acid formation and the acid catalyzed trigger pull for the 25 compounds shown in Figure 5.17. On the y-axis, there is a clear separation of compounds based on their thermal stability, with only a few exceptions. Compounds with an uncatalyzed Ea below 45 kcal/mol have poor thermal stabilities and above 45 kcal/mol have good thermal stabilities. On the x-axis, compounds are separated based on their difference between uncatalyzed and acid catalyzed decomposition energies. Compounds with a negative value are predicted to decompose via the uncatalyzed pathway and a positive value would suggest acid catalyzed decomposition is favored. This means that compounds with a positive value are likely to decompose autocatalytically. Experimentally we found this analysis to have good predictability. For example, body-11 compounds do not undergo autocatalysis and on the plot these
compounds are located around 0 on the x-axis. Conversely, body-3 compounds do undergo autocatalysis and these compounds have values greater than 0 on the x-axis. Another example where the model accurately predicts the reactivity is between compounds \textit{6HB} and \textit{6AB}. These two compounds only differ by their trigger type, \textit{6HB} has a hydroxyl trigger and \textit{6AB} has an acetate trigger. The model predicts that \textit{6AB} will decompose autocatalytically but \textit{6HB} will not. We experimentally confirmed this to be accurate (Chapter 3). Using this model, we can predict compounds that will potentially function as useful acid amplifiers for EUV resists.
Figure 5.21 Structures of 25 compounds and the result of their thermal stabilities.
Figure 5.22  Model results predict compounds with an uncatalyzed decomposition Ea below 45 will be thermally unstable to resist processing temperatures.

5.3 Summary
Two models were discussed in this chapter. The first model simulated acid diffusion and AA reactivity in resist films. The model results predicted that AAs can simultaneously improve the resist sensitivity and acid concentration gradient at a line edge. The second model used thermodynamic calculations to predict AA reactivity. The model results agree with experimental AAs thermal stabilities and reaction kinetics. These models can be used to guide synthetic efforts to make new AAs with improved properties.
References


CHAPTER 6

ACID AMPLIFIER SYNTHESIS PROCEDURES

6.1 General Procedures

In this chapter, we give detailed procedures to synthesize, purify and characterize the AAs presented in this thesis. Reagents were purchased or donated from commercial suppliers and used without further purification unless noted. Reaction solvents were purchased as anhydrous grade or dried on an MSPS-MBRAUN solvent purifier. Chromatography was performed on Adedge silica gel (32-63 μm diameter, 6 nm pore size). Nuclear magnetic resonance spectra were recorded on Bruker 400 NMR spectrometer or a 300MHz JEOL Eclipse NMR spectrometer and the chemical shifts are reported in parts per million [1,2,3]. $^1$H NMR data are referenced to the residual solvent peaks, CDCl$_3$ (7.24 ppm), DMSO (2.50 ppm) or acetone-d$_6$ (2.05 ppm) and $^{19}$F data are referenced to C$_6$F$_6$ (-164.9 ppm) [4]. IR spectra were recorded on a Perkin Elmer 1600 FTIR using an ATR accessory. Elemental analyses were performed by Gailbraith or Midwest Microlab LLC.
6.2 Body 1

6.2.1 2-(2-Phenyl-1,3-dioxolane-2-yl)ethyl 4-methylbenzenesulfonate (1EA)

\[
\begin{align*}
\text{CH}_2\text{Cl}_2 & \quad + \\
\underbrace{\text{TEA}}_{\text{DMAP}} & \quad \text{CH}_2\text{Cl}_2
\end{align*}
\]

\( p \)-Toluenesulfonyl chloride (0.485 g, 2.54 mmol) and 4-dimethylamino pyridine (DMAP) (0.054 g, 0.44 mmol) were weighed into a 100 mL single-neck round bottom flask. The flask was sealed with a rubber septum and purged with nitrogen. The contents were dissolved in dichloromethane (10 mL). Triethylamine (0.309 g, 3.05 mmol) was added to the flask and the solution was stirred for several minutes. In a separate flask, 2-(2-phenyl-1,3-dioxolane-2-yl)ethanol [5] (0.440 g, 2.27 mmol) was weighed and dissolved in dichloromethane (10 mL). The alcohol solution was added to the sulfonyl chloride and the solution was stirred at room temperature overnight. The solution was washed with 10 wt% aqueous ammonium chloride (2 \( \times \) 25 mL) and saturated aqueous sodium chloride (1 \( \times \) 25 mL). The organics were dried over sodium sulfate and concentrated to give a yellow oil (0.502 g). The crude product was purified by column chromatography using silica gel as the stationary phase and hexanes / ethyl acetate as the elutant. The starting alcohol and the desired product were both isolated. The alcohol eluted from the column first then the desired product [6,7,8]. \(^1\)H NMR (400 MHz CDCl\(_3\)) \( \delta \) 7.73 (d, 2 H, \( J = 8.2 \) Hz), 7.36-7.26 (m, 7 H), 4.14 (t, 2 H, \( J = 7.3 \) Hz), 3.91 (m, 2 H), 3.70 (m, 2 H), 2.43 (s, 3 H), 2.25 (t, 2 H, \( J = 7.3 \) Hz).
6.2.2 2-(2-Phenyl-1,2-dioxolane-2-yl)ethyl 4-(trifluoromethyl)benzene-sulfonate (1EB)

\[
\begin{align*}
\text{CH}_2\text{Cl}_2 & \quad \text{SO}_2\text{Cl} \\
\text{TEA} & \quad \text{DMAP}
\end{align*}
\]

4-(Trifluoromethyl)benzene-1-sulfonyl chloride (1.409 g, 5.76 mmol) and DMAP (0.126 g, 1.03 mmol) were weighed into a 100 mL single necked round bottom flask. The flask was sealed with a rubber septum and purged with nitrogen. Dichloromethane (10 mL) and triethylamine (0.695 g, 6.87 mmol) were added to the flask and the solution was stirred for several minutes. In a separate flask, 2-(2-phenyl-1,3-dioxolane-2-yl)ethanol (1.009 g, 5.20 mmol) was weighed and dissolved in dichloromethane (10 mL). The alcohol solution was added to the reaction flask and the solution was stirred at room temperature overnight. The solution was washed with 10 wt% aqueous ammonium chloride (2 × 25 mL), 5 wt% aqueous sodium bicarbonate (1 × 25 mL) and lastly with saturated aqueous sodium chloride (25 mL). The organics were dried over sodium sulfate and concentrated to give a pink solid (1.719 g). The desired product was purified by silica column chromatography using a gradient of ethyl acetate and hexanes as the eluting solvent followed by recrystallization from carbon tetrachloride and hexanes. \(^1\)H NMR (400 MHz CDCl\(_3\)) \(\delta\) 7.91 (d, 2 H, \(J = 8.1\) Hz), 7.79 (d, 2 H, \(J = 8.1\) Hz), 7.30 (m, 5 H), 4.21 (t, 2 H, \(J = 7.2\) Hz), 3.92 (m, 2 H), 3.70 (m, 2 H), 2.28 (t, 2 H, \(J = 7.2\) Hz).
6.3 Body 2

The next two acid amplifiers, \textit{2AA} and \textit{2AB} are cyclic 1,3-diesters with an acetate trigger and either tolenesulfonate or \textit{p}-trifluoromethylbenzenesulfonate as the acid precursor. The synthesis of these AAs was done by Dr. Srividya Revuru. Both AAs are very reactive and readily decomposed. The decomposition was prevented by addition of a stabilizer, DMAP.

6.3.1 Dimethyl 2-hydroxysuccinate

2-Hydroxysuccinic acid (10.0 g, 74.6 mmol), \( \text{H}_2\text{SO}_4 \) (0.2 mL, 18 N) and methanol (75 mL) were mixed together and refluxed for 48 h. The reaction mixture was concentrated to remove the solvent and the residue was diluted with ethyl acetate (2 × 100 mL) and was washed with DI water (2 × 25 mL). The organic layer was washed with brine (2 × 25 mL) and dried and concentrated to afford a pure product (9.634 g, 89 %). \(^1\text{H} \text{NMR} \) (400 MHz \text{CDCl}_3) \( \delta \ 4.50 - 4.51 \) (m, 1 H), 4.10 (m, 1 H), 3.78 (s, 3 H), 3.69 (t, 3 H), 2.80 - 2.89 (m, 2 H).
6.3.2 Methyl 3,4-dihydroxybutanoate

The diester dimethyl 2-hydroxysuccinate (2 g, 12.3 mmol) was dissolved in THF (12 mL). BH$_3$·Me$_2$S (12.3 mL) was added dropwise as gas evolved. The solution was stirred for 30 min and NaBH$_4$ (0.042 g, 11.10 mmol) was added. The reaction mixture was stirred overnight and quenched with methanol. The solution was concentrated under reduced pressure and the resulting mixture was purified by running through a pad of silica gel (5/95 MeOH/CH$_2$Cl$_2$) to afford a pure product (1.534 g, 92.7 %). $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 4.11 (broad s, 1 H), 3.71 (s, 3 H), 3.65 (m, 2 H), 3.54 (m, 2 H), 2.50 - 2.56 (m, 2 H).
6.3.3 4-Hydroxydihydrofuran-2(3H)-one

The diol methyl 3,4-dihydroxybutanoate (1.534 g, 11.436 mmol) was dissolved in CHCl₃ (12 mL) and camphorsulfonic acid (0.318 g, 1.37 mmol) was added. The reaction mixture was refluxed for 24 h. The solvent was removed under reduced pressure to afford a pure product (0.98 g, 84%). $^1$H NMR (400 MHz CDCl₃) δ 4.67 (m, 1 H), 4.40 (dd, 1 H), 4.28 (d, 1 H), 3.37 (broad s, 1 H), 2.75 (dd, 1 H), 2.52 (1H, d).
6.3.4 5-Oxotetrahydrofuran-3-yl 4-methylbenzenesulfonate

\[
\text{The lactone 4-Hydroxydihydrofuran-2(3H)-one (2.00 g, 19.6 mmol) was dissolved in}\ CH_2Cl_2 (20 \text{ mL}). \text{Pyridine (2.324 g, 29.4 mmol) was added at 0 °C, followed by the addition of } p\text{-toluenesulfonyl chloride (5.60 g, 29.4 mmol). The reaction mixture was brought to room temperature and stirred for 5 h. The reaction was quenched with 5 % aq. HCl (20 mL) and diluted with CH}_2Cl_2 (50 \text{ mL}). \text{The organic layer was washed with 5 % aq. HCl (2} \times 25 \text{ mL), H}_2O (3 \times 30 \text{ mL}) \text{ and brine (1} \times 25 \text{ mL}). \text{The organic layer was dried over Na}_2SO_4 \text{ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography to get a white solid (1.95 g, 39 %). }^1H \text{ NMR (400 MHz CDCl}_3) \delta 7.77 (d, 2 \text{ H, } J = 8.3 \text{ Hz}), 7.37 (d, 2 \text{ H, } J = 8.0 \text{ Hz}), 5.26 (dt, J = 4.5 \text{ Hz, } J = 2.3 \text{ Hz}), 4.53 - 4.32 (m, 2 \text{ H}), 2.69 (m, 2 \text{ H}), 2.45 (s, 3 \text{ H}).} \]
The lactone 4-Hydroxydihydrofuran-2(3H)-one (2.00 g, 19.6 mmol) was dissolved in CH₂Cl₂ (20 mL). Pyridine (2.324 g, 29.4 mmol) was added at 0 °C, followed by 4-(trifluoromethyl)benzene-1-sulfonyl chloride (7.188 g, 29.4 mmol). The reaction mixture was brought to room temperature and stirred for 5 h. The reaction was then quenched with 5 % aq. HCl (20 mL) and diluted with CH₂Cl₂ (50 mL). The organic layer was then washed with 5 % aq. HCl (2 × 25 mL), H₂O (3 × 30 mL), brine (1 × 25 mL). The organic layer was dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was precipitated from hexane to give a white solid (2.05 g, 34 %). ¹H NMR (400 MHz CDCl₃) δ 8.05 (d, 2 H, J = 8.2 Hz), 7.86 (d, 2 H, J = 8.2 Hz), 5.37 (m, 1 H), 4.48 (m, 2 H), 2.79 (dt, 2 H).
6.3.6 4-(Tosyloxy)tetrahydrofuran-2-yl acetate (2AA)

