Mechanisms of EUV exposure: photons, electrons and holes

Amrit Kausik Narasimhan
University at Albany, State University of New York, ANarasimhan@sunypoly.edu

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Mechanisms of EUV Exposure:
Photons, Electrons and Holes

By Amrit Narasimhan

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Submitted to the University at Albany, State University of
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Abstract

The microelectronics industry’s movement toward smaller and smaller feature sizes has necessitated a shift to Extreme Ultra-Violet (EUV) lithography to be able to pattern sub 20-nm features, much like earlier shifts from i-line to 248 nm. However, this shift from 193-nm lithography to EUV (13.5 nm) poses significant obstacles. EUV is the first optical lithography to operate in an energy range (92 eV per photon vs. 6.4 eV per photon for 193 nm lithography) above the electron binding energies of common resist atomic species. This significant energy increase complicates resist design. For exposures of equal dose, resists receive 14 times fewer photons in EUV relative to 193 nm. Thus, for EUV photoresists to be able to reap the benefits of smaller resolution they must also maximize absorption while still maintaining photo-reactivity. In order to design EUV resists for manufacturing, the first step is to understand the mechanisms of exposure involved in EUV photochemistry.

In this Thesis, we present three studies performed to understand the behavior and reactivity of electrons and holes in chemically amplified photoresists. These three studies can be characterized by their approaches—computational and experimental, and serve to develop better resist models for EUV reactions and mechanisms.

The first study discusses the adaptation and improvement of a Monte Carlo electron-resist simulation program to understand EUV photochemistry by modeling total electron yield, thickness loss, and sub-10 eV electron-resist interactions. The second study evaluates the mechanism of internal excitation as a possible pathway for acid generation in EUV resists by the investigation of electron-induced fluorescence. The third study aims to investigate the reactivity of electrons and holes in chemically amplified resists and determine their relative contributions to acid production.
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Publications

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This Thesis is Dedicated to

My friends, for keeping me sane

My cousins, aunts, and uncles, for their encouragement and affection

My grandparents, for their blessings and well wishes

And especially to

My brother, for his friendship and inspiration

And my parents, for their love and support
Chapter 1: Introduction

1.1 Integrated Circuit Manufacturing and Photolithography

Modern computers are built upon integrated circuits which rely on the fundamental physics of semiconductors. Integrated Circuits (or ICs) are systems of physical devices known as transistors built in silicon chips that take advantage of the controllable conductivity of semiconductors to convert analog electrical signals into binary for the purpose of carrying out logical and arithmetic calculations.\(^1\) The semiconductor industry takes advantage of multiple physical processes to build transistors in the silicon itself.\(^2\) Semiconducting and insulating films are used to construct and isolate transistors while metal (originally aluminum, and now copper) is used to wire these transistors together.

ICs are made of billions (or trillions) of transistors connected in intricate circuits designed with precision to carry out computation. Construction of these transistors, ranging from microns (10 microns in 1971) to a few nanometers (14 nm in 2016) in size, involves many complicated steps, including photolithography, reactive ion etches, vapor deposition (chemical or physical), wet deposition, and even mechanical planarization.\(^3\) Furthermore, increasing demands for computation speed and efficiency have required the shrinking of transistors by 50% in area every 1.5-2 years; this observation by Gordon Moore in 1965 is known as Moore’s Law.\(^4\) In order to maintain the semiconductor industry’s pace, new targets in reliability must be met for every process involved in IC manufacturing.

The primary avenue through which feature sizes are shrunk is through the photolithographic process. In photolithography (or lithography), a material known as a photoresist is exposed to light
through a mask. Exposure through the mask transfers the pattern for the devices into the resist. Resists retain this knowledge through photochemistry—areas that are exposed to light undergo a chemical change that allows a wet development process to dissolve either the exposed or unexposed regions (Figure 1.1). Following exposure and development, the resist that remains on the surface of the silicon substrate resists the subsequent etch processes that carve away the bare silicon to build transistors or the metal interconnects (Figure 1.2).

![Diagram](image)

**Figure 1.1.** Exposure of the photoresist to light causes a chemical change. Subsequent development rinses away the unexposed region (negative tone resist) or the exposed region (positive tone resist).
Figure 1.2. Following photoresist exposure and development, an anisotropic etch process is used to etch into the silicon substrate. Areas covered by the remaining resist are protected from the etch (the photoresist resists the etch), and then the resist is removed to reveal the bare substrate underneath.

1.2 Reduction in Feature Size via Wavelength Reduction

To keep pace with Moore’s law (and the economic demands placed on the semiconductor industry), the feature sizes printed by lithography have had to shrink over time. Occasionally, the wavelength used by in lithography is deemed no longer sufficient to print features small enough to keep pace, so a new photolithographic technology is developed. Incremental improvements made by increasing the numerical aperture (or NA) of the light source in accordance with Rayleigh’s Criterion (Figure 1.3) can only carry a lithographic technology so far—eventually, a new wavelength is required.
Photolithography began with g-line (436-nm) sources, then shifted to h-line (405-nm), i-line (365-nm), deep UV (DUV, 248-nm), and finally 193-nm by 2004. The lifetime of 193-nm lithography was extended by the advent of immersion lithography, where a meniscus of water between the optics and the resist serves to increase the NA, and then further extended by multiple patterning. Multiple patterning, or the use of successive lithographic steps without development in between, allows for the printing of features of smaller size by using multiple masks slightly offset from each other. However, at some point, this extension of 193-nm lithography will no longer meet the needs of the industry, and a shift to a new technology is required.

**Figure 1.3.** Lithographic technologies have moved to smaller wavelengths of light over time to print smaller and smaller feature. Current devices (2017) are manufactured using 193-nm light produced by ArF laser sources.
1.3 Extreme Ultra-Violet (EUV) Lithography and Resists

EUV lithography (13.5-nm) is the leading candidate to replace 193-nm immersion lithography and multiple patterning for the 7-nm node and beyond. EUV presents advantages over 193-nm lithography in terms of fewer patterning steps, higher resolution, and sharper printed features (Figure 1.4), but comes at the cost of vastly more complex source and mask issues. However, this shift from 193-nm lithography to EUV poses significant obstacles. EUV is the first optical lithography to operate in an energy range (92 eV) above the electron binding energies of common resist atomic species.

Figure 1.4. Modern EUV resists are chemically amplified; they take advantage of the production of strong catalytic acids created by PAG reactions upon exposure in order to deprotect multiple groups and generate many solubility-changing reactions from one photon absorption.\(^6\)
This significant energy increase complicates resist design. For exposures of equal dose, resists receive 14-times fewer photons in EUV relative to 193 nm. Thus, for EUV photoresists to be able to reap the benefits of smaller resolution they must also maximize absorption while still maintaining photo reactivity. Furthermore, 193-nm lithography will rarely cause ionization within the resist, but ionization is a main mechanism through which photons are absorbed in EUV. EUV exposure liberates electrons at energies (~75-82 eV) which can cause further ionization or other reactions. It is these electrons and their radical-cation holes that provide the chemical transformations needed to produce solubility changes in photoresists. Therefore, understanding the reactivity of electrons and holes is key to optimizing the performance of future EUV photoresists.

Since the beginning of EUV research in 1986, remarkable progress has been made in the development of the source technology, mask and pellicles, and in resists. Resist requirements for the feature sizes to be printed by EUV are demanding—resists must meet new targets in resolution capability, line-edge roughness (LER), and sensitivity (or dose) to be implemented in high-volume manufacturing. However, these three parameters are inversely related to each other through what is known as the RLS trade-off. In other words, improvement in one parameter will likely result in a diminishing in at least one of the other two.