5-Oxotetrahydrofuran-3-yl 4-methylbenzenesulfonate (2.00 g, 7.8 mmol) was dissolved in CH₂Cl₂ (20 mL) and DIBAL-H (1 M in toluene) (7.8 mL, 7.8 mmol) was added at -78 °C. The reaction mixture was stirred for 2 h at -78 °C. DMAP (1.144 g, 9.36 mmol), pyridine (2.469 g, 31.21 mmol) and acetic anhydride (2.343 g, 39.01 mmol) were added and reaction mixture was allowed to warm to room temperature and stirred for 24 h. The reaction mixture was quenched with NH₄Cl (5 mL) and stirred for 20 min. The contents were then transferred to a separatory funnel and washed with 1 M NaHSO₄ (3 × 50 mL), saturated NaHCO₃ (2 × 25 mL), brine (1 × 10 mL) and dried over Na₂SO₄. The solvent was removed under reduced pressure to give a crude product which was purified by column chromatography. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, 2 H, J = 8.3 Hz), 7.34 (d, 2 H, J = 8.0 Hz), 6.46 – 6.19 (m, 1 H), 5.20 (tt, 1 H), 4.24 – 3.95 (m, 3 H), 2.44 (s, 3 H), 2.43 - 2.37 (m, 1 H), 2.29 (ddd, 1 H), 2.01 (d, 3 H).
6.3.7 4-(4-(Trifluoromethyl)phenylsulfonyloxy)tetrahydrofuran-2-yl acetate (2AB)

The lactone 4-Hydroxydihydrofuran-2(3H)-one (0.400 g, 1.29 mmol) was dissolved in CH$_2$Cl$_2$ (10 mL) and DIBAL-H (1 M in toluene) (1.29 mL, 1.29 mmol) was added at -78 °C. The reaction mixture was stirred for 2 h at -78 °C. DMAP (0.189 g, 1.547 mmol), pyridine (0.408 g, 5.16 mmol) and acetic anhydride (0.387 g, 6.44 mmol) were added and the reaction mixture was allowed to warm to room temperature and stirred for 24 h. The reaction mixture was quenched with NH$_4$Cl (5 mL) and stirred for 20 min. The contents were then transferred to a separatory funnel and washed with 1 M NaHSO$_4$ (3 × 50 mL), saturated NaHCO$_3$ (2 × 25 mL), brine (1 × 10 mL) and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure to give a crude product which was purified by column chromatography. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, 2 H, J = 8 Hz), 7.83 (d, 2 H, J = 8 Hz), 6.43 - 6.22 (m, 1 H), 4.24 - 4.01 (m, 2 H), 5.38 - 5.13 (m, 1 H), 2.01 (d, 3 H, J = 4.8, Hz), 2.52 - 2.26 (m, 2 H). $^{19}$F NMR: δ -66.43.
6.4 Body 3

6.4.1 3-Hydroxy-3-methylbutyl methanesulfonate (3HD)

\[
\begin{align*}
\text{OH} & \quad + \quad \text{Me-SO}_2\text{Cl} \\
\text{CH}_2\text{Cl}_2 & \quad \text{TEA} \\
\rightarrow & \quad \text{OH} \quad \text{O}_2\text{S}
\end{align*}
\]

3-Methyl-1,3-butanediol (1.258 g, 12.1 mmol), triethylamine (2.067 g, 20.43 mmol) and dichloromethane (50 mL) were added to a 250 mL two-neck flask that was purged with nitrogen. The flask was cooled to 0 °C and the solution was stirred for five minutes. Methanesulfonyl chloride (1.136 g, 9.9 mmol) [9] dissolved in 1 mL dichloromethane was added dropwise to the flask and the solution was stirred at 0 °C for 25 minutes. Hydrochloric acid (1.6 M, 10 mL) was added to the solution at 0 °C. The organics were washed with DI water (2 × 25 mL) and saturated sodium chloride (25 mL). The organics were dried over sodium sulfate and concentrated to give an oil (0.777 g, 4.26 mmol, 43 %). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 1.27 (s, 6 \text{ H}), 1.94 (t, 2 \text{ H}, J = 8.0 \text{ Hz}), 3.00 (s, 3 \text{ H}), 3.39 (t, 2 \text{ H}, J = 8.0 \text{ Hz}).\)
6.4.2 3-hydroxy-3-methylbutyl (7,7-dimethyl-2-oxobicyclo[2.2.1]-heptan-1-yl)methanesulfonate (3HK)

To a solution of 3-methyl-1,3-butane diol (2.08 g, 20 mmol), TEA (1.54 g, 15 mmol) and DMAP (0.24 g, 2 mmol) in CH$_2$Cl$_2$ (30 mL) was added camphorsulfonyl chloride (2.50 g, 10 mmol) dissolved in CH$_2$Cl$_2$ (20 mL). The solution was stirred at room temperature for 22 h. The organics were washed with 0.5 M HCl (3 × 50 mL), saturated aqueous NaHCO$_3$ (50 mL) and saturated aqueous NaCl (50 mL). The organics were dried over Na$_2$SO$_4$ and concentrated to give the pure product (1.92 g, 60%). $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 4.45 (m, 2 H), 3.58 (d, 1 H, 15 Hz), 2.97 (d, 1 H, J = 15 Hz), 2.42 (m, 2 H), 2.18 (t, 1 H, J = 4.5 Hz), 2.03 (m, 1 H), 1.95 (d, 1 H, J = 4.1 Hz), 1.92 (d, 2 H, 7.1 Hz), 1.65 (m, 1 H), 1.42 (ddd, 1 H, J = 12 Hz, J = 9 Hz, J = 4 Hz), 1.27 (s, 6 H), 1.09 (s, 3 H), 0.86 (s, 3 H).
6.4.3 3-hydroxy-3-methylbutyl 4-methylbenzenesulfonate (3HA)

To a solution of 3-methyl-1,3-butane diol (5.22 g, 50 mmol) in pyridine (40 mL) was added toluenesulfonyl chloride (4.8 g, 25 mmol). The solution was stirred at 0 °C for 5 h. The reaction mixture was diluted with ethyl acetate (100 mL) and washed with 1 M HCl (10 × 50 mL), saturated aqueous NaHCO₃ (50 mL) and saturated aqueous NaCl (50 mL). The organics were dried over Na₂SO₄ and concentrated to give a white solid [10] (4.27 g, 66 %). ¹H NMR (400 MHz CDCl₃) δ 7.77 (d, 2 H, J = 8.3 Hz), 7.33 (d, 2 H, J = 8.3 Hz), 4.18 (t, 2 H, J = 6.8 Hz), 2.43 (s, 3 H), 1.84 (t, 2 H, J = 6.8 Hz), 1.19 (s, 6 H).
6.4.4 3-Hydroxy-3-methylbutyl 4-(trifluoromethyl)benzenesulfonate (3HB)

To a solution of 3-methyl-1,3-butane diol (1.9 g, 18.2 mmol) in pyridine (15 mL) was added 4-(trifluoromethyl)benzene-1-sulfonyl 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 NaHCO₃ (50 mL) and saturated aqueous NaCl (50 mL). The organics were dried over Na₂SO₄ and concentrated to give a white low melting solid [11-13] (3.33 g, 71 %). ¹H NMR (400 MHz CDCl₃) 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 C₁₂H₁₅F₃O₄S: C, 46.15; H 4.84. Found: C, 46.14; H, 4.90.
6.4.5 3-Hydroxy-3-methylbutyl 2-(trifluoromethyl)benzenesulfonate (3HF)

To a solution of 3-methyl-1,3-butane diol (2.5 g, 21 mmol) and TEA (1.63 g, 16 mmol) in CH₂Cl₂ (15 mL) was added 2-(trifluoromethyl)benzene-1-sulfonyl chloride (2.03 g, 8.3 mmol) dissolved in CH₂Cl₂ (20 mL). The solution was stirred at room temperature for 7 h. The reaction mixture was diluted with CH₂Cl₂ (75 mL) and washed with 1 M HCl (2 × 25 mL), saturated aqueous NaHCO₃ (25 mL) and saturated aqueous NaCl (25 mL). The organics were dried over Na₂SO₄ and concentrated to give a crude mixture. Silica gel chromatography with ethyl acetate in hexanes yielded the desired product as an oil (1.73 g, 66%). ¹H NMR (400 MHz CDCl₃) 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 C₁₂H₁₅F₃O₄S: C, 46.15; H 4.84. Found: C, 45.73; H, 4.88.
6.4.6 3-Hydroxy-3-methylbutyl 2,3,4,5,6-pentafluorobenzenesulfonate (3HG)

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$_2$Cl$_2$ (7 mL) at 0 °C was added pentafluorobenzenesulfonyl 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 room temperature for 15 min. The organics were extracted with CH$_2$Cl$_2$ and washed with 0.5 M HCl (20 mL) and saturated aqueous NaCl (20 mL). The organics were dried over Na$_2$SO$_4$ 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 solid (0.69 g, 66 %). $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 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$_5$O$_4$S: C, 39.53; H 3.32. Found: C, 39.54; H, 3.22.
6.4.7 2-Methyl-4-(tosyloxy)butan-2-yl acetate (3AA)

To a mixture of the alcohol 3HA (0.500 g, 1.937 mmol), ZrOCl₂·8H₂O (0.0031 g, 0.5 mol%) in CH₂Cl₂ (5 mL), acetyl chloride (0.304 g, 3.87 mmol) was added and the reaction was stirred overnight at room temperature [14]. The reaction was diluted with CH₂Cl₂ (5 mL) and washed with saturated sodium bicarbonate (2 × 10 mL), brine (1 × 10 mL) and dried. The solvent was evaporated to get a crude product which was purified by silica gel chromatography. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, 2 H, J = 8.2 Hz), 7.33 (d, 2 H, J = 7.9 Hz), 4.26 (dt, 3 H, J = 13.5 Hz, J = 6.9 Hz), 2.43 (s, 3 H), 2.14 - 2.07 (m, 2 H), 1.54 (s, 6 H), 1.59 (s, 3 H).

The alcohol 3HA (0.753 g, 2.91 mmol) and DMAP (0.178 g, 1.46 mmol) were weighed into a 100 mL single necked round bottom flask with a small stir bar. The flask was sealed with a rubber septum and purged with nitrogen. Dichloromethane (24 mL) was added to the flask followed by TEA (1.192 g, 11.78 mmol). Lastly, acetic anhydride (1.196 g, 11.72 mmol) was added dropwise. The solution was stirred overnight at room temperature. The reaction was quenched with saturated aqueous sodium bicarbonate and washed with saturated aqueous ammonium chloride to remove the DMAP and TEA. The organic phase was dried over sodium sulfate and concentrated to give an oil (0.549 g crude). The crude product was purified on a silica column to give an orange oil (0.329 g, 34 % ).
To a mixture of the alcohol 3HB (0.500 g, 1.6 mmol), in CH₂Cl₂ (5 mL) was added ZrOCl₂·8H₂O (0.0025 g, 0.5 mol%) and acetyl chloride (0.251 g, 3.2 mmol). The reaction was stirred overnight at room temperature. The reaction on was diluted with CH₂Cl₂ (5 mL) and washed with saturated sodium bicarbonate (2 × 10 mL), brine (1 × 10 mL) and dried. The solvent was evaporated to get a crude product which was purified by silica gel chromatography. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, 2 H, J = 8.0 Hz, 7.82 (d, 2 H, J = 8.0 Hz), 4.33 (t, 2 H, J = 6.8 Hz), 2.14 (t, 2 H, J = 6.8 Hz), 1.60 (s, 3 H), 1.56 (s, 6 H).
6.4.9 3-methoxy-3-methylbutyl (7,7-dimethyl-2-oxobicyclo[2.2.1]-heptan-1-yl)methanesulfonate (3MK)

To a solution of 3-methoxy-3-methylbutane-1-ol (2.32 g, 20 mmol), TEA (1.52 g, 15 mmol) and DMAP (0.24 g, 2 mmol) in CH$_2$Cl$_2$ (30 mL) was added camphorsulfonyl chloride (2.51 g, 10 mmol) dissolved in CH$_2$Cl$_2$ (20 mL). The solution was stirred at room temperature for 22 h. The organics were washed with 0.5 M HCl (3 x 50 mL), saturated aqueous NaHCO$_3$ (50 mL) and saturated aqueous NaCl (50 mL). The organics were dried over Na$_2$SO$_4$ and concentrated to give a crude mixture. Silica gel chromatography with ethyl acetate in hexanes yielded the desired product (2.24 g, 60%).

$^1$H NMR (400 MHz CDCl$_3$) $\delta$ 4.37 (m, 2 H), 3.58 (d, 1 H, J = 15 Hz), 3.27 (s, 3 H), 2.96 (d, 1 H, J = 15 Hz), 2.42 (m, 2 H), 2.10 (t, 1 H, J = 4.5 Hz), 2.02 (m, 1 H), 1.95 (d, 2 H, J = 7.3 Hz), 1.91 (d, 1 H, 3.6 Hz), 1.64 (ddd, 1 H, J = 14 Hz, J = 9 Hz, J = 4.7 Hz), 1.42 (ddd, 1 H, J = 12.5 Hz, J = 9 Hz, J = 4 Hz), 1.18 (s, 6 H), 1.10 (s, 3 H), 0.86 (s, 3 H).
6.4.10 3-methoxy-3-methylbutyl 4-methylbenzenesulfonate (3MA)

To a solution of 3-methoxy-3-methylbutane-1-ol (8.86 g, 75 mmol), TEA (5.17 g, 50 mmol) in dichloromethane (75 mL) was added p-toluenesulfonyl chloride (4.76 g, 25 mmol). The solution was stirred at room temperature for 7 h. The reaction mixture was washed with 1 M HCl (3 × 50 mL), saturated aqueous NaHCO₃ (50 mL) and saturated aqueous NaCl (30 mL). The organics were dried over Na₂SO₄ and concentrated to give an oil. The crude mixture was purified by silica chromatography to give the desired product (4.60 g, 67%). ¹H NMR (400 MHz CDCl₃) δ 7.77(d, 2 H, J = 8.1 Hz), 7.32 (d, 2 H, J = 8.1 Hz), 4.11 (t, 2 H, J = 7.3 Hz), 3.08 (s, 3 H), 2.43 (s, 3 H), 1.85 (t, 2 H, J = 7.3 Hz), 1.10 (s, 6 H).
6.4.11 3-Methoxy-3-methylbutyl 4-(trifluoromethyl)benzenesulfonate (3MB)

To a solution of 3-methoxy-3-methylbutane-1-ol (0.58 g, 4.9 mmol) in pyridine (5 mL) was added 4-(trifluoromethyl)benzene-1-sulfonyl chloride (0.98 g, 4 mmol). The solution was stirred at room temperature 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 NaHCO₃ (25 mL) and saturated aqueous NaCl (25 mL). The organics were dried over Na₂SO₄ and concentrated to give an oil (0.53 g, 40%). ¹H NMR (400 MHz CDCl₃) 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 C₁₃H₁₇F₃O₄S: C, 47.85; H 5.25. Found: C, 47.72; H, 5.05.
6.4.12 3-Methoxy-3-methylbutyl 2-(trifluoromethyl)benzenesulfonate (3MF)

To a solution of 3-methoxy-3-methylbutane-1-ol (2.8 g, 24 mmol) and TEA (1.6 g, 16 mmol) in CH₂Cl₂ (15 mL) was added 2-(trifluoromethyl)benzene-1-sulfonyl chloride (1.9 g, 8 mmol) dissolved in CH₂Cl₂ (20 mL). The solution was stirred at room temperature for 4 h. Saturated aqueous NaHCO₃ (15 mL) was added to the solution and the mixture was stirred at room temperature for 30 min. The organics were extracted with CH₂Cl₂ (75 mL) and washed with 1 M HCl (2 × 25 mL), saturated aqueous NaHCO₃ (25 mL) and saturated aqueous NaCl (25 mL). The organics were dried over Na₂SO₄ and concentrated to give a crude mixture. Silica gel chromatography with ethyl acetate in hexanes yielded the desired product (2.1 g, 81 %). ¹H NMR (400 MHz CDCl₃) 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, 3 H), 1.92 (t, 2 H, J = 7.5 Hz) 1.13 (s, 6 H). Anal. Calcd. For C₁₃H₁₇F₃O₄S: C, 47.85; H 5.25. Found: C, 47.95; H, 5.11.
6.4.13  3-Methoxy-3-methylbutyl  2,3,4,5,6-pentafluorobenzene-
sulfonate (3MG)

To a solution of 3-methoxy-3-methylbutane-1-ol (1.07 g, 9 mmol) and TEA (0.61 g, 6 mmol) in CH₂Cl₂ (12 mL) was added pentafluorobenzenesulfonyl chloride (0.99 g, 3.7 mmol). The solution was stirred at room temperature for 2 h. Saturated aqueous NaHCO₃ (12 mL) was added to the solution and the mixture was stirred at room temperature for 30 min. The organics were extracted with CH₂Cl₂ (50 mL) and washed with 0.5 M HCl (3 × 40 mL), saturated aqueous NaHCO₃ (40 mL) and saturated aqueous NaCl (40 mL). The organics were dried over Na₂SO₄ and concentrated to give a crude mixture. Silica gel chromatography with ethyl acetate in hexanes yielded the desired product as an oil (0.68 g, 51 %). ¹H NMR (400 MHz CDCl₃) 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 C₁₂H₁₃F₅O₄S: C, 41.38; H, 3.76. Found: C, 41.37; H, 3.77.
6.5 Body 4

6.5.1 General Strategy

We identified 3-hydroxybutan-2-one [15] as a versatile starting material for the synthesis of acid amplifiers with a range of reactivity. This compound is commercially available and inexpensive. With this synthon, acid amplifiers are synthesized with only two synthetic transformations. AA reactivity is further modified with a third transformation. The first reaction is to attach an acid precursor by reacting a sulfonyl chloride with the alcohol. The second step is to react the ketone with a Grignard reagent yielding a tertiary alcohol. The trigger is modified in a third reaction by converting the alcohol to an ether or ester. Many acid amplifiers with a range of reactivity can be synthesized by combining various sulfonyl chlorides, Grignard reagents, and trigger options.

![Figure 6.1](image)

**Figure 6.1** Generic synthetic scheme for acid amplifiers starting with 3-hydroxybutan-2-one.

The starting compound 3-hydroxy-2-butanone purchased from Aldrich comes as a solid dimer. We determined this from solubility properties and $^1$H NMR. Reactions using the dimer resulted in poor yields and mixtures of products. However, we thermally crack the dimer by short path distillation to give a pale yellow liquid.
6.5.2 3-Oxobutane-2-yl 4-methylbenzenesulfonate

\[\text{AcOH} + \text{phenylsulfonic acid} \xrightarrow{\text{TEA, } \text{CH}_2\text{Cl}_2} \text{AcO} - \text{O} - \text{S} - \text{O}_2\text{S} - \text{Ph}\]

\(p\)-Toluenesulfonyl chloride (10.009 g, 52.5 mmol) was weighed into a 500 mL single-neck round bottom flask with a medium spin bar. The flask was sealed with a rubber septum and purged with nitrogen. Dichloromethane (105 mL) was added to the flask via syringe. The flask was cooled to 0 \(^\circ\)C and triethylamine (18.3 mL, 131.3 mmol) was added. The solution was stirred for ~3 minutes then 3-hydroxy-2-butanone (9.269 g, 105.2 mmol) was added. The solution was stirred for 0.5 h at 0 \(^\circ\)C and 21 h at room temperature. The solution was rinsed with saturated aqueous ammonium chloride until the pH became acidic, then once with saturated aqueous sodium chloride. The organics were dried over sodium sulfate and concentrated to give an oil (6.561 g, 27.1 mmol, 52 %). \(^1\)H NMR (400 MHz CDCl\(_3\)) \(\delta\) 7.79 (d, 2 H, \(J = 8.1\) Hz), 7.34 (d, 2 H, \(J = 8.1\) Hz), 4.73 (q, 1 H, \(J = 7.0\) Hz), 2.44 (s, 3 H), 2.19 (s, 3 H), 1.33 (d, 3 H, \(J = 7.0\) Hz).
6.5.3 3-Oxobutan-2-yl 4-(trifluoromethyl)benzenesulfonate

\[
\begin{align*}
\text{CH}_3\text{C(O)OH} & \quad + \quad \begin{array}{c}
\text{F}_3\text{C} \quad \text{SO}_2\text{Cl}
\end{array} \\
\xrightarrow{\text{TEA}} \\
\text{CH}_2\text{Cl}_2 \\
\end{align*}
\]

4-(Trifluoromethyl)benzene-1-sulfonyl chloride (7.954 g, 20.4 mmol) was weighed into a 250 mL single-neck round bottom flask with a medium spin bar. The flask was sealed with a rubber septum and purged with nitrogen. The flask was cooled to 0 °C and dichloromethane (100 mL) was added followed by triethylamine (7 mL, 50 mmol). The solution was stirred for ~3 minutes then 3-hydroxy-2-butanone (7.954 g, 90.3 mmol) was added. The solution was stirred for 3 h at 0 °C. The solution was rinsed with saturated aqueous ammonium chloride until the pH became acidic. The organics were dried over sodium sulfate and concentrated to give an oil (15.25 g, 95 % purity, 17 mmol, 87 %).

\textsuperscript{1}H NMR (400 MHz CDCl\textsubscript{3}) \(\delta\) 8.06 (d, 2 H, \(J = 8.4\) Hz), 7.83 (d, 2 H, \(J = 8.4\) Hz), 4.87 (q, 1 H, \(J = 7.0\) Hz), 2.22 (s, 3 H), 1.40 (d, 3 H, \(J = 7.0\)).
6.5.4 3-Hydroxy-3-methylbutan-2-yl 4-methylbenzenesulfonate (4HA)

\[
\begin{align*}
\text{MeMgBr} & \quad \text{Et}_2\text{O} \\
\text{3-Oxobutan-2-yl 4-methylbenzene-sulfonate (6.47 g, 26.7 mmol) was weighed into a} & \\
\text{500 mL two-necked round bottom flask with a large spin bar. The flask was sealed with} & \\
rubber septum and purged with nitrogen. The compound was dissolved in diethyl ether & \\
(300 mL) and the solution was cooled to \(-78^\circ\text{C}\). Methylmagnesium bromide [16] (3 M,} & \\
11 mL, 33 mmol) was added dropwise to the solution and the mixture was stirred at \(-78^\circ\text{C}\) for 1.5 h. The reaction was quenched with acetic acid at \(-78^\circ\text{C}\). The solution was brought to room temperature and saturated aqueous ammonium chloride was added to dissolve the precipitates. The solution was extracted with diethyl ether and the extracts were combined and washed with saturated aqueous sodium bicarbonate. The organic phase was dried over sodium sulfate and concentrated to give an oil which turns green upon vacuum drying. The crude product was purified by silica chromatography using hexane/ethyl acetate as the mobile phase. The starting material elutes from the column first then the desired product (4.398 g, 17.0 mmol, 64%). \( ^1\text{H NMR (400 MHz CDCl}_3\) \(\delta 7.79 \text{ (d, 2 H, J = 8.0 Hz), 7.33 (d, 2 H, J = 8.0 Hz), 4.28 (q, 1 H, J = 6.5 Hz), 2.43 (s, 3 H), 1.22 (d, 3 H, J = 6.5 Hz), 1.14 (s, 3 H), 1.13 (s, 3 H).} \)
6.5.5 3-Hydroxy-3-methylbutan-2-yl 4-(trifluoromethyl)benzenesulfonate (4HB)

3-Oxobutan-2-yl 4-(trifluoromethyl)benzenesulfonate (2.011 g, 6.8 mmol) was weighed into a 250 mL two-neck round bottom flask with a medium stir bar. The flask was sealed with rubber septum and purged with nitrogen. The compound was dissolved in diethyl ether (70 mL) and the solution was cooled to -78 °C. Methylmagnesium bromide (3 M, 2.9 mL, 8.7 mmol) was added dropwise to the solution and the mixture was stirred at -78 °C for 1.5 h. The reaction was quenched with acetic acid at -78 °C. The solution was brought to room temperature and saturated aqueous ammonium chloride was added to dissolve the precipitates. The solution was extracted with diethyl ether and the extracts were combined and washed with saturated aqueous sodium bicarbonate. The organic phase was dried over sodium sulfate and concentrated to give an oil. The crude product was purified by silica chromatography using hexane/ethyl acetate as the mobile phase. After purification an orange oil was collected (0.728 g, 2.3 mmol, 34 %). The product turned to a green solid after drying in vacuo overnight. $^1$H NMR (400 MHz CDCl$_3$) δ 8.05 (d, 2 H, J = 8.2 Hz), 7.81 (d, 2 H, J = 8.2 Hz), 4.60 (q, 1 H, J = 6.5 Hz), 1.27 (d, 3 H, J = 6.5 Hz), 1.18 (s, 3 H), 1.16 (s, 3 H).
6.5.6 2-Methyl-3-(tosyloxy)butan-2-yl acetate (4AA)