Modern EUV resists (based on 193-nm resists) take advantage of chemical amplification in order to produce solubility changes upon exposure to light (Figure 1.5). Typically, these resists are composed of phenolic polymers with deprotection groups such as t-butyl acrylate. These groups are deprotected upon reaction with acid to form carboxylic acids that are easily developed away by rinses in aqueous tetramethylammonium hydroxide (TMAH, pH 13.9). The exposure process is used to generate the acid via the photon and electron reactions of photo-acid generators.
(PAGs). These PAGs generate strong acids such as triflic or perfloro-1-butanesulfonic acid which are capable of diffusing through the polymer matrix and catalytically deprotecting multiple (as high as 50-100) groups. In this way, one PAG reaction can cause many solubility-changing reactions, so the effect of one photon absorption is chemically amplified.

Other resists, often developed in academia, take advantage of more intricate chemistry, such as acetal-based deprotection,\textsuperscript{11-14} chain-scission resists,\textsuperscript{14-16} fluorine-rich resists,\textsuperscript{17,18} or even metal-based resists that take advantage of increased EUV absorbance to improve sensitivity and stochastics.\textsuperscript{19-28} These resists seek to deliver improved LER, sensitivity, or resolution capabilities over traditional chemically amplified resists. The mechanisms of exposure for these more exotic resist platforms will not be discussed in this thesis, but may have similarities with the mechanisms described in Chapters 2, 5, and 6.

![Chemical reaction diagram](image)

**Figure 1.5.** Modern EUV resists are chemically amplified; they take advantage of the production of strong catalytic acids created by PAG reactions upon exposure in order to deprotect multiple groups and generate many solubility-changing reactions from one photon absorption.
1.4 EUV Photochemistry in Chemically Amplified Photoresists

This thesis covers an experimental and computational investigation of the mechanisms involved in EUV photochemistry for the purpose of contributing knowledge that may better aid resist chemists in developing new resists technologies. EUV resist chemistry, dominated by electron interactions, is vastly more complicated than the resist chemistry of previous lithographic technologies. This work will discuss several fundamental physical and chemical mechanisms that play a role in resist interactions (Figure 1.6). Primarily, this thesis will seek to answer the questions:

1. Does modifying the underlying physical and chemical models of EUV exposure to incorporate low-energy electron-resist interactions improve simulation?
2. What is the contribution of internal excitation to acid generation?
3. What is the relationship between and the relative contributions of electron-trapping and hole-initiated chemistry to acid production in resists?

This thesis will address these questions in the order given:

- Chapter 2: A mechanistic overview of the EUV exposure process will provide the framework for the rest of thesis.
- Chapter 3: An introduction to Monte Carlo modeling of electron-matter interactions will serve to provide the background for question 1.
- Chapter 4: A more in-depth look at improvements in computational modeling of EUV photochemical mechanisms will address question 1.
- Chapter 5: Internal excitation is discussed and experimental data is shown to answer question 2.

- Chapter 6: An experimental exploration of the mechanisms of electron-trapping and hole-initiated chemistry and their respective contributions to acid production will seek to answer question 3.

- Chapter 7: A brief conclusion of the work described in this thesis will pull together the questions outlined above and their answers, as well as look to provide direction for future work.

**Figure 1.6.** A summary of the physical interactions and chemical mechanisms of EUV exposure.
1.5 References


Chapter 2: Mechanisms of Resist Exposure to EUV

2.1 Introduction

As described in the previous chapter, the large change in wavelength between 193-nm and 13.5-nm (EUV) light produces enormous improvements in resolution, yet it also creates new challenges for resist chemists since the mechanism of EUV exposure is completely different than the mechanisms previously encountered using 193- or 248-nm light. In particular, the absorbance of 193-nm photons causes molecular electrons to be excited from ground state to an excited state within the same molecule. In contrast, the absorption of EUV photons causes molecular electrons to be ejected from the molecules with ~75-82 eV energy, leaving a radical-cation “hole” in the molecule.1-5 These liberated electrons have sufficient energy to undergo other ionization reactions or other reactions. It is these electrons and their holes that provide the chemical transformations needed to produce solubility changes in photoresists. Therefore, understanding the reactivity of electrons and holes is key to optimizing the performance of future EUV photoresists.

The exposure mechanisms that occur in chemically amplified resists during exposure to 193- or 248-nm light are well understood.6,7 For example, either the photon is absorbed by a Photo-Acid Generator (PAG) creating an excited state in the PAG. Or, the photon is absorbed by the polymer which can then sensitize a PAG molecule. At these wavelengths, the resist components can be tailored to minimize photon absorption in the polymer and maximize photon absorption by the PAG.6 Because the concentration of reacting species is known, the quantum yields (QYs) of these reactions are also known. Furthermore, at these longer wavelengths the quantum yields of PAG exposure do not exceed 100%.8
However, in EUVL, the underlying physical and chemical mechanisms of EUV exposure are areas of active research and many of the fundamental questions remain unanswered. This chapter aims to address some of these topics and provide an overview of research that attempts to answer specific questions, namely:

1. What are the elementary physical and chemical mechanisms in EUV photochemistry? (Section 2.2 and 2.3)

2. What is the total number of electrons generated (total electron yield, TEY) during EUV exposure? (Section 2.4 and 2.5)

3. How does TEY impact our mechanistic understanding of EUV chemistry, specifically in chemically amplified resists? (Section 2.6)

4. How far do electrons generated in EUV exposure travel in resists? (Section 2.7)

### 2.2 The Physics of EUV Exposure Mechanisms

In EUVL, photons can interact strongly with any resist components, generating electrons through photoionization. An initial photoelectron with an energy of about 75-82 eV may cause further ionization in the resist, generating additional electrons that contribute to the chemical reactions during exposure. In this section, we describe the physics of the interactions of these electrons as they interact with molecules from their initial creation ~80 eV until they decay to ~2 eV.

There are several underlying elementary interactions between these ~2-80 eV photo- and secondary electrons\(^9\) (Figure 2.1): (1) **Photo-ionization**: a photon is absorbed by an atom and liberates an electron with enough kinetic energy to interact further. The ionized resist component may yield further electrons or charged ion fragments through electronic and atomic relaxation processes.\(^5\) (2) **Electron ionization**: a ballistic electron scatters off an atom and produces another
electron such that the total kinetic energy of the two electrons is equal to the energy of the incident electron less the binding energy of the “daughter” electron. (3) Plasmon generation: an incident electron scatters off an atom, losing energy and causing a coherent displacement wave in the bound electrons. At the moment, it is unclear if plasmons can be an additional source of electron-hole pairs. (4) Elastic scattering: the trajectory of an incident electron is altered by the Coulombic potential of an atom with no associated energy loss. In chemically amplified resists, ionization and plasmon generation of PAG or polymer may directly produce acid.²

![Diagram of electron interactions](image)

**Figure 2.1.** A schematic drawing of the four elementary physical electron-matter interactions described above.

In order to understand the interactions of electrons with molecules in resist films, we must learn from the excellent research being conducted in the gas phase by atmospheric scientists. These gas-phase experiments can provide precise and useful data to help the EUV community understand EUV resist mechanism. However, these experiments do not account for phenomena
such as molecular dampening or cage recombination that are present in condensed-phase interactions, and thus must be interpreted with care. An excellent review of electron-induced chemistry by W.F. van Dorp\textsuperscript{1} provides a summary of this work and suggests applications to EUV resist exposure mechanisms. This work divides these eight interactions (Figure 2.2) into three broad categories: (1) electron impact ionization, (2) electron attachment, and (3) electron excitation. In electron impact ionization (Figure 2.2, eq. 1-3), following the interaction of a molecule with the initial electron, charged species are created, either in the form of the charged molecule and additional electrons, or at least one charged molecular component is generated (i.e. a bond is broken) sometimes accompanied by an additional electron. (2) In electron attachment (Figure 2.2, eq. 5-6), an electron can attach to a molecule, occupying a higher energy orbital, and creating a charged molecule, which may ultimately lead to the dissociation of the molecule (known as dissociative electron attachment, or internal excitation). (3) In electron excitation, (Figure 2.2, eq. 4, 7-8) an energetic electron may donate some energy to a nearby molecule, elevating a bound electron to a higher energy, and thus exciting the molecule. This excited molecule may then dissociate into neutral species.
\[ AB + e^- \rightarrow AB^{n+} + e_{\text{scattered}}^{-} + n e_{\text{emitted}}^{-} \]  
\[ \rightarrow A + B^+ + e_{\text{scattered}}^{-} + e_{\text{emitted}}^{-} \]  
\[ \rightarrow A^+ + B^- + e_{\text{scattered}}^{-} \]  
\[ \rightarrow AB^* + e_{\text{scattered}}^{-} \]  
\[ \rightarrow AB^- * \]  
\[ \rightarrow A + B^- \]  
\[ \rightarrow A + B + e_{\text{scattered}}^{-} \]  
\[ \rightarrow A^* + B + e_{\text{scattered}}^{-} \]  