3-Hydroxy-3-methylbutan-2-yl 4-methylbenzenesulfonate (0.752 g, 2.9 mmol) and DMAP (0.178 g, 1.4 mmol) [17] were weighed into a 100 mL single-neck round bottom flask with a small spin bar. The flask was sealed with a rubber septum and purged with nitrogen. Dichloromethane (24 mL) was added to the flask followed by triethylamine (1.192 g, 11.7 mmol) and acetic anhydride (1.196 g, 11.7 mmol). The solution was stirred at room temperature for 24 h. The reaction was quenched with aqueous sodium bicarbonate. The organic layer was separated and washed with aqueous ammonium chloride until the pH became acidic. The organics were dried over sodium sulfate and concentrated. The crude product was purified by silica gel chromatography using hexane/ethyl acetate as the mobile phase. The first compound to elute from the column is the desired product. After purification an orange oil was collected (0.392 g, 0.9 mmol, 31%). The product is stable in the freezer for 1 month but decomposes and turns black overnight at room temperature. $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 7.78 (d, 2 H, $J = 8.0$ Hz), 7.32 (d, 2 H, $J = 8.0$ Hz), 4.95 (q, 1 H, $J = 6.5$ Hz), 2.42 (s, 3 H), 1.85 (s, 3 H), 1.39 (s, 6 H), 1.20 (d, 3 H, $J = 6.5$ Hz).
6.5.7 2-Methyl-3-(4-(trifluoromethyl)phenylsulfonyloxy)butan-2-yl acetate (4AB)

\[
\begin{align*}
\text{OH} & \quad \text{O} \\
\text{S} & \quad \text{O}_2 \quad \text{CF}_3 \\
\end{align*}
\]

3-(3-(hydroxypropan-2-yloxy)-3-methylbutan-2-yl 4-(trifluoromethyl)benzenesulfonate (0.05 g, 0.15 mmol) and DMAP (0.01 g, 0.075 mmol) were weighed into a 10 mL single-neck round bottom flask with a small spin bar. The flask was sealed with a rubber septum and purged with nitrogen. Dichloromethane (2 mL), triethylamine (0.3 g, 3 mmol) and acetic anhydride (0.6 g, 6 mmol) were added to the flask. The solution was stirred at -40 °C for 1 h. The reaction was diluted with dichloromethane and washed with aqueous sodium bicarbonate until the formation of bubbles had stopped. The organic layer was separated and washed with aqueous ammonium chloride and sodium chloride then dried over sodium sulfate and concentrated. The synthesis of this compound was not successful. All attempts led to the final product immediately decomposing upon work up.
6.5.8 3-Hydroxy-3-methylhex-5-en-2-yl 4-methylbenzenesulfonate

A clean oven dried 25 mL single-neck round bottom flask with a small stir bar was sealed with a rubber septum and purged with nitrogen. The flask was cooled to -78 °C. In a separate flask 3-oxobutane-2-yl 4-methylbenzenesulfonate (0.108 g, 0.44 mmol) was diluted in anhydrous diethyl ether (1.5 mL) and added to the reaction flask. Allylmagnesium bromide (1 M, 0.4 mL, 0.4 mmol) was added to the reaction flask and the solution was stirred for 1 h. The reaction was quenched with acetic acid (0.4 mmol) at -78 °C. The solution was extracted with diethyl ether (3 × 10 mL) and the extracts were combined, dried over sodium sulfate and concentrated to give an oil (0.059 g, 0.21 mmol, 53 %). \(^1\)H NMR (400 MHz CDCl\(_3\)) \(\delta 7.78\) (d, 2 H, \(J = 8.0\) Hz), \(7.32\) (d, 2 H, \(J = 8.0\) Hz), \(5.77\) (m, 1 H), \(5.12\) (m, 2 H) \(4.53\) (q, 1 H, \(J = 4.2\)), \(2.43\) (s, 3 H), \(2.20\) (m, 2 H), \(1.23\) (d, 3 H, \(J = 4.2\) Hz), \(1.09\) (s, 3 H).
6.6 Body 5

The synthesis of body of body 5 AAs and their intermediates were done by Sarah Gibbons, Dan Freedman (Ph.D.) and Preeti Dahr (Ph.D.) in the chemistry department at SUNY New Paltz, NY.

6.6.1 1-phenylcyclohexane-1,2-diol

\[
\text{A} = \text{I}_2, \text{K}_2\text{CO}_3, \text{K}_2\text{OsO}_2(\text{OH})_4 \text{ and Quinuclidine}
\]

Iodine, I\(_2\), (7.23 g, 28.5 mmol), potassium carbonate, K\(_2\)CO\(_3\), (7.88 g, 57 mmol), potassium osmate, K\(_2\)OsO\(_2\)(OH)\(_4\), (0.035 g, 0.095 mmol), and quinuclidine, (0.0528 g, 0.475 mmol) were placed into a round bottom flask. Water (25 mL) and tert-butanol (25 mL) were added and the mixture was heated with a heat gun until two distinct layers were formed [18]. Subsequently, 1-phenylcyclohexene (3.00 g, 19 mmol) was added dropwise. The reaction was stirred in the dark for three days. Sodium sulfite, Na\(_2\)SO\(_3\), (5.8 g, 46 mmol) was added slowly and the resulting solution was stirred for an additional 2 days. The solution was extracted with dichloromethane (3 × 50 mL) and the organic phase was dried over MgSO\(_4\). The solvent was removed via rotary evaporation followed by drying in vacuo. The product was isolated as a white solid with a yield of (2.58 g, 70.5 %). \(^1\)H NMR (CDCl\(_3\), 300MHz) \(\delta\) 7.48-7.52 (m, 2 H), 7.40-7.34 (m, 2 H), 7.28-7.23 (tt, 1 H), 3.99 (dd, 1 H, \(J = 11.0\) Hz, \(J = 4.7\) Hz), 1.93-1.25 (m, 8 H).
6.6.2 2-hydroxy-2-phenylcyclohexyl 4-(trifluoromethyl)benzene-sulfonate (5HB)

1-phenylcyclohexane-1,2-diol (2.13 g, 11.1 mmol) was placed into a three-neck round bottom flask equipped with a stir bar and N\textsubscript{2} inlet. Dichloromethane (20 mL) was added. Triethylamine (5.60 g, 55.3 mmol) was added to the flask through a 5 cm column of activated alumina. 4-(trifluoromethyl)benzene-1-sufonyl chloride (2.98 g, 12.2 mmol) was added to the flask and the reaction was stirred for 14 hours. The solution was washed with saturated sodium bicarbonate (2 × 30 mL) and a 10 % aqueous triethylamine solution (25 mL). The organic phase was dried over MgSO\textsubscript{4} and the solvent was removed via rotary evaporation. The crude product was purified by filtering it through ~3 cm of silica gel in a glass fritted funnel using 50/50 hexane/ethyl acetate. Addition of hexane precipitated the product as a white solid. (1.25g, 30 %) \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz) δ 7.47 (d, 2 H, J = 8.53 Hz), 7.41 (d, 2 H, J = 8.53 Hz), 7.20-7.06 (m, 5 H), 4.87 (dd, 1 H, J = 11.3 Hz, J = 5.5 Hz), 3.31-1.42 (m, 8 H).
6.6.3 1-phenyl-2-(4-(trifluoromethyl)phenylsulfonyloxy)cyclohexyl acetate (5AB)

![Chemical Structure]

Compound 5HB (0.5 g, 1.25 mmol) was weighed into a three-neck flask equipped with a stir bar and a N\textsubscript{2} inlet. Acetonitrile (25 mL), acetic anhydride (0.255 g, 2.5 mmol) and cobalt (II) chloride (0.00812 g, 0.0625 mmol) were added and the reaction was refluxed for 3 hours [19]. The solvent was removed \textit{via} rotary evaporation to give an oil. Silica gel chromatography with 9:1 hexane/ethyl acetate gave the pure product. The product was isolated as a white solid (0.224 g, 40 %). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz) \(\delta\) 7.50 (d, 2 H, \(J = 8.81\) Hz), 7.45 (d, 2 H, \(J = 8.81\) Hz), 6.99-7.16 (m, 5 H), 4.36 (t, 1 H, \(J = 7.43\) Hz), 2.96 (ddd, 1 H, \(J = 17.2\) Hz, \(J = 5.5\), Hz \(J = 3.0\) Hz), 2.15 (s, 3 H), 2.27-1.20 (m, 7 H). IR (ATR) \(v_{C=O}\) = 1721 cm\textsuperscript{-1}.
6.7 Body 6

6.7.1 1-Methylcyclohexane-1,2-diol

Potassium ferricyanide, K₃Fe(CN)₆, (20.5 g, 62.4 mmol), potassium carbonate, K₂CO₃, (8.62 g, 62.4 mmol), potassium osmate, K₂OsO₂(OH)₄, (0.092 g, 0.312 mmol), and quinuclidine, C₇H₁₃N, (0.139 g, 1.56 mmol) were placed into a round bottom flask. Water (25 mL) and tert-butanol (25 mL) were added and the mixture was heated with a heat gun until one distinct layer was formed [20]. 1-methylcyclohexene (2.991 g, 31.1 mmol) was added dropwise and the reaction was stirred in the dark for three days. Sodium sulfite, Na₂SO₃, (15.7 g, 124.8 mmol) was added slowly, followed by water (35 mL) and the resulting solution was stirred for an additional hour. The solution was poured into a separator funnel with 50 mL dichloromethane and water was added until the aqueous layer became on top of the dichloromethane. The solution was extracted with dichloromethane (4 × 50 mL) and the organic phase was dried over Na₂SO₄. The solvent was removed via rotary evaporation followed by drying in vacuo. The product was isolated as a white solid (2.675 g, 66%). mp 69-70 °C. ¹H NMR (CDCl₃, 400 MHz) δ 3.38 (m, 1 H), 1.26-1.77 (m, 8 H), 2.01 (s, 1 H), 1.90 (s, 1 H), 1.22 (s, 3 H)
6.7.2 2-Hydroxy-2-methylcyclohexyl 4-(trifluoromethyl)benzene-sulfonate (6HB)

To a solution of 1-methylcyclohexane-1,2-diol (1.57 g, 12 mmol) in pyridine (17 mL) was added 4-(trifluoromethyl)benzene-1-sulfony chloride (2.44 g, 10 mmol). The solution was stirred at room temperature for 20 hours. The solution was diluted with ethyl acetate (25 mL) and washed with 1 M hydrochloric acid (6 × 25 mL), saturated sodium bicarbonate (1 × 25 mL) and saturated sodium chloride (25 mL). The organics were dried over sodium sulfate and concentrated to give an oil. The crude product was purified by column chromatography using silica gel as the stationary phase and eluting with 70 % hexane / 30 % ethyl acetate to give the desired product as a white solid (2.31 g, 6.8 mmol, 68 %). mp 59-60 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ, 8.04 (d, 2 H, J = 8.2 Hz), 7.81 (d, 2 H, J = 8.2 Hz), 4.47 (d, 1 H), 1.23-1.89 (m, 9 H), 1.60 (s, 3 H); $^{13}$C NMR (400 MHz, CDCl$_3$) δ 141.28, 135.60 (q), 128.40, 126.52, 124.61, 122.01, 88.53, 70.88, 37.88, 28.44, 27.12, 23.68, 20.82. $^{19}$F NMR (400 MHz, CDCl$_3$/C$_6$F$_6$) δ -66.37. IR (ATR) 3544, 3453, 2936, 2863, 1736, 1365, 1319, 1170, 1129, 1062, 879, 838, 712 cm.$^{-1}$ Anal. Calcd. For C$_{14}$H$_{17}$SO$_4$F$_3$: C, 49.7; H, 5.0. Found C, 49.7; H, 5.0.
6.7.3  1-Methyl-2-(4-(trifluoromethyl)phenylsulfonyloxy)cyclohexyl acetate (6AB)