(1) – ionization, single or multiple  
(2) – dissociative ionization  
(3) – ion pair formation  
(4) – excitation  
(5) – attachment  
(6) – dissociative attachment  
(7) – dissociation into neutrals  
(8) – dissociation into excited neutrals

**Figure 2.2.** The physical interactions of electrons with molecular species as chemical equations. (Adapted from Ref. 1.)

### 2.3 The Chemistry of EUV Exposure Mechanisms

Researchers\(^{2,3,7,8,11-15}\) have proposed that the dominant chemical mechanisms involved in EUV chemically amplified resists include: (1) electron trapping (or dissociative electron attachment), (2) hole-initiated chemistry, or (3) internal excitation (or dissociative electron excitation), as described below (Figure 2.3). In electron trapping, a low energy electron (perhaps 0-5 eV\(^{13}\)) may be trapped by a PAG molecule, occupying an antibonding orbital in the PAG. This leads to a change in the electronic structure of the PAG, causing the molecule to fall apart.\(^{2,9,10}\) (2) Holes left in ionized atomic species within the resist may also contribute to resist chemistry.\(^{2,10}\) A hole on a polymer may lead to a disproportionation reaction with other polymer side-chains, ultimately producing acid on its own. Additionally, (3) electrons of higher energy (10-80 eV) in resists may deposit energy by exciting electrons from bonding to anti-bonding states in PAG molecules. This excited PAG molecule may then dissociate to produce acid.\(^{12}\)
Electrons also interact with polymers directly.\textsuperscript{13,16,17} Enomoto \textit{et al.}\textsuperscript{13} exposed different polymers to increasing doses of electron beam (90 keV) and analyzed the resulting resist through gel permeation chromatography. They observed that PHS-type chemically amplified photoresists exhibited cross-linking, while poly-2-methyladamantane-2-methacrylate underwent chain scission upon exposure, similar to PMMA. High dose e-beam exposure of polystyrene was also posited by Narasimhan \textit{et al.}\textsuperscript{11} to cause a high degree of backbone conjugation that ultimately lead to e-beam induced fluorescence. Fedynyshyn \textit{et al.} have demonstrated the relationship between resist polymer composition and clearing dose, \(E_0\),\textsuperscript{16} and calculated chain scission and cross-linking reaction quantum yields in polymers due to EUV exposure.\textsuperscript{17} These direct electron-polymer interactions may play an additional role in acid production.

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\textbf{Figure 2.3.} Chemical mechanisms of EUV exposure. \\
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2.4 Maximum Quantum Yield in Chemically Amplified Photoresists

Research by Higgins et al.\textsuperscript{18,19} and Hirose, Kozawa, and Tagawa\textsuperscript{20} determined film quantum yields (FQYs) of acid production during EUV exposure by formulating chemically amplified resists with an acid-sensitive dye (Coumarin-6) to measure the concentration of acid in a film with UV/Vis absorbance spectroscopy. These researchers determined FQYs for resists containing three different PAGs at concentrations ranging from 0-1000 mM. Ultimately, the FQYs of these resists were shown (Figure 2.4) to plateau at PAG concentrations greater than 600 mM, with iodonium PAGs producing more acid than sulfonium or nonionic PAGs at all concentrations. More importantly, this work demonstrated a maximum FQY of 4.9-5.9 acids per photon for the iodonium PAGs.\textsuperscript{18-20}

\textbf{Figure 2.4.} Film quantum yields (FQYs) for an iodonium, sulfonium, and non-ionic PAG measured by two groups using absorbance measurements of protonated Coumarin-6. (Data from Refs. 18 and 20 used with permission from SPIE and The Japan Society of Applied Physics, respectively.)
2.5 Total Electron Yield (TEY) in EUV Photoresists

In EUVL, FQYs for photoacid generators have been shown to exceed 100%. In a single initial ionization process one EUV photon is absorbed so greater than unity quantum yields indicate that the number of electrons generated plays a large role in resist sensitivity. Work carried out by several groups suggests that the total electron yield (or TEY) from EUV absorption is ~2-4 electrons per absorbed photon (e⁻/hν). The exact TEY value is not important, but these greater than unity numbers influence the mechanistic understanding of the EUV exposure process. In general, these studies are approached through either experimentation or modeling. In either case, studies may build upon assumptions that are carried over from research that may or may not be directly applicable to EUV (e.g. gas phase, exposure with keV electrons or photons).

Quantum yield measurements of acid produced in EUV exposure carried out by the Brainard group and Kozawa and Tagawa have shown film quantum yields up to ~6 acids per absorbed EUV photon. Typical photochemical reactions have yields of 60-100%, so it may seem that 6-10 electrons are required to yield 6 H⁺. To investigate this claim, several groups have used Monte Carlo modeling to simulate EUV exposures. LESiS (Low energy Electron Scattering in Solids, Chapters 3 and 4), developed by Ocola and Brainard, predicted 1.8 ± 0.8 e⁻/hν. Similar modeling, developed by Biafore et al. and used with PROLITH by De Schepper et al. predicts 3.69 ± 0.08 e⁻/hν. Additionally, Kozawa and Tagawa, using assumptions from higher energy radiation physics, predict 4.2 e⁻/hν.
Similar electron scattering models developed by two different groups predict different total electron yields (TEY) based on different handling of input parameters such as ionization (or inelastic) cross sections.

Experiments by De Schepper et al.\textsuperscript{4} estimates $4.2 \pm 0.3$ e$^-$/h\textnu for a standard EUV resist. They contacted the back of a conductive substrate to ground through an ammeter, and then coated a 50-nm resist on top. They then measured the current flowing into the substrate while exposing the resist to 5-500 nm light. In this experiment, the charge imbalance created by electrons scattering out of the film is compensated by a current into the substrate. By measuring the compensating current, and adjusting for the resist absorption at the exposure wavelengths, the group then calculated the total electron yield. Further experimentation should be carried out to validate these results.
2.6 Mechanisms of Acid Generation in Chemically Amplified Resists

Kozawa and Tagawa of Osaka University have conducted excellent work in understanding the photo- and radio-chemistry of photoresists. Of particular importance to EUVL is their work in pulse radiolysis to understand electron-polymer and electron-PAG interactions. Their review of this work in 2010 summarizes many of their findings.¹²

Due to the difficulty of studying thin polymer films, and especially of generating EUV photons, many early pulse radiolysis experiments were conducted with model resist solutions and 75+ keV electrons. In these pulse radiolysis experiments,²²²⁻²⁴ a quartz cell is loaded with a chosen solution, in many cases a polymer, PAG, and sometimes Coumarin-6, all dissolved in tetrahydrofuran. High energy electrons are injected into the system and the transient UV-Vis-IR absorbance is measured. The reaction of the high-energy electron, now solvated, with solution components can be monitored via the absorbance of the solution (at a particular wavelength) over a short period, usually several picoseconds. This is referred as a kinetic trace in these experiments (Figure 2.6). Such experiments allow the monitoring of thermalized electrons over time as they react with other solvated species, such as PAGs. Figure 2.6 shows the reaction (and depletion) of solvated electrons in solutions of increasing PAG concentration, demonstrating the effect of PAG concentration on electron lifetime (in solution). Similar experiments prove difficult in solid phase—electron-PAG reactions must be measured differently in resist films, as discussed in Chapters 5 and 6.

These kinetic traces are useful for monitoring the rate of reactions of “thermalized” (< 1 eV) electrons in the presence of different polymers or PAGs. Through this work, as well as measurements of acid yield through acid-sensitive dye experiments (Section 7.4.3), Kozawa and Tagawa have arrived at a proposed mechanism for acid production in chemically amplified EUV resists. Their proposal is best summarized by Thackeray et al. (Figure 2.7).¹⁰
Figure 2.6. Kinetic traces (absorbance at 1300 nm vs. time) for several concentrations of the PAG triphenylsulfonium tris(trifluoromethansulfonyl)methane. High energy electrons are injected at $t = 100$ ps and are thermalized (i.e. their energies are $< 1\text{-}2\text{ eV}$) by approximately 200 ps. It can be observed that these thermalized electrons react (and thus their signal decays) faster with increasing concentrations of PAG in solution. [Reproduced from Ref. 2 with permission; Copyright (2010) The Japan Society of Applied Physics]
Figure 2.7. A mechanism for the generation of acid in chemically amplified resists, proposed by Kozawa and Tagawa, and summarized by Thackeray et al. (Reprinted with permission from Ref. 10.)

**Hole-Initiated Chemistry.** In this mechanism (Figure 2.7), (1) an EUV photon is directly absorbed by the polymer matrix, liberating a photoelectron and leaving a charged radical on the polymer side group. (2) The radical cation polymer undergoes a disproportionation reaction with a nearby unexposed polymer unit, creating a neutral radical and a cationic polymer group. (3) The primary electron, or any other secondary electron, interacts with a PAG through electron trapping (dissociative electron attachment) to release the acid anion. (4) The acid anion reacts with the radical polymer group created in step 2, and the acid is “released.”

This mechanism is built on several assumptions – principally, that direct acid generation due to the absorption of EUV photons by PAG molecules is rare, and only becomes appreciable at high
PAG concentrations. Traditional photoacid generators and EUV resist polymers have similar EUV optical densities so this assumption seems reasonable.\textsuperscript{7,25} A second assumption, implicit in the proposed mechanism, is that hole-initiated chemistry and electron trapping are both required in order to produce acid. In other words, acid production is a function of \textit{co-dependent} electron trapping and hole-initiated chemistry. However, there is some evidence that these mechanisms may be able to operate independently in EUV resists.

Acid quantum yield measurements were made by Nakano \textit{et al.}\textsuperscript{24} using Coumarin-6 in two different polymers with the same PAG. Two similar resists were exposed, one consisting of poly-4-hydroxytyrene (PHS) polymer and the other of poly-4-methoxystyrene (PMS), to 75 keV e-beam and the protonation of Coumarin-6 through absorbance spectroscopy was measured. They observed almost double the acid quantum yield in the PHS resist than in the PMS resist and attributed this difference to the relative ease of deprotonation in PHS \textit{vs.} PMS (Figure 2.8). This was further supported by molecular dynamics calculations made by Endo \textit{et al.}\textsuperscript{26} which calculated a smaller activation energy required for the deprotection of PHS than for PMS. However, the key piece of data is that a PMS resist \textit{does} produce acid. Chapter 6 addresses further investigation in this area, particularly: to what extend does hole-initiated chemistry contribute to acid yield in resists?
**Figure 2.8.** Film quantum yields for resists composed of poly-4-hydroxystyrene (PHS) and poly-4-methoxystyrene containing the same PAGs at the same concentrations. The higher absorption of the PHS resist at $\lambda = 530$ nm indicates a higher acid quantum yield. [Reproduced and adapted from Ref. 24 with permission; Copyright (2006) The Japan Society of Applied Physics]

**Electron Trapping.** The production of acid in a PMS-based film lends support to the independent operation of electron-PAG reactions to produce acid. PMS has been shown, through pulse radiolysis and calculation, to have a higher energetic barrier to deprotonation. This high energetic barrier effectively “knocks out” the hole-induced chemistry pathway for the PMS resist, and yet acid is still produced, presumably entirely from the PAG. In addition, Thackeray *et al.*, Goldfarb *et al.*, and Tarutani *et al.* have shown that PAG reduction potential correlates well with EUV clearing dose, $E_0$, and acid yield, indicating that PAG electron affinity directly relates
to acid production in EUV exposure (Figure 2.9). Further research, discussed in Chapter 6, demonstrates that direct electrolysis of PAGs can produce acid.

Co-dependent electron trapping and hole-initiated chemistries would require a full 6-10 electron-holes pairs to produce the 5-6 H⁺ observed by acid quantum yield measurements (Section 2.4 and Chapter 6). Fully independent operation of these mechanisms may instead push the number of required e/p⁺ pairs down to 3-5, more in line with TEY predictions and measurements. There is yet a third assumption built into the proposed mechanism of Kozawa and Tagawa—their mechanism requires that an acid anion is released near to the polymer-bound proton. Generally, the bound proton is thought to be immobile, so electrons must be confined to short distances from their ionization sites in order to provide the anion release needed for efficient acid production. If acid production mechanisms can instead operate independently, this confinement of electron range is no longer required. Therefore, it is important to investigate how far electrons can travel in resists (Section 2.7 and Chapter 4).

Figure 2.9. Thackeray et al.¹⁰ and Tarutani et al.¹⁵ have shown that PAG reduction potential correlates well with EUV photospeed (E₀) and acid yield. (Reprinted from Ref. 10 and Ref. 15, respectively.)
**Internal Excitation.** The discrepancy between the analysis of acid and total electron yields poses a challenge in understanding EUV photochemistry. If 6 acids can be produced by up to 4 electrons, then either electrons can produce multiple acids (perhaps via internal excitation), or holes left behind by ionization can independently generate acid, or some other mechanism(s) must account for this discrepancy. Internal excitation (Figure 2.10) provides a potential avenue for many acids to be generated without the consumption of an electron. An electron may donate the relatively small amount of energy, 2-3 eV, required to promote a bound electron to an excited state, and then continue on to the next interaction. Chapter 5 discusses experimental evaluation of internal excitation as a possible pathway for acid production in chemically amplified resists.

![Figure 2.10. Model of acid production via internal excitation.](image)

**2.7 Electron Travel Distance in Photoresists**

The distance travelled by an electron from the site of ionization until it can no longer cause reactions due to a loss in energy is called the “electron travel”. This distance has been estimated by a few groups to be on the order of 2-4 nm. This distance is consistent with the electron travel range for the linked mechanism proposed by Kozawa and Tagawa. However, experiments
conducted at CNSE (Figure 2.11, Chapter 4) and at CXRO, have shown that low energy electrons (15-250 eV) can penetrate up to 10+ nm in resists.\textsuperscript{9,27} In both studies, thickness loss due to low energy e-beam exposure was measured with ellipsometry. Additionally, models based on dielectric response theory\textsuperscript{27} and simulations in LESiS\textsuperscript{28} have shown agreement between electron penetration depth calculations and experimentation. The methodologies for the experimentation and modeling carried out at CNSE are discussed in Chapter 4.