![Chemical Structure]

Compound 6HB (2.27 g, 6.7 mmol) and DMAP (0.2 g, 1.6 mmol) [17] were weighed into a 50 mL single-neck flask equipped with a stir bar and reflux condenser. The flask was purged with nitrogen. Dichloromethane (15 mL), TEA (0.84 g, 8.3 mmol) and acetic anhydride (3.426 g, 33.5 mmol) were added to the flask via syringe. The solution was refluxed for 22 h. The solution was diluted with dichloromethane (25 mL) and washed with 1 M HCl (1 × 25 mL), saturated aqueous NaHCO₃ (2 × 25 mL) and saturated aqueous NaCl (1 × 25 mL). The organics were dried over Na₂SO₄ and concentrated to give an oil. Silica gel chromatography with hexane and ethyl acetate yielded the desired product as a white solid (1.174 g, 3.0 mmol, 45 %). mp 110-111 °C. IR (ATR) νC=O = 1736 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, 2 H, J = 8.0 Hz), 7.80 (d, 2 H, J = 8.4 Hz), 4.55 (m, 1 H), 2.55 (m, 1 H), 1.90 (m, 4 H), 1.68 (m, 2 H), 1.45-1.33 (m, 7 H). ¹³C NMR (400 MHz, CDCl₃) δ 169.95, 141.39, 135.44 (q), 128.28, 126.60, 124.47, 121.81, 86.85, 81.37, 33.08, 28.49, 22.80, 22.34, 20.94. ¹⁹F NMR (400 MHz, CDCl₃/C₆F₆) δ -66.42. IR (ATR) 2937, 2860, 1735, 1366, 1321, 1230, 1178, 1132, 1064, 714 cm⁻¹

6.8 Body 7
The synthesis of body of body 5 AAs and their intermediates were done by Sarah Gibbons, Dan Freedman (Ph.D.) and Preeti Dahr (Ph.D.) in the chemistry department at SUNY New Paltz, NY.

6.8.1 1-benzyl-1-cyclohexanol

Ether was passed through activated aluminum oxide into a round bottom flask containing magnesium turnings (1.01 g, 41.5 mmol). Benzyl bromide (7.10 g, 41.5 mmol) was added dropwise. The reaction was cooled with an ice bath as needed. Cyclohexanone (3.4 g, 34.6 mmol) was added dropwise and the mixture was stirred overnight under nitrogen. The solution was poured over ice and 3N HCl was added until the solids completely dissolved. The mixture was extracted with diethyl ether (3 × 50 mL). The diethyl ether layer was washed with saturated sodium bicarbonate and saturated sodium chloride and then dried over MgSO₄. The solvent was removed via rotary evaporation, yielding 1-benzyl-1-cyclohexanol as an oil (6.50 g, ca. 100 %). ¹H NMR indicated that the product was contaminated with 1,2-diphenylethane. ¹H NMR (CDCl₃, 300 MHz) δ 7.36-7.17 (m, 5 H), 2.76 (s, 2 H), 1.70-1.10 (m, 10 H).
6.8.2 1-Benzylcyclohexene

1-benzyl-1-cyclohexanol (6.37 g, 33.5 mmol), toluene (40mL), and \( p \)-toluenesulfonic acid, monohydrate (0.20 g, 1.05 mmol) were placed into a 100 mL round bottom flask equipped with a Dean-Stark trap. The mixture was refluxed overnight to yield 1-benzylcyclohexene (5.79 g, ca. 100 %). \(^1\)H NMR showed that the product was contaminated with a small amount of 1,2-diphenylethane. \(^1\)H NMR data matches literature values [21].
Potassium ferricyanide, K₃Fe(CN)₆, (3.82 g, 11.6 mmol), potassium carbonate, K₂CO₃, (1.60 g, 11.6 mmol), potassium osmate, K₂OsO₂(OH)₄, (0.0213 g, 0.058 mmol), and quinuclidine, C₇H₁₃N, (0.032 g, 0.29 mmol) were placed into a round bottom flask. Water (25 mL) and tert-butanol (25 mL) were added and the mixture was heated with a heat gun until two distinct layers were formed [20]. 1-Benzylcyclohexene (1.00 g, 5.8 mmol) was added dropwise and the reaction was stirred in the dark for three days. Sodium sulfite, Na₂SO₃, (2.92 g, 23 mmol) was added slowly and the resulting solution was stirred for an additional 2 days. The solution was extracted with dichloromethane (3 × 50 mL) and the organic phase was dried over MgSO₄. The product was obtained as a white powder after recrystallization from CH₂Cl₂/hexane (0.582 g, 49 %). ¹H NMR (CDCl₃, 300 MHz) δ 7.36-7.20 (m, 5 H) 3.44 (dd, 1 H, J = 9.6 Hz, J = 4.4 Hz), 2.92 (d, 1 H, J = 13.2 Hz), 2.86 (d, 1 H, J = 13.2 Hz), 1.80-1.11 (m, 8 H).
1-Benzylocyclohexane-1,2-diol (0.623 g, 3.02 mmol) was placed into a three-neck round bottom flask equipped with a stir bar and N₂ inlet. Dichloromethane (20 mL) was added. Triethylamine (4.35 g, 43 mmol) was added to the flask through a ca. 5 cm column of activated alumina. 4-(Trifluoromethyl)benzene-1-sulfonyl chloride (0.813 g, 3.32 mmol) was added to the flask and the reaction was stirred for 14 hours. The solution was washed with saturated sodium bicarbonate (2 × 30 mL) and a 10 % aqueous triethylamine solution (25 mL). The organic phase was dried over MgSO₄ and the solvent was removed via rotary evaporation. Silica gel column chromatography eluting with 80/20 hexane/ethyl acetate gave the desired product as a white solid (0.841 g, 67.8 %). \( ^1H \text{NMR (CDCl}_3, 300 \text{ MHz}) \delta 8.06 (d, 2 H, J = 8.26 \text{ Hz}), 7.81 (d, 2 H, J = 8.53 \text{ Hz}), 7.33-7.13 (m, 5 H), 4.60 (dd, 1 H, J = 9.91 \text{ Hz}, J = 4.13 \text{ Hz}), 2.97 (d, 1 H, J = 13.5 \text{ Hz}), 2.65 (d, 1 H, J = 13.7 \text{ Hz}), 1.99-1.11 (m, 8 H).
6.8.5  1-Benzyl-2-(4-(trifluoromethyl)phenylsulfonyloxy)cyclohexyl acetate (7AB)

![Chemical Structure]

Compound 7HB (0.841 g, 2.04 mmol) was placed into a three-neck flask equipped with a stir bar and a N₂ inlet. Acetonitrile (25 mL), acetic anhydride (0.417 g, 4.08 mmol) and cobalt (II) chloride (0.0132 g, 0.102 mmol) [19] were added and the reaction was refluxed for 3 hours. Silica gel chromatography was carried out with 9:1 hexane/ethyl acetate. The product was isolated as a white solid (0.765 g, 80 %). \(^1\)H NMR (CDCl₃, 300 MHz) δ 8.00 (d, 2 H, J = 8.53 Hz), 7.77 (d, 2 H, J = 8.26 Hz), 7.35-7.10 (m, 5 H), 5.00 (m, 1 H), 3.46 (d, 1 H, J = 14.03 Hz), 3.24 (d, 1 H, J = 14.03 Hz), 2.30-2.15 (m, 1 H), 1.75 (s, 3 H), 2.10-1.10 (m, 7 H). IR (ATR) \(\nu_{C=O} = 1736 \text{ cm}^{-1}\).
6.9 Body 8

6.9.1 4-Hydroxy-4-methylpentan-2-yl methanesulfonate (8HD)

\[
\text{CH}_2\text{Cl}_2 \quad \text{TEA} \quad \text{Me-SO}_2\text{Cl} \quad \text{CH}_2\text{Cl}_2
\]

2-Methylpentane-2,4-diol (4.010 g, 33.9 mmol), triethylamine (4.570 g, 45.2 mmol) and dichloromethane (60 mL) were added to a 100 mL two-neck flask that was purged with nitrogen. The flask was cooled to 0 °C and the solution was stirred for 5 minutes. Methanesulfonyl chloride (2.616 g, 22.8 mmol) was added dropwise to the flask and the solution was stirred at 0 °C for 2 hours. The solution was washed with 50 mL of hydrochloric acid (1.6 M) and 50 mL of saturated sodium chloride. The organics were dried over sodium sulfate and concentrated to give an oil (2.663 g, 13.5 mmol, 59 %). \(^1\)H NMR (400 MHz, CDCl\(_3\) ) \(\delta\) 5.09 (m, 1 H), 3.01 (s, 3 H), 1.98 (dd, 1 H, \(J = 15\) Hz, \(J = 8\) Hz), 1.90 (broad, 1 H), 1.67 (dd, 1 H, \(J = 15\) Hz, \(J = 3\) Hz), 1.46 (d, 3 H, \(J = 6.2\) Hz), 1.27 (s, 6 H).
6.9.2  4-Hydroxy-4-methylpenane-2-yl 4-methylbenzenesulfonate (8HA)

\[
\begin{align*}
\text{CH}_2\text{Cl}_2 + \text{Pyridine} &\rightarrow \text{OH} \quad \text{CH}_2\text{O} \quad \text{SO}_2\text{Cl} \\
&\text{OH} \quad \text{O} \quad \text{SO}_2\text{Cl}
\end{align*}
\]

2-Methylpentane-2,4-diol (4.077 g, 34.5 mmol) and pyridine (20 mL) were weighed into a 50 mL two-neck flask that was purged with nitrogen. The flask was cooled to 0 °C and the solution was stirred for 5 minutes. p-Toluenesulfonyl chloride (4.384 g, 23 mmol) was added to the flask and the solution was stirred at 0 °C for 1 hour then at room temperature for 3.5 hours. The solution was diluted with ethyl acetate (50 mL) and washed with hydrochloric acid (1.6 M, 8 × 50 mL) DI water (4 × 50 mL) and saturated sodium chloride (50 mL). The organics were dried over sodium sulfate and concentrated to give an oil. The crude product was purified by column chromatography using silica as the stationary phase and eluting with 95 % hexane / 5 % ethyl acetate to give the desired product as (3.579 g, 13.1 mmol, 57 %). \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.78 (d, 2 H, \(J = 8\) Hz), 7.31 (d, 2 H, \(J = 8\) Hz), 4.96 (m, 1 H), 2.41 (s, 3 H), 1.90 (m, 1 H), 1.84 (s, 1 H), 1.63 (dd, 1 H, \(J = 15\) Hz, \(J = 4.2\) Hz), 1.25 (d, 3 H, \(J = 6.2\) Hz), 1.19 (s, 6 H).
2-Methylpentane-2,4-diol (0.952 g, 8 mmol) and pyridine (6 mL) were weighed into a 25 mL two-neck flask that was purged with nitrogen. The flask was cooled to 0 °C and the solution was stirred for 3 minutes. 4-(Trifluoromethyl)benzene-1-sulfonyl chloride (0.975 g, 4 mmol) was added to the flask and the solution was stirred for 7 hours during which time the solution reached room temperature. The solution was diluted with ethyl acetate (25 mL) and washed with hydrochloric acid (1.6 M, 3 × 25 mL), DI water (4 × 25 mL) and saturated sodium chloride (25 mL). The organics were dried over sodium sulfate and concentrated to give an oil. The crude product was purified by column chromatography using silica as the stationary phase and eluted with 95 % hexane / 5 % ethyl acetate to give the desired product (0.927 g, 2.84 mmol, 71 %). ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, 2 H, J = 8.0), 7.80 (d, 2 H, J = 8.0), 5.08 (m, 1 H), 1.96 (dd, 1 H, J = 15 Hz, 7.4 Hz), 1.67 (m, 1 H), 1.32 (d, 3 H, J = 6.2), 1.22 (s, 6H). ¹³C NMR (400 MHz, CDCl₃) δ 141.31, 135.6, 128.39, 126.50, 124.58, 121.87, 79.53, 69.85, 49.56, 30.39, 29.48, 22.78. ¹⁹F NMR (400 MHz, CDCl₃/C₆F₆) δ -66.28. IR (ATR) 3519, 3410, 2967, 1734, 1319, 1309, 1127, 1061, 880 cm⁻¹. Anal. Calcd. For C₁₃H₁₇SO₄F₃: C, 47.8; H, 5.2. Found C, 47.5; H, 5.4.
6.9.4 4-Hydroxy-4-methylpenane-2-yl 2-(trifluoromethyl)benzene-sulfonate (8HF)