The results by CNSE and CXRO show that electrons can travel up to 20 nm in EUV resists, potentially outside the reaction-accessible range of a polymer-bound proton, suggesting that electron trapping and hole-initiated chemistry need not occur near each other to generate acid. Further investigation is needed to characterize electron travel distances in different resists platforms. Such studies may aid in determining the mechanisms of EUV exposure, both in chemically amplified resists, or other more exotic platforms. In either case, however, this work may be important in determining the ultimate resolution capabilities for EUV resists.
Figure 2.11. Thickness loss in an open source chemically amplified positive tone resist due to e-beam exposure at CNSE (experimental data in squares) compared with LESiS simulation (dashed lines). 80 eV electrons are shown to penetrate up to 20 nm at high doses, in agreement with simulation.\textsuperscript{9,27,28} (Adapted from Ref. 28.)
2.8 Conclusions

The basic physical interactions involved in EUV photochemistry are well known, but their impact on EUV photochemistry remains an active area of research. The total electron yield has been narrowed to a range of 2-4 e\(^{-}/\)hv through modeling, and the acid yield in chemically amplified photoresists has been determined to be a maximum of 6 acid/hv. Experimentation is needed to make final conclusions on electron yield and evaluate acid yield with EUV. Further work is needed to determine if the total electron yield or acid yield can be improved to produce better resists for manufacturing. However, some of the underlying chemical mechanisms involved in EUV exposure are still not well understood. Experimental evidence supports a mechanism in which direct electron-trapping by PAGs can produce acid, and that polymers are also involved in acid production mechanisms, but further research is required to determine if electron trapping and hole-initiated chemistry operate co-dependently or independently. Future work should also be directed to applying mechanistic analysis and experimentation to the development of more exotic metal-based or nanoparticle resist systems.
2.9 References


25. The Center for X-Ray Optics (CXRO) at Lawrence Berkeley National Laboratory. 

http://henke.lbl.gov/optical_constants/filter2.html


Chapter 3: Monte Carlo Modeling of Electron-Matter Interactions

3.1 Introduction: Monte Carlo Modeling

Monte Carlo modeling is essentially a probabilistic approach to simulating the behavior of systems. It takes advantage of probabilistic information in cases where analytic predictions may be too difficult or impossible to find. Monte Carlo simulations, named for their reliance on random numbers, are useful in analyzing systems with many coupled subunits and degrees of freedom, such as in the case of large-scale financial analysis, failure analysis, or even evolutionary algorithms in computer science. However, Monte Carlo methods may be most used in analyses of complex physical systems, such as fluid simulation, solid-phase ordering, molecular modeling, and cellular interaction modeling. In principle, Monte Carlo modeling may be applied to any system in which behavior is probabilistic in nature, and these probabilities (and uncertainties) are known. In addition, Monte Carlo approaches are particularly useful if the system to be modeled has the property of “memorylessness”, or, in other words, the future behavior of the system can be determined entirely from the present state of the system and the relevant probabilistic distributions. This allows for multiple (often, thousands to millions) of independent simulations to determine overall statistical probabilities for extremely complex systems.

Monte Carlo modeling is particularly useful in modeling particle-particle, or particle-material interactions. In these cases, simulations are used to generate information about many interactions in a manner in which the underlying physics can be investigated with ease. Often, experimental approaches may be time consuming, laborious, materials-limited, or instrument-limited. For these
situations, Monte Carlo modeling may be seen as an idealized “experiment”, with perhaps less
time consumption and little materials consumption (if any). Simulations can be carried out on
simple, single core computers, or on multi-core supercomputers depending on system complexity.

Of particular relevance to this work is the large body of Monte Carlo approaches for electron-
matter interaction simulations. Primarily, Monte Carlo programs developed for this purpose are
used for electron and ion microscopy simulation (*e.g. Casino, Penelope, Win X-ray, LMS-MC, and
Electron Flight Simulator*). However, there is long history of Monte Carlo simulation of electron-
matter interactions for lithography purposes (Figure 3.1), beginning with Green and Murata in the
late 1960s and early 70s, and then Kyser, Murata, and Liljequist in the 80s. Further work was
carried out in the 90s, and, recently, this work has become more important with the advent of e-
beam and EUV lithography in manufacturing. The improvement in modeling and increase in
computational power over time has allowed for the simulation of low and lower electron energies,
approaching the boundary between physics and chemistry.

This chapter will focus on two separate Monte Carlo approaches, one developed by Dapor and
used in *PROLITH*, and the other developed by Ocola, Han, and Cerrina, and implemented in *LESiS*.
Both of these approaches implement Monte Carlo code for e-beam and EUV exposure modeling.
*LESiS* (Low-energy Electron Scattering in Solids) is used in this work, and some simple
demonstrations of its capabilities are shown here (with more advanced capabilities shown in
Chapter 4).
Figure. 3.1 Lithographically motivated Monte Carlo simulations of electron interactions has a long history, beginning in the 60s and continuing on today. As models improve and computational power increases with time, the lower bound of energies able to be investigated has fallen from $10^4$ eV down to under $10^2$ eV.

3.2 Monte Carlo Approaches for Electron-Matter Simulations

Monte Carlo simulation of particle-matter interactions (primarily electron-matter interactions) began in the 1970s and was primarily motivated by the field of electron microscopy and e-beam lithography.\textsuperscript{1} As such, much of this work relied upon scattering data relevant only in the high energy regime ($> 10$ KeV), such as Bethe’s theory for inelastic scattering,\textsuperscript{2} Mott’s ionization cross sections,\textsuperscript{3} and Rutherford’s elastic scattering cross sections.\textsuperscript{4} Initial work, carried out by Everhart and Hoff\textsuperscript{5} and Kyser and Murata,\textsuperscript{6} began with elastic scattering cross-sections derived from
Rutherford and then eventually Mott, and utilized a Continuous Slowing Down Approximation (CSDA) for continuous energy losses at high energies which eventually morphed into a hybrid model.

More recent work has shifted to modeling at lower energies; Liljequist\textsuperscript{7,8} applied dielectric response theory from Ritchie, Ashley, and Tung to push modeled energies to 100 eV, and other work by Kotera,\textsuperscript{9} Murata,\textsuperscript{10} and Ho\textsuperscript{11} applied discrete energy losses described by Gryzinski-Vriens cross-sections. The work carried out by Ho was computationally implemented (with minor adjustments) as LESiS in 1996 by Leonidas E. Ocola, using Mott elastic cross-sections calculated by Fink, dielectric stopping powers calculated by Ritchie, Ashley, and Tung, and ionization cross-sections from Gryzinski-Vriens theory.\textsuperscript{1} For electrons with energies lower than 100 eV, these mechanisms are aided by the CSDA (down to ~25 eV). Below 25 eV, only Mott elastic-cross sections and ionization cross-sections are used to model electron behavior.

In general, there are two main Monte Carlo strategies used to model electron-matter interactions.\textsuperscript{12-14} The first utilizes the \textit{continuous slowing-down approximation} (CSDA), which assumes that electrons lose energy continuously as they travel through a material. Changes in direction are covered by simple probabilistic models of elastic scattering (usually using the elastic mean free path). This method is advantageous for calculations results that do not require intimate knowledge of electron behavior in the material, e.g. determination of electron backscatter coefficients, or the depth-distribution of “absorbed” electrons. This method is computationally efficient and is used by many SEM simulation programs.

If, on the other hand, accurate information of the inelastic scattering events in the material are required (as is the case in this work), then the \textit{energy straggling} approach is taken. This approach simulates inelastic scattering events along the electron trajectory, along with the elastic events, and
takes into consideration the discrete energy losses associated with ionization and plasmon excitations. In this manner, discrete energy loss events contribute to variations in electron range, otherwise known as straggling. This approach is usually built on top of the CSDA approach, as the CSDA is used to simulate energy regimes for which the program does not have interaction data.