2-Methylpentane-2,4-diol (0.360 g, 3 mmol) and pyridine (4.5 mL) were weighed into a 25 mL two-neck flask that was purged with nitrogen. The flask was cooled to 0 °C and the solution was stirred for 3 minutes. 2-(Trifluoromethyl)benzene-1-sulfonyl chloride (0.488 g, 2 mmol) was added to the flask and the solution was stirred for 16 hours during which time the solution reached room temperature. The solution was diluted with ethyl acetate (25 mL) and washed with hydrochloric acid (1.6 M, 3 × 25 mL), DI water (4 × 25 mL) and saturated sodium chloride (25 mL). The organics were dried over sodium sulfate and concentrated to give an oil. The crude product was purified by column chromatography using silica as the stationary phase and eluted with 95 % hexane / 5 % ethyl acetate to give the desired product as an oil (0.145 g, 0.44 mmol, 15 %). 1H NMR (400 MHz, CDCl3) δ 8.23 (m, 1 H), 7.87 (m, 1 H), 7.73 (m, 2 H), 5.13 (m, 1 H), 1.97 (m, 1 H), 1.84 (broad, 1 H), 1.69 (dd, 1 H, J = 15 Hz, J = 4.8 Hz), 1.31 (d, 3 H, J = 6.4 Hz), 1.20 (s, 6 H).
6.10 Body 11

6.10.1 3-Hydroxybutyl 4-(trifluoromethyl)benzenesulfonate (11HB)

To a solution of 1,3-butane diol (4.34 g, 48 mmol) and TEA (3.19 g, 31.5 mmol) in CH₂Cl₂ (20 mL) at 0 °C was added 4-(trifluoromethyl)benzene-1-sulfonyl chloride (3.97 g, 16.2 mmol) dissolved in CH₂Cl₂ (20 mL). The solution was stirred at 0 °C for 2 h. Saturated aqueous NaHCO₃ (15 mL) was added to the solution and mixture was stirred at room temperature for 40 min. The organics were extracted with CH₂Cl₂ (50 mL) and washed with 1 M HCl (3 × 25 mL) and saturated aqueous NaCl (25 mL). The organics were dried over Na₂SO₄ and concentrated to give the desired product (3.28 g, 65 %). ¹H NMR (400 MHz CDCl₃) δ 8.02 (d, 2 H, J = 8.2 Hz), 7.80 (d, 2 H, J = 8.3 Hz), 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).

6.10.2 3-Hydroxybutyl 2-(trifluoromethyl)benzenesulfonate (11HF)

To a solution of 1,3-butane diol (2.18 g, 24 mmol) and TEA (1.64 g, 16 mmol) in CH₂Cl₂ (15 mL) at 0 °C was added 2-(trifluoromethyl)benzene-1-sulfonyl chloride (2 g, 8 mmol) dissolved in CH₂Cl₂ (20 mL). The solution was stirred at 0 °C for 2 h. Saturated aqueous NaHCO₃ (15 mL) was added to the solution and the mixture was stirred at room temperature for 45 min. The organics were extracted with CH₂Cl₂ (150 mL) and washed with 0.5 M HCl (2 × 80 mL) and saturated aqueous NaCl (50 mL). The organics were dried over Na₂SO₄ and concentrated to give a crude mixture. Silica gel chromatography (50 % ethyl acetate in hexanes) yielded the desired product (2 g, 84 %).¹H NMR (400 MHz CDCl₃) 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 C₁₁H₁₃F₃O₄S: C, 44.29; H 4.39. Found: C, 44.29; H, 4.28.
6.10.3  3-Hydroxybutyl 2,3,4,5,6-pentafluorobenzenesulfonate (11HG)

\[
\begin{align*}
\text{OH} & \quad + \\
\text{F} & \quad \text{SO}_2\text{Cl} \\
\text{F} & \quad \text{TEA} \\
\text{CH}_2\text{Cl}_2 & \quad \rightarrow \\
\text{OH} & \quad \text{O} \\
\text{F} & \quad \text{SO}_2 \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F}
\end{align*}
\]

To a solution of 1,3-butane diol (0.9 g, 10 mmol) and TEA (0.61 g, 6 mmol) in CH\(_2\)Cl\(_2\) (4 mL) at 0 °C was added pentafluorobenzenesulfonyl chloride (0.53 g, 2 mmol) dissolved in CH\(_2\)Cl\(_2\) (4 mL). The solution was stirred for 6 h over which time the solution slowly warmed to room temperature. Saturated aqueous NaHCO\(_3\) (25 mL) was added to the solution and the mixture was stirred at room temperature for 30 min. The organics were extracted with CH\(_2\)Cl\(_2\) (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\(_2\)SO\(_4\) 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\(_3\)) \(\delta\) 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\(_9\)F\(_5\)O\(_4\)S: C, 37.51; H 2.83. Found: C, 37.70; H, 2.93.
6.10.4 3-Methoxybutyl 4-(trifluoromethyl)benzenesulfonate (11MB)

To a solution of 3-methoxybutane-1-ol (0.58 g, 4.9 mmol) in pyridine (5 mL) was added 4-(trifluoromethyl)benzene-1-sulfonyl chloride (0.98 g, 4 mmol). The solution was stirred at room temperature 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 NaHCO₃ (25 mL) and saturated aqueous NaCl (25 mL). The organics were dried over Na₂SO₄ and concentrated to give an oil (0.53 g, 40 %). $^1$H NMR (400 MHz CDCl₃) 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 C₁₂H₁₅F₃O₄S: C, 46.15; H, 4.84. Found: C, 45.99; H, 4.64.
6.10.5 3-Methoxybutyl 2-(trifluoromethyl)benzenesulfonate (11MF)

\[
\begin{array}{c}
\text{O} \\
\text{CH} \\
\text{CH}_2 \\
\text{OH}
\end{array}
\quad +
\quad \begin{array}{c}
\text{SO}_2\text{Cl} \\
\text{CF}_3
\end{array}
\quad \xrightarrow{\text{TEA}}
\quad \begin{array}{c}
\text{O} \\
\text{CH} \\
\text{CH}_2 \\
\text{SO}_2
\end{array}
\quad \begin{array}{c}
\text{F}_3 \\
\text{C}
\end{array}
\quad \begin{array}{c}
\text{CF}_3
\end{array}
\quad \begin{array}{c}
\text{CF}_3
\end{array}
\quad \begin{array}{c}
\text{CF}_3
\end{array}
\quad \begin{array}{c}
\text{CF}_3
\end{array}
\]

To a solution of 3-methoxybutane-1-ol (0.63 g, 6.0 mmol) and TEA (0.42 g, 4.1 mmol), in CH$_2$Cl$_2$ (5 mL) was added 2-(trifluoromethyl)benzene-1-sulfonyl chloride (0.50 g, 2.0 mmol). The solution was stirred at room temperature for 2 h. The reaction mixture was diluted with CH$_2$Cl$_2$ (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$_2$SO$_4$ 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$_3$) $\delta$ 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$_3$O$_4$S: C, 46.15; H 4.84. Found: C, 46.30; H, 4.88.
6.10.6 3-Methoxybutyl 2,3,4,5,6-pentafluorobenzenesulfonate (11MG)

To a solution of 3-methoxybutane-1-ol (0.78 g, 7.5 mmol) and TEA (0.388 g, 3.8 mmol), in CH$_2$Cl$_2$ (15 mL) was added pentafluorobenzenesulfonyl chloride (0.79 g, 3.0 mmol). The solution was stirred at room temperature for 4 h. Saturated aqueous NaHCO$_3$ (10 mL) was added to the solution and the mixture was stirred at room temperature for 30 min. The organics were extracted with CH$_2$Cl$_2$ (30 mL) and washed with 0.5 M HCl (2 × 20 mL) and saturated aqueous NaCl (20 mL). The organics were dried over Na$_2$SO$_4$ 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$_5$O$_4$S: C, 39.53; H 3.32. Found: C, 39.83; H, 3.45.
6.11 Body 29

6.11.1 1,1,1-trifluoro-4-methylpent-4-en-2-yl 2,3,4,5,6-pentafluorobenzenesulfonate (29OG)

\[ \text{CH}_2\text{Cl}_2 \text{TEA}^+ \]

1,1,1-Trifluoro-4-methylpent-4-en-2-ol (0.355 g, 2.3 mmol) and triethylamine (0.23 g, 2.3 mmol) were weighed into a 25 mL single-neck flask equipped with a stir bar. The flask was sealed with a rubber septum and purged with nitrogen. Dichloromethane (10 mL) was added to the flask followed by pentafluorobenzenesulfonyl chloride (0.52 g, 1.95 mmol). The solution was stirred for 5 hours at room temperature. The solution was diluted with dichloromethane (25 mL) and washed with hydrochloric acid (1 M, \(3 \times 20\) mL), saturated sodium bicarbonate (20 mL) and saturated sodium chloride (20 mL). The organics were dried over sodium sulfate and concentrated to give an oil. The crude product was purified by column chromatography using neutral alumina as the stationary phase and eluted with 90 % hexane / 10 % ethyl acetate to give the desired product (0.535 g, 1.39 mmol, 70 %). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.14 (m, 1 H), 4.86 (m, 2 H), 2.55 (m, 2 H), 1.77 (s, 3 H). \(^{19}\)F NMR (400 MHz, CDCl\(_3\)/C\(_6\)F\(_6\)) \(\delta\) -79.7 (d, 3 H), -136.7 (m, 2 H), -145.5 (t of t, 1 H), -160.9 (m, 2 H).
6.11.2 1,1,1-trifluoro-4-methylpent-4-en-2-yl trifluoromethane-sulfonate (29OC)

1,1,1-Trifluoro-4-methylpent-4-en-2-ol (0.30 g, 2 mmol) and pyridine (0.33 g, 4.2 mmol) were weighed into a 25 mL single-neck flask equipped with a stir bar. The flask was sealed with a rubber septum and purged with nitrogen. Dichloromethane (6 mL) was added to the flask and the solution was cooled to -40 °C. A solution of trifluoromethanesulfonic anhydride (0.645 g, 2.3 mmol) in 3 mL of dichloromethane was added dropwise to the reaction flask [22]. The solution was stirred for 1 hour at -40 °C. The solution was diluted with dichloromethane (10 mL) and washed with saturated sodium chloride (2 × 20 mL). A small amount (<0.001 g) of polyvinyl pyridine was added to the organic phase and the dichloromethane was removed under reduced pressure [23]. The crude product was purified by column chromatography using silica as the stationary phase and eluted with 80 % pentane / 20 % ethyl formate. Polyvinyl pyridine (<0.001 g) was added to the organics and the product was concentrated under reduced pressure. The desired product was obtained as a colorless liquid (0.30 g, 1 mmol, 50 %).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.07 (m, 3 H), 5.61 (m, 2 H), 1.79 (s, 3 H).
6.11.3  1,1,1-trifluoro-4-methylpent-4-en-2-yl 1,1,2,2,3,3,4,4,4-nonafluoro-butane-1-sulfonate (29OE)

\[
\begin{align*}
&\text{CF}_3 \quad \text{OH} \quad + \quad \text{N}_2\text{O} \quad \xrightarrow{\text{Pyridine}} \quad \text{CF}_3 \\
&\text{CH}_2\text{Cl}_2
\end{align*}
\]

1,1,1-Trifluoro-4-methylpent-4-en-2-ol (0.15 g, 1 mmol) and pyridine (0.16 g, 2 mmol) were weighed into a 25 mL single-neck flask equipped with a stir bar. The flask was sealed with a rubber septum and purged with nitrogen. Dichloromethane (10 mL) was added to the flask and the solution was cooled to -40 °C. A solution of 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonic anhydride (0.62 g, 1 mmol) in dichloromethane (4 mL) was added dropwise to the reaction flask. The solution was stirred for 1 hour at -40 °C over which time a precipitate formed and the solution color turned red. The solution was stirred overnight at room temperature. The reaction was quenched with saturated sodium chloride (25 mL) and the organics were extracted with dichloromethane (4 × 25 mL). The organics were concentrated and the crude product was purified on a silica prep-TLC plate by eluting with 90 % hexane / 10 % ethyl acetate. The desired product was obtained as a colorless liquid (0.036 g, 0.08 mmol, 8 %). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.12 (m, 1 H), 5.04 (broad s, 1 H), 4.96 (broad s, 1 H), 2.61 (m, 2 H), 1.79 (s, 3 H).
6.12 Polymer-Bound Acid Amplifiers

6.12.1 3-Hydroxy-3-methylbutyl 4-(bromomethyl)benzenesulfonate (3HJ)

3-Methyl-1,3-butane diol (2.52 g, 24 mmol) and pyridine (5 mL) were weighed into a flask and dissolved with dichloromethane (10 mL). 4-(Bromomethyl)benzene-1-sulfonyl chloride (5.39 g, 20 mmol) was weighed into a single-neck flask that was purged with nitrogen and cooled to 0 °C. The alcohol solution was added to the sulfonyl chloride and the mixture was stirred for 2 h. The solution was diluted with dichloromethane (30 mL) and washed with hydrochloric acid (1 M, 3 × 20 mL) and saturated aqueous NaCl (1 × 25 mL). The organics were dried over Na₂SO₄ and concentrated to give an oil (1.832 g, 27 %). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, 2 H, J = 8.3 Hz), 7.56 (d, 2 H, J = 8.3 Hz), 4.61 (s, 2 H), 4.23 (t, 2 H, J = 6.8 Hz), 1.86 (t, 2 H, J = 6.8 Hz), 1.21 (s, 6 H).
6.12.2 3-Methoxy-3-methylbutyl 4-(bromomethyl)benzenesulfonate (3MJ)

![Chemical structure diagram]

3-Methyl-1,3-butane diol (2.84 g, 24 mmol) and pyridine (5 mL) were added to a 50 mL two-neck flask that had been purged with nitrogen. The flask was cooled to 0 °C. 4-(Bromomethyl)benzene-1-sulfonyl chloride (5.39 g, 20 mmol) dissolved in dichloromethane (15 mL) was added to the flask and the solution was stirred for 2 hours. The solution was diluted with dichloromethane (30 mL) and washed with 1 M HCl (3 × 25 mL) and saturated aqueous NaCl (1 × 25 mL). The organics were dried over Na₂SO₄ and concentrated to give an oil (2.316 g, 33 %). ¹H NMR (400 MHz, CDCl₃) δ 7.86 (m, 2 H), 7.55 (m, 2 H), 4.47 (s, 2 H), 4.13 (t, 2 H, J = 7.3 Hz), 3.06 (s, 3 H), 1.84 (t, 2 H, J = 7.3 Hz), 1.09 (s, 6 H).
6.12.3 Polyhydroxystyrene-t-butlyacrylate Co-polymer (65/35)

![Reaction Diagram]

Acetoxystyrene (52.7 g, 325 mmol), t-butylacrylate (22.4 g, 175 mmol) and isopropyl alcohol (200 mL) were added to a 500 mL two-necked and degassed with nitrogen for 30 min. The free radical initiator 2,2’-azobis-(2-methylbutyronitrile) (AMBN) (2.88 g, 15 mmol) was weighed into a flask and dissolved in acetonitrile (25 mL). The AMBN solution was added dropwise to the monomer solution while refluxing. After 22 h, ammonium acetate (30 g, 390 mmol) dissolved in DI water (40 mL) was added to the refluxing solution. The solution was refluxed for 24 h then cooled to room temperature [24]. The solution was divided into two parts and dripped into beakers of ice water (600 mL) while vigorously stirring. A white solid polymer precipitated out of solution. The polymer was filtered, dried and dissolved in isopropanol. The polymer was precipitated in ice water a second time, filtered, and dried. The polymer was ground into a fine power, washed with dichloromethane (2 L), and dried.
6.12.4 Polymer-Bound Acid Amplifier (PHS/AA/TBA)

![Chemical structure]

Synthesis of polymer-bound AAs. $R = H \ (3HJ)$, $R = Me \ (3MJ)$.

<table>
<thead>
<tr>
<th></th>
<th>AA (g)</th>
<th>Polymer (g)</th>
<th>$K_2CO_3$ (g)</th>
<th>Product (g)</th>
<th>PHS/AA/TBA (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3HJ</td>
<td>0.170</td>
<td>3.004</td>
<td>0.137</td>
<td>1.7</td>
<td>62/3/35</td>
</tr>
<tr>
<td>3HJ</td>
<td>0.410</td>
<td>3.012</td>
<td>0.337</td>
<td>1.4</td>
<td>59/6/35</td>
</tr>
<tr>
<td>3MJ</td>
<td>0.176</td>
<td>3.000</td>
<td>0.136</td>
<td>1.5</td>
<td>62/3/35</td>
</tr>
<tr>
<td>3MJ</td>
<td>0.430</td>
<td>3.000</td>
<td>0.336</td>
<td>2.3</td>
<td>58/7/35</td>
</tr>
</tbody>
</table>

Table 6.1 Reagents and product quantities used to synthesize 4 polymer-bound AAs.

The co-polymer of PHS/TBA (65/35) and potassium carbonate were weighed into a 50 mL single-neck round bottom flask. The flask was sealed and purged with nitrogen. Acetonitrile (20 mL) was added to the flask via syringe and heated to reflux. Acid amplifier (3HJ or 3MJ) was dissolved in acetonitrile (10 mL) and added dropwise to the reaction. The solution was refluxed for 4 h then cooled to room temperature. The acetonitrile was removed under reduced pressure and the remaining solids were dissolved in isopropanol. The polymer solution was dripped into a beaker of ice water (400 mL) while vigorously stirring. The precipitated polymer was filtered, dried, ground into a fine power and washed with dichloromethane until all of the unreacted AA was removed.
References


CHAPTER 7

SUMMARY, AND FUTURE DIRECTIONS:
GENERATION-3 ACID AMPLIFIERS

7.1 Summary

Next generation lithography technologies must be developed to keep pace with transistor scaling. Extreme ultraviolet lithography (EUV, 13.5 nm) continues to be one of the leading candidates because of its capability to print features that are 22 nm and smaller [1]. One major obstacle to the implementation of EUV is the need for highly sensitive photoresists that meet 22 nm resolution and LER requirements [2,3]. We propose that the best way to get all three properties in the same resist is to increase the number of strong acids generated in the exposed regions and we assert that acid amplifiers may be one of the best ways to achieve this goal [4-6].

Publications prior to our work suggest that acid amplifiers designed for use in photoresists must have three properties [7,8]. First, AAs must be thermally stable toward resist process conditions. Second, AAs must rapidly decompose in the presence of catalytic acid. Third, AAs must generate strong (fluorine-containing sulfonic) acids capable of participating in the photoresist chemistry.

The majority of acid amplifiers in this thesis generate moderately strong, fluorinated sulfonic acids. The focus of this thesis was to synthesize, characterize and implement acid amplifiers in EUV resists. We synthesized over 40 AAs with systematic variations in chemical structure to give a range of reactivities. We developed useful characterization techniques to analyze critical AA properties. We used $^{19}$F NMR to
measure AA decomposition kinetics in the presence and absence of base. This allowed us to measure AA thermal stability and to identify AAs that decompose autocatalytically. We used thermally-programmed spectroscopic ellipsometry to measure decomposition temperatures of AAs in resist films. We learned that the polymer platform can influence AA stability. More specifically, we found that AAs are more stable in polymers that do not have phenol. We hypothesize that phenol groups act as nucleophiles and displace the acid precursors on AAs. We used $^1$H NMR to identify AA decomposition products and found that phenol reacts with AAs. Most importantly, we evaluated the lithographic performance of EUV resists with added AAs and demonstrated that some AAs can simultaneously improve resist resolution, LER and sensitivity.

We classify AAs as Generation-1, Generation-2 and Generation-3 base on the strength of the acids that they generate and their thermal stability (Figure 7.1). Generation-1 AAs generate weak nonfluorinated acids such as toluenesulfonic acid. Generation-2 AAs generate moderately strong fluorinated sulfonic acids such as $p$-(trifluoromethyl)benzenesulfonic acid. Generation-3 AAs generate strong fluorinated sulfonic acids such as triflic acid and the AAs are thermally stable in the absence of catalytic acid. At the time of our first communication on this topic [4] there were only twenty-seven acid amplifiers in the literature, none of which meet all three requirements for use in photoresists. All but two of these published AAs are Generation-1 [9]. In this thesis work we developed Generation-2 AAs and showed that they improve the lithographic performance of EUV resist, but we have not made our ideal AA. We will develop new AAs that are thermally stable, that generate strong acids such as triflate or nonaflate and that generate acids with low diffusion in resist films.
Figure 7.1 Examples of Generation-1 (3HA), Generation-2 (3HB), and Generation-3 (29OC) AAs.

7.2 Generation-3 Acid Amplifiers
In this section we present two Generation-3 AAs and show some preliminary data. To improve the AA acid strength we need to improve the AA thermal stability. We showed through reaction kinetics (Chapter 3) and decomposition measurements (Chapter 4) that AA thermal stability is inversely correlated to the AA acid strength. We learned that there are two thermal (non-acid catalyzed) decomposition pathways that effect AA stability, SN2 and SN1 decomposition mechanisms. We must inhibit both decomposition pathways to improve the AA stability.

Figure 7.2 shows the SN2 and SN1 decomposition mechanism for a generic olefin trigger AA with and without a CF3 group alpha to the sulfonate ester. During SN2 decomposition a nucleophile (Nu:) displaces the sulfonate ester. Steric hindrance is the best way to reduce nucleophilic attack. During SN1 decomposition the sulfonate ester bond breaks to give a carbocation intermediate. Generation-2 AAs are prone to SN1 decomposition because fluorinated sulfonates are good leaving groups. Reducing the electron density at the C-O sulfonate bond inhibits SN1 reactions. We control both SN2 and SN1 reactions by incorporating a CF3 group alpha to the sulfonate ester. This group sterically hinders the sulfonate ester from nucleophilic attack and is highly electron
withdrawing to destabilize carbocation formation. We call compounds with this new design Generation-3 AAs.

![SN1 and SN2 reactions](image)

**Figure 7.2** CF$_3$ alpha to the sulfonate ester inhibits SN$_2$ and SN$_1$ reactions.

Figure 7.3 show the chemical structures of the two Generation-3 AAs that we synthesized, 29OG and 29OC. Both AAs have an olefin trigger that isomerizes in the presence of acid to form an olefin that is allylic to the sulfonate ester. The acid precursors are pentafluorobenzene (29OG) sulfonate and triflate (29OC). This is our first successful AA that generates triflic acid. We characterized these compounds with our thermal stability measurements, $^{19}$F NMR kinetic measurements and evaluated the additive effects of 29OG in our OS2 resist formulation.

![Chemical structures of Generation-3 AAs](image)

**Figure 7.3** Chemical structures of Generation-3 AAs 29OG and 29OC.
Figure 7.4 shows the thermally-programmed spectroscopic ellipsometric analysis of $OS_2$ resist and $OS_2$ with 70 mM added $29OG$, $29OC$ or $11HG$. Resist films of 70 nm were coated on silicon substrates and soft baked at 90 °C for 60 s. The film thickness was measured as a function of temperature at a temperature ramp rate of 10 °C/min. The steepest part of the curve indicates the decomposition temperature. The $OS_2$ ESCAP polymer decomposed at 195 °C. Our most thermally stable Generation-2 AA with a pentafluorobenzene sulfonate acid precursor ($11HG$) has a decomposition temperature of 125 °C. Remarkably, resists with $29OG$ and $29OC$ have the same film thickness curve as the control $OS_2$ resist. We conclude that these AAs decompose at a temperature higher than the ESCAP polymer.

Figure 7.4 Thermally-programmed spectroscopic ellipsometry shows that AAs $29OG$ and $29OC$ are more thermally stable than the resist ESCAP polymer.
Figure 7.5 shows 50 nm L/S imaging results of OS2 resist with 0, 70, 140 or 280 mM added 29OG. The resist films were coated to 60 nm thickness and soft baked at 110 °C for 60 s. The films were exposed to EUV radiation at Albany on the micro exposure tool with annular illumination, post exposed baked at 130 °C for 90 s and developed in TMAH for 45 s. The sizing dose for OS2 is 15.0 mJ·cm⁻² and 16.7, 16.8 and 15.6 mJ·cm⁻² for resist with 70, 140 and 280 mM 29OG respectively. Even though 29OG does not improve the resist sensitivity, it does improve LER from 8.2 ± 0.5 nm (OS2) to 6.4 ± 0.5 nm. We think that 29OG is not reactive enough during PEB to generate a sufficient amount of acid to have a sensitivity effect. We also think the LER improvements are due to dissolution inhibition properties of 29OG.