### 3.2.1 The Continuous Slowing-Down Approximation

This approach first calculates the step length, or, in other words, the distance between elastic scattering events (changes in electron direction). The step length ($\Delta s$) is calculated by:

$$\Delta s(E) = -\lambda_{el}(E) \ln(\mu)$$  \hspace{1cm} (3.1)

where $\lambda_{el}$ is the elastic mean free path (usually tabulated for materials, and can be calculated from atomic composition, and a function of electron energy), and $\mu$ is a random number uniformly distributed in the interval $[0,1]$. The elastic mean free path is generally calculated by:

$$\lambda_{el}(E) = \frac{1}{\sum_i n^i \sigma_{el}^i(E)}$$  \hspace{1cm} (3.2)

where $n^i$ is the number density of atoms of element $i$, and $\sigma_{el}^i$ is the total elastic cross section for element $i$ (dependent on electron energy). Then, the new trajectory is calculated using polar and
The energy loss ($\Delta E$) along the step length is calculated using the stopping power of the material (tabulated for many materials by NIST\textsuperscript{15}):

$$\Delta E = -\frac{dE}{ds}\Delta s(E)$$ (3.3)

The program terminates the simulation of a particular electron below a specific energy cutoff, often user defined, and then begins the simulation of a new electron. This approach is generally ignorant of the statistical fluctuations of the energy losses involved in inelastic scattering, and as a result, should be avoided for applications where knowledge of the energy loss mechanisms is required. However, this strategy is useful for more simple calculations, such as backscatter coefficient determination, and is useful as a catch-all floating parameter in more complicated approaches.

**3.2.2 The Energy Straggling Approach**

The energy straggling approach requires cross-sectional data for all the inelastic scattering events included in the model (usually ionization, plasmon, and phonon interactions). The step-length is calculated as before, but the elastic mean free path is replaced by
\[ \lambda = \frac{1}{\sum_i n^i (\sigma_{el}^i + \sigma_{in}^i)} \]  

(3.4)

where \( \sigma_{in}^i \) is the total inelastic scattering cross section (a sum of the ionization, plasmon, and other cross sections).

Then, at the end of every step-length, a second random number is generated. If this random number is less than or equal to the probability of inelastic scattering \( (p_{in}) \):

\[ p_{in} = \frac{\sum_i n^i \sigma_{in}^i}{\sum_i n^i (\sigma_{el}^i + \sigma_{in}^i)} \]  

(3.5)

then an inelastic event is triggered; otherwise, the scattering event at the end of the step-length is elastic. The particular type of inelastic event is chosen by generating additional random variables and comparing against the relative likelihoods of those events. The energy loss of that event is either drawn from a table or decided by generating a final random number and comparing against the cumulative distribution function (CDF) of probability vs. energy loss for that event (Figure
3.2). Then, new trajectories are calculated using the appropriate formulae.\textsuperscript{12} This method is directly implemented in PROLITH for EUV and e-beam exposure simulation.

**Figure 3.2.** The cumulative distribution function for probability of a particular energy loss is used to determine the energy loss associated with a discrete inelastic event. A random number uniformly distributed on \([0,1]\) is generated and compared with the CDF. The energy loss could be calculated by applying the inverse CDF to the random number, or interpolating the energy loss from a tabulated CDF (more common).
**3.3 PROLITH Monte Carlo Implementation**

PROLITH, originally developed by Chris Mack, is a computational lithography software that simulates the lithographic process from exposure (include a full set of optical features and illumination styles) to development. For traditional optical lithography, photon absorption in the resist is handled by a simple Monte Carlo implementation of the Beer-Lambert absorption law, using tabulated absorption data for different materials. For EUV (and e-beam) exposure simulation, it became necessary to simulate electron-matter interactions, so the energy straggling approach was implemented.

For this implementation, it is necessary to determine the inelastic mean free paths of resist materials, so the PROLITH team devised an approach based on dielectric response theory. With this approach, probabilities of inelastic events for particular materials could be determined by optical measurements covering the range of 10-100 eV.

Here, the stopping power, inverse inelastic mean free path and the differential inelastic cross sections are calculated from three given equations (3.6-3.9), and the imaginary part of the negative reciprocal of the complex dielectric function is given by the optical constants \( n \) (index of refraction) and \( k \) (extinction coefficient) (Figure 3.3). As an example, Figure 3.3 shows the energy
loss function for polystyrene, determined from the CXRO X-ray database (for > 10 eV). For energies below 10 eV, optical data from UV/Vis spectroscopy or ellipsometry is needed.

\[-\frac{dE}{dS} = \frac{me^2}{\pi \hbar^2 E} \int_0^{\frac{E}{2}} \text{Im} \left[ -\frac{1}{\varepsilon(0, \hbar \omega)} \right] G_e \left( \frac{\hbar \omega}{E} \right) \hbar \omega \, d(\hbar \omega) \]  

(3.6)

\[\lambda_{inel}^{-1} = \frac{me^2}{2\pi \hbar^2 E} \int_0^{\frac{E}{2}} \text{Im} \left[ -\frac{1}{\varepsilon(0, \hbar \omega)} \right] L_e \left( \frac{\hbar \omega}{E} \right) d(\hbar \omega) \]  

(3.7)

\[\frac{d\lambda_{inel}^{-1}}{d(\hbar \omega)} = \frac{me^2}{2\pi \hbar^2 E} \text{Im} \left[ -\frac{1}{\varepsilon(0, \hbar \omega)} \right] \ln \left( \frac{cE}{\hbar \omega} \right) \]  

(3.8)

\[\text{Im} \left[ -\frac{1}{\varepsilon(0, \hbar \omega)} \right] = \frac{\text{Im}[\varepsilon(0, \hbar \omega)]}{|\varepsilon(0, \hbar \omega)|^2} = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2} = \frac{2n(\hbar \omega)k(\hbar \omega)}{(n(\hbar \omega)^2 + k(\hbar \omega)^2)^2} \]  

(3.9)
Figure 3.3. The imaginary part of the negative reciprocal of the complex dielectric function, or the energy loss function, shown for polystyrene for energies of 0-60 eV. (Reprinted with permission from Ref. 16.)

Using this approach, PROLITH is able to simulate photon absorption and electron energy loss events\textsuperscript{16,17} predict total electron yield\textsuperscript{18,19} and simulate complex exposure patterns such as dense lines, contact holes, and other features involved in IC manufacturing.

3.4 LESiS Monte Carlo Implementation

The LESiS approach to modeling electron-matter interactions is a modification of the energy straggling approach. LESiS applies a fully stochastic energy loss model. Particle (electron or photon) sources are defined with a given area or volume and trajectory. Materials are modeled in layer geometries, with each layer defined with given dimensions and atomic composition. The photon or electron is generated randomly in the source field with the given trajectory.
Absorption of photons is handled via Beer’s Law. Absorption coefficients necessary for this model are calculated by summing over all photo-ionization cross-sections weighted by atomic composition. An inversion method is then used to calculate absorption location, whereupon the probability of electron emission is calculated using the photo-ionization cross-sections of each atomic shell. For low Z elements (such as carbon and oxygen), this probability is close to 1.

The source-generated incident electron, or the electron emitted via photo-ionization takes steps of size < 1 nm (0.1 nm was used in this study) through the material and ionization, plasmon, and elastic cross sections are calculated on the fly. At each step, the probability of scattering via all mechanisms is totaled and added to prior probabilities. When this accumulated probability exceeds a random number $0 < R < 1$, the scattering condition is fulfilled. LESiS then uses the atomic total and differential interaction cross sections to identify and record the scattering type (elastic, ionization, or plasmon), the scattering atom species, scattering event location, the scattering trajectory, and corresponding energy loss.

LESiS provides data about the location and type of energy loss events, particle trajectories, particle energies, and atomic information (element, energy level, and orbital) about individual scattering targets. With the aid of analysis scripts developed by our group, we can analyze and distil the large volume of information in each simulation to extract relevant data.

Currently, LESiS incorporates four interaction mechanisms (Figure 3.4): (1) **Photo-ionization**: a photon is absorbed by an atom and liberates an electron with kinetic energy equal the photon energy less the binding energy. (2) **Electron ionization**: a ballistic electron scatters off an atom and in the process liberates another electron such that the total kinetic energy of the two electrons is equal to the energy of the incident electron less the binding energy of the “daughter” electron. (3) **Plasmon generation**: an incident electron scatters off an atom, losing energy and
causing a coherent displacement wave in the bound electrons. (4) **Elastic scattering:** the trajectory of an incident electron is altered by the Coulombic potential of an atom with no associated energy loss. The **Continuous Slowing Down Approximation** handles the “residual” energy loss, and is calculated from literature stopping power information (discussed in more detail by Ocola). The ionization and plasmon cross sections are subtracted from the literature stopping power to produce the CSDA residue that LESiS uses to handle non-discrete energy loss. Possible mechanisms relevant to EUV resist chemistry such as electron trapping, or hole-initiated chemistry, are discussed in Chapter 4.

![Diagram of electron-matter interactions](image)

**Figure 3.4.** A schematic drawing of the four elementary physical electron-matter interactions described above.

### 3.5 LESiS Simulation of Electron Yield

LESiS is capable of modeling electron yield in resists. In simple terms, LESiS is used to simulate EUV absorption, and the resulting electron yield is tallied for each absorbed photon. The average
and standard deviation of these numbers is reported at the total electron yield (TEY). Our previous work reported a TEY of $1.8 \pm 0.8 \text{ e}^-/\text{hv}$ in an open source chemically amplified resist. An analysis of this prior work shows how the original 92 eV of energy in the incoming photon contributes to energy loss in the LESiS simulation (Figure 3.5). In this case, the majority of energy (22% to plasmon generation and 50% to the continuous slowing down approximation) is lost to mechanisms that do not produce electrons.

However, we can adjust the parameters of our model to yield different results. Specifically, we will discuss the possibility of plasmon generation contributing to electron yield, as well as modification of the CSDA to adjust the energy loss to this interaction.

### Energy

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>EUV Absorption $\rightarrow$ 1 e-/p+ pair</td>
<td>13%</td>
</tr>
<tr>
<td>Electron Ionization $\rightarrow$ 1 e-/p+ pair</td>
<td>15%</td>
</tr>
<tr>
<td>Plasmons $\rightarrow$ 0 electrons</td>
<td>22%</td>
</tr>
<tr>
<td>CSDA $\rightarrow$ 0 electrons</td>
<td>50%</td>
</tr>
</tbody>
</table>

**Electron Yield: $1.8 \pm 0.8 \text{ e}^- $ per EUV hv**

**Figure 3.5.** LESiS simulates multiple energy loss mechanisms when modeling EUV absorption. Roughly 50% of the energy of the original 92 eV photon is consumed by the CSDA. The remaining 50% is split between plasmon generation, electron ionization, and the original EUV absorption.

By modifying the assumptions of electron interactions in a controlled manner, we investigated the effects of these changes on predicted TEY. First, we examined the effects of plasmon
generation contributing to electron yield. We considered the case where each plasmon yields a secondary electron by including plasmon events in the tallying process for TEY. In this way, we do not modify LESiS to generate electrons from plasmons, so we avoid dealing with fundamental physics that needs more investigation before implementation in the code. With this adjustment, LESiS predicts an increased electron yield of $3.4 \pm 1.0 \text{ e}^-/\hbar\nu$ (Figure 3.6). Here, the 22% of energy involved in plasmon generation contributes directly to total electron yield.

% Energy

<table>
<thead>
<tr>
<th>Phenomenon</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>EUV Absorption $\rightarrow$ 1 e-/$p+$ pair</td>
<td>13%</td>
</tr>
<tr>
<td>Electron Ionization $\rightarrow$ 1 e-/$p+$ pair</td>
<td>15%</td>
</tr>
<tr>
<td>Plasmons $\rightarrow$ 1 e-/$p+$ pair</td>
<td>22%</td>
</tr>
<tr>
<td>CSDA $\rightarrow$ 0 electrons</td>
<td>50%</td>
</tr>
</tbody>
</table>

**Electron Yield: 3.4 ± 1.0 e⁻ per EUV hv!**

**Figure 3.6.** When we include plasmon generation in the tally process to calculate TEY, we find that LESiS predicts at TEY of $3.4 \pm 1.0 \text{ e}^-/\hbar\nu$.

We additionally modified the CSDA (Continuous Slowing-Down Approximation). The CSDA allows many particle-matter simulation codes to account for high energy particles coming to a rest within the system. In LESiS, the CSDA uses tabulated stopping power data to calculate small energy losses of electrons as they move through matter. We modified the CSDA by scaling the stopping power data; for this study, the original stopping power data is labeled “100% CSDA”, and multiplication of the data by 0.5 or 0.1 are labeled “50% CSDA” and “10% CSDA” respectively. By modifying the CSDA, we observed increased electron yield, even without
considering plasmon contributions to electron yield. The results are summarized below (Figure 3.7). Adjustment to CSDA from 100% to 50% to 10% results in less energy “lost”—the amount of the original 92 eV energy consumed by the CSDA drops from 50% to 36% and 25%. This energy is instead redistributed almost entirely to electron ionization, contributing directly to increased TEY predictions. In the case of “10% CSDA”, LESiS predicts electron yields of 3.7 ± 0.7 (if plasmons do not produce electrons) and 4.7 ± 0.8 e-/hν (if plasmons do produce electrons).

Work carried out by several groups\textsuperscript{16-18} suggests that the total electron yield (or TEY) from EUV absorption is ~2-4 electrons per absorbed photon (e-/hν). In general, these studies are approached through either experimentation or modeling. In either case, studies may build upon assumptions that are carried over from research that may or may not be directly applicable to EUV (e.g. gas phase, exposure with keV electrons or photons).

Modeling by Biafore \textit{et al.} and used with PROLITH by De Schepper \textit{et al.} predicts 3.69 ± 0.08 e-/hν.\textsuperscript{17,18} Additionally, Kozawa and Tagawa, using assumptions from higher energy radiation physics, predict 4.2 e-/hν.\textsuperscript{21} Our results here show that predictions for TEY, especially those based on simulation and modeling, may vary drastically (~2X) with simple modifications to fundamental assumptions and parameters. The exact TEY value is not important, but the resist and exposure models involved in these predictions greatly influence the mechanistic understanding of the EUV exposure process.
Figure 3.7. Adjustment of the continuous slowing down approximation results in increased electron yield in both the cases where plasmons do and do not contribute to electron generation. Furthermore, almost all the energy no longer lost to CSDA is reallocated to electron ionization.

### 3.6 LESiS Dynamic Charge Modeling

LESiS tracks the outcome of each photon or electron interaction event (and its position) in a table with an associated incoming and outgoing direction and energy. Not only does this data become unmanageable at larger numbers of incident particles, but it does not provide information about how the resist is being changed by the exposure process. The solution to this problem was the addition of real time binning code that monitors electrons being simulated. When an interaction
event occurs, the result of that event is ‘binned’ – added to a bin which represents a section of the sample.

The binning code stores data it acquires into a three-dimensional matrix of bins that spans the sample. Each bin is a cube of a specified size (1 nm$^3$ in this study). Memory for a bin is only allocated as needed to conserve resources. These bins are far more memory efficient then the raw data output, so the bins for the entire sample can be held in memory at the same time. This allows LESiS to efficiently keep track of changes to the resist as they happen.

Real time binning tracks the energy deposited due to each inelastic event. Each energy deposition bin contains the sum of energy lost by electrons due to inelastic events inside that bin’s volume. This provides a map of where energy is deposited in a resist, and could be used to model electron-PAG interactions in a chemically amplified resist. LESiS does not model any of the possible mechanisms for PAG breakdown, but energy transferred modeled with LESiS has been correlated with thickness loss.$^{22}$

Real time binning also tracks the number of photoionization and electron ionization events, along with the number of electrons that fall below the 5-eV energy cutoff. By making the assumption that an electron falling below this threshold is trapped by a molecule within the resist,$^{23-25}$ this can be interpreted as a negative charge being deposited in the bin. This allows the code to construct a charging matrix, where ionization events create positive charge, and trapped electrons create negative charge. Currently, LESiS does not model hole recombination, so positive charges can only be eliminated when a negative charge is tabulated in the same bin, and vice versa.