![No AA](image)

**Figure 7.5** SEM images of OS2 resist with 0, 70, 140 and 280 mM added 29OG. Images are 50 nm dense lines and spaces.

We showed that these new AAs are extremely thermally stable in resists films and that 29OG does not improve resist sensitivity under normal resist process conditions. One
possible reason that \textbf{290G} did not improve the resist sensitivity is that it does not undergo acid catalyzed decomposition. We therefore investigated the reaction kinetics of \textbf{290G} and \textbf{290C} in solution in sealed NMR tubes to determine if acid catalyzes the decomposition of these compounds.

The thermal decomposition kinetics of the AAs were measured using $^{19}$F NMR. Solutions of AAs (70 mM) in 50/50 wt\% C$_6$D$_6$/m-ethylphenol in the presence and absence of 1.2 eq. of added 2,4,6-tri-\textit{t}-butylpyridine were monitored. We chose to measure the rate constants at 145 °C because the compounds are exceptionally stable and decompose very slow at lower temperatures.

Figure 7.6 shows the decomposition kinetics of \textbf{290G} and \textbf{290C} in the presence (Figure 7.6A) and absence (Figure 7.6B) of added base. Figure 7.6A shows the thermal (uncatalyzed) decomposition of \textbf{290G} and \textbf{290C}. The natural log of AA concentration \textit{versus} time yields the first-order rate constants for \textbf{290G} and \textbf{290G} to be $0.009 \times 10^{-5}$ s$^{-1}$ and $0.43 \times 10^{-5}$ s$^{-1}$ respectively. At these slow decomposition rates, \textbf{290G} decompose only 20 \% after heating at 145 °C for 29 days. Both compounds are more thermally stable than any Generation-2 AA that we measured. Figure 7.6B shows the decomposition of \textbf{290G} and \textbf{290C} in the absence of base. The AA concentration \textit{versus} time shows the characteristic profile of autocatalytic decomposition. Initially, there is no indication of decomposition but once a small amount of acid is thermally generated, both compounds decompose rapidly over a very short time period. The autocatalytic rate constants for \textbf{290G} and \textbf{290C} are the same within experimental error, $0.11$ (Ms)$^{-1}$ and $0.12$ (Ms)$^{-1}$ respectively.
Figure 7.6 Thermal decomposition of 29OG and 29OC: A) With added base B) In the absence of base.

Table 7.1 compares uncatalyzed rate constants (k_{Base}) and ratios of autocatalytic/uncatalyzed (k_{No Base} / k_{Base}) rate constants for some of our best Generation-2 and Generation-3 AAs. Of the Generation-2 AAs, 3HF has the best k_{No Base} / k_{Base} ratio (at 100 °C) of 1390, 3HG has a k_{No Base} / k_{Base} ratio of 300 (at 100 °C) but is the best ratio of the AAs that generate pentafluorobenzenesulfonic acid and 11HG has a k_{No Base} / k_{Base} ratio (at 100 °C) of 1.0, but is the most thermally stable AA that generates pentafluorobenzenesulfonic acid. 6AB is also a Generation-2 AA and has the best thermal stability with a k_{Base} of $0.49 \times 10^{-5}$ s$^{-1}$ and $13 \times 10^{-5}$ s$^{-1}$ at 100 °C and 145 °C, respectively. The k_{No Base} / k_{Base} ratio is 490 and 270 at 100 °C and 145 °C, respectively. The high thermal stability and moderate k_{No Base} / k_{Base} ratio is partially due to the relatively weak fluorinated sulfonic acid precursor, 4-(trifluoromethyl)benzene sulfonate.

In comparison, both Generation-3 AAs have far superior k_{Base} and k_{No Base} / k_{Base} ratios than our best Generation-2 AAs. 29OC and 29OG have a k_{Base} of $0.43 \times 10^{-5}$ s$^{-1}$ and $0.009 \times 10^{-5}$ s$^{-1}$ at 145 °C respectively. Even though they generate strong fluorinated sulfonic acids, pentafluorobenzene sulfonic acid and triflic acid, they are 30 and 1,400 ×
more stable than 6AB. 29OC and 29OG also have unprecedented k_{No Base} / k_{Base} ratios of 28,000 and 1,000,000 respectively. With such promising results, Generation-3 AAs provide an opportunity to make our ideal AA.

<table>
<thead>
<tr>
<th></th>
<th>Generation-2 Acid Amplifiers</th>
<th>Generation-3 Acid Amplifiers</th>
</tr>
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<tbody>
<tr>
<td>k_{Base} at 100 °C (small is better)</td>
<td>5.1 73 33 0.49</td>
<td>- -</td>
</tr>
<tr>
<td>k_{Base} at 145 °C (smaller is better)</td>
<td>- - - 13</td>
<td>0.43 0.009</td>
</tr>
<tr>
<td>k_{No Base} / k_{Base} at 100 °C (bigger is better)</td>
<td>1390 300 1 490</td>
<td>- -</td>
</tr>
<tr>
<td>k_{No Base} / k_{Base} at 145 °C (bigger is better)</td>
<td>- - - 270</td>
<td>28,000 1,000,000</td>
</tr>
</tbody>
</table>

Figure 7.1 k_{Base} and k_{No Base} / k_{Base} rate constants at 100 °C and 145 °C for selected AAs. k_{Base} units are × 10^{-5} s^{-1}

7.3 Future Directions

Generation-3 AAs have great thermal stability but react too slow in a photoresist to provide any sensitivity improvements. We propose to synthesize new Generation-3 AAs with improved reactivities. Figure 7.8 shows our synthetic strategy and the chemical structures of target AAs. The current Generation-3 body type provides the thermal stability that we desire and the reactivity can be tuned by changing the trigger type. For example, methoxy or hydroxyl triggers are used for Generation-2 AAs and they have fast reactivity’s. Another approach is to destabilize carbocation formation when the acid precursor is released by moving the alpha CF₃ group farther from the sulfonate ester or reducing the number of fluorine on the beta carbon.
Lastly, we propose to reduce AA acid diffusion by attaching the acid to the resist polymer. In Chapter 2 we demonstrated that polymer-bound AAs improve resist sensitivity without impacting the exposure latitude. The high thermal stability of Generation-3 AAs provides the opportunity to make polymer-bound AAs that generate strong fluorinated sulfonic acids. Figure 7.9 shows the chemical structure of one possible AA that could be attached to a polymer. The acrylate functionality provides a route for free radical polymerization of the AA with resist monomers. This would yield a resist polymer with the AA in the backbone of the polymer chain. Generation-2 AAs are not thermally stable enough to survive free radical polymerization conditions. In conclusion, based on our extensive investigation of AAs we propose that polymer-bound AAs that generate strong fluorinated sulfonic acids will provide EUV resist systems that can break the RLS tradeoff.

![Stability vs Reactivity Diagram](attachment:image1)

Figure 7.8 Chemical structures of target AAs with high thermal stability and fast reactivity.

![Chemical Structure](attachment:image2)

Figure 7.9 Chemical structure of an AA monomer that can be polymerized in a future EUV resist polymer.
References


Appendix A. $^1$H NMR Spectra

Figure A.1 $^1$HNMR spectra of \textit{1EA} in CDCl$_3$. 
Figure A.2 $^1$HNMR spectra of $1EB$ in CDCl$_3$.

Figure A.3 $^1$HNMR spectra of $2AA$ in CDCl$_3$. 
Figure A4 $^1$HNMR spectra of $2AB$ in CDCl$_3$.

Figure A.5 $^1$HNMR spectra of $3HD$ in CDCl$_3$. 
Figure A.6 $^1$HNMR spectra of 3HK in CDCl$_3$.

Figure A.7 $^1$HNMR spectra of 3HA in CDCl$_3$. 
Figure A.8 $^1$HNMR spectra of 3HB in CDCl$_3$.

Figure A.9 $^1$HNMR spectra of 3HF in CDCl$_3$. 
Figure A.10 $^1$HNMR spectra of 3HG in CDCl$_3$.

Figure A.11 $^1$HNMR spectra of 3MA in CDCl$_3$. 
Figure A.12 $^{1}$HNMR spectra of $3MK$ in CDCl$_3$.

Figure A.13 $^{1}$HNMR spectra of $3MB$ in CDCl$_3$. 
Figure A.14 $^1$HNMR spectra of $3MF$ in CDCl$_3$.

Figure A.15 $^1$HNMR spectra of $3MG$ in CDCl$_3$. 
Figure A.16 $^1$H NMR spectra of 3-Oxobutane-2-yl 4-methylbenzenesulfonate in CDCl$_3$.

Figure A.17 $^1$H NMR spectra of 3-Oxobutan-2-yl 4-(trifluoromethyl)benzenesulfonate in CDCl$_3$. 
Figure A.18 $^1$HNMR spectra of $4HA$ in CDCl$_3$.

Figure A.19 $^1$HNMR spectra of $4HB$ in CDCl$_3$. 
Figure A.20 $^1$HNMR spectra of 4AA in CDCl$_3$.

Figure A.21 $^1$HNMR spectra of 3-Hydroxy-3-methylhex-5-en-2-yl 4-methylbenzenesulfonate in CDCl$_3$. 

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Figure A.22 $^1$HNMR spectra of 1-phenylcyclohexane-1,2-diol in CDCl$_3$.

Figure A.23 $^1$HNMR spectra of 5HB in CDCl$_3$. 
Figure A.24 $^1$HNMR spectra of $5AB$ in CDCl$_3$.

Figure A.25 $^1$HNMR spectra of $7HB$ in CDCl$_3$. 
Figure A.26 $^1$HNMR spectra of 6AB in CDCl$_3$.

Figure A.27 $^1$HNMR spectra of 1-benzylcyclohexane-1,2-diol in CDCl$_3$. 
Figure A.28  $^1$HNMR spectra of 7HB in CDCl$_3$.

Figure A.29  $^1$HNMR spectra of 7AB in CDCl$_3$. 
Figure A.30 $^1$HNMR spectra of $8\text{HD}$ in CDCl$_3$.

Figure A.31 $^1$HNMR spectra of $8\text{HA}$ in CDCl$_3$. 
Figure A.32 $^1$HNMR spectra of $8HB$ in CDCl$_3$.

Figure A.33 $^1$HNMR spectra of $8HF$ in CDCl$_3$. 
Figure A.34 $^1$HNMR spectra of $11HB$ in CDCl$_3$.

Figure A.35 $^1$HNMR spectra of $11HF$ in CDCl$_3$. 
Figure A.36 $^1$HNMR spectra of $11HG$ in CDCl$_3$.

Figure A.37 $^1$HNMR spectra of $11MB$ in CDCl$_3$. 

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Figure A.38 $^1$HNMR spectra of $11MF$ in CDCl$_3$.

Figure A.39 $^1$HNMR spectra of $11MG$ in CDCl$_3$. 
Figure A.40 $^1$HNMR spectra of $29OG$ in CDCl$_3$.

Figure A.41 $^1$HNMR spectra of $29OC$ in CDCl$_3$. 
Figure A.42 $^1$HNMR spectra of 29OE in CDCl₃.

Figure A.43 $^1$HNMR spectra of 3HJ in CDCl₃.
Figure A.44 $^1$HNMR spectra of 3MJ in CDCl$_3$.

Figure A.45 $^1$HNMR spectra of PHS/TBA (65/35) co-polymer in DMSO.
Figure A.46 $^1$HNMR spectra of polymer-bound $3HJ$ in DMSO, PHS/AA/TBA (62/3/35).

Figure A.47 $^1$HNMR spectra of polymer-bound $3HJ$ in DMSO, PHS/AA/TBA (59/6/35).
**Figure A.48** $^1$HNMR spectra of polymer-bound $3MJ$ in DMSO, PHS/AA/TBA (62/3/35).

**Figure A.49** $^1$HNMR spectra of polymer-bound $3MJ$ in DMSO, PHS/AA/TBA (58/7/35).