This data can be fed back into the simulation to model time dependent effects. Before binning was implemented, LESiS treated each new particle as if it was the first particle to enter the sample. However, in both EUV and e-beam exposures charge builds up in the resist which either deflects
or attracts subsequent electrons. Using real time binning, LESiS can now model the coulombic attraction due to this charge build up.

![Diagram of electron trapping and coulombic force modeling]

**Figure 3.8.** Graphics describing the two new capabilities of LESiS due to the implementation of binning.

The coulombic force due to charge build up significantly effects e-beam exposures, which can involve high beam currents and doses. This experiment, in which 1700 EUV photons were run – simulating a dose of 27.2 mJ/cm², modeled the effect of charging in EUV exposures. A 10x10 nm EUV photon source exposed a 60-nm resist film on top of a silicon substrate; 10 nm of vacuum separated the resists and the source. Figure 3.9 shows the energy deposited in the sample with and without coulombic force modeling.
The addition of coulombic force modeling allows LESiS to adjust the trajectories and energies of free electrons in the resist by calculating the attractive or repulsive effects of static holes or “trapped” electrons tracked using real time binning.

As can be seen, the effects of charge build up in the EUV process simulated here is negligible. In both simulations, the amount of energy deposited in each bin was found to be the same (indicated by the same colors at each location in Figure 3.9). These experiments used the same random seed, so each electron event had identical results. The only difference was the very small contribution from the electric field attracting or deflecting generated electrons. These effects were too small to cause electrons to travel differently or deposit more or less energy in this simulation. At extremely high e-beam or EUV doses (far beyond typical exposure doses), charging may begin to be important.
3.7 Conclusions

Monte Carlo modeling is a powerful tool for understanding electron-matter interactions, and is particularly useful in simulating EUV or e-beam lithography, where actual exposures may be limited by materials or tool time. In these cases, building accurate modeling software is important for providing guidance to resist chemists to design next generation resists. Furthermore, these sophisticated modeling programs may yield insight into the fundamental interactions involved in EUV photochemistry.

In this chapter, we have described the theoretical framework of Monte Carlo electron-matter interaction simulators, and discussed the two most common methods in use today. Furthermore, we have described LESiS, which is the modeling software used in this work, and described some of its capabilities. The next chapter will discuss two additional, more complex uses of LESiS and the modification of several internal mechanisms in order to more accurately model low-energy electron-resist interactions involved in EUV exposures.
3.8 References


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Chapter 4: Simulation of E-beam Thickness Loss and Electron Energy Loss Spectroscopy using LESiS

4.1 Introduction

Chapter 3 outlines the underlying operation of LESiS and some of its uses. This chapter covers more in-depth explorations of LESiS use and modification to include physical understanding and data from experiments.

The first part of this chapter will cover the simulation and modeling of photoresist thickness loss caused by e-beam exposure and subsequent resist processing (bake, development). The experiment itself will be discussed briefly before a lengthier discussion of the simulation. The simulation was carried out in two phases—the first in 2015, and the second in 2016. In phase one, the general model and approach was developed, but the results showed discrepancies between the experiment and computational modeling. In phase two, the model was updated to include a computational analogue of electron trapping (discussed in Chapters 2 and 6); this updated model showed better agreement between experiment and modeling.

The second part of this chapter covers the study of several resists and resist components via Electron Energy-Loss Spectroscopy (EELS), and the subsequent incorporation of that experimental data into LESiS to bolster the functionality of the simulations in the low-energy regimes (< 50 eV). A brief discussion of the experimentation carried out by the Bartynski group at Rutgers University precedes the incorporation of experimental data into the underlying computational structure of LESiS.
4.2 Thickness Loss Experimentation

4.2.1 Materials

The resists used in this study include four open source EUV resists, labelled OS2, OS4, OS12, and OS14, along with PMMA and a commercially available resist. The open source resists were formulated as 4 wt.% solids in propylene glycol monomethyl ether acetate (PMA); of the solids, 83.5 wt% was a polymer, 15 wt% was a Photoacid Generator (PAG), and 1.5 wt% was a base (Figures 4.1 and 4.2). All resists tested were positive tone. These formulations were spun coat on silicon wafers to a thickness of 60.0 nm ± 1.0 nm, and subjected to a post-application bake at 120 °C for 1 minute. These wafers were then stored in containers in a dry environment and exposed no more than 1 week after application.

**Figure 4.1.** Formulation of the resist heretofore known as OS2. It is composed of an aromatic polymer (65% hydroxystyrene, 20% styrene, and 15% t-butyl Acrylate), an Iodonium Nonaflate PAG, and TBAL (a base).
4.2.2 Exposure and Post-Exposure Processing

Strips cleaved from these wafers were exposed under e-beam in vacuum (10^{-7} torr). A Kimball Physics© electron gun system with a reported electron energy spread of ± 0.5 eV was used to expose the resists. Exposures were carried out at four representative energies; 80, 250, 700, and 2000 eV. The focus of the electron beam was controlled such that the beam at each energy had a full-width at half-maximum (FWHM) of 5 mm, with 95% of beam intensity falling within 10 mm. E-beam currents were measured using a Faraday cup, and currents during exposure were limited to under 1μA, with variation to expedite exposures. Exposure doses spanned four orders of magnitude in µC/cm². Each exposure was carried out on a region of unexposed resist.

Exposed resist samples were extracted from the vacuum chamber and immediately subjected to post-exposure bakes (PEB) at 120 °C for 1.5 minutes. The PEB serves to promote the acid-catalyzed decomposition of t-butyl acrylate that results in the increased solubility of the resist film.
in developer. Resists were developed in 0.26 M tetramethylammonium hydroxide (TMAH) for 45 s. Ellipsometry was used to measure thickness loss.

4.2.3 LESiS Thickness-Loss Simulation Methodology

Within LESiS, an electron source was defined to cover an area of 20x20 nm. Material layer geometries were confined to these same lateral dimensions. A 2-nm thick layer of vacuum was included in the model for completeness. A 200-nm thick layer of OS2, whose atomic composition was calculated, was defined, followed by a 50-nm thick layer of pure silicon (Figure 4.3). OS2 was chosen for modeling because it showed the most consistent results in thickness loss experiments of all the resists tested.

One hundred thousand electrons were generated in each simulation (corresponding to a dose of ~4000 μC/cm²), and four simulations were carried out, corresponding to the four chosen energies in section 2.1 (80, 250, 700, and 2000 eV). The resulting data files were analyzed computationally to simulate thickness loss experiments.
4.3 Thickness Loss Results and Discussion

4.3.1 Experimental Results

Ellipsometry was carried out on these wafer strips, with data gathered on a grid with 0.7 mm spacing covering the exposed regions of photoresist. The ellipsometry model was developed using the Cauchy dispersion law to three terms. Ellipsometry was used to determine the beam intensity profile in the plane of the resist surface using a method developed in the group. A beam current-density function was extracted from post-exposure ellipsometry data by comparing thickness loss relative to exposure dose. These current density functions were calculated for each energy and then the true exposure dose was calculated by integrating under the density functions over the exposure areas. Figure 4.4 shows a sample ellipsometry scan with 80 eV electrons, where each spot represents a single exposure on a fresh region of photoresist. The median of the lowest ten...
measured thicknesses in a given exposure spot was reported as the thickness loss for that exposure dose.

Figure 4.4. (a) Thickness loss as measured by ellipsometry vs. position along the length of a wafer strip, with exposures (spots) of increasing dose (in μC/cm²) from left to right. (b) Contour map (color online) of post-development film thickness along the entire strip, with redder colors representing larger thickness as shown in the color scale. Rings of thickness loss correspond with electron exposure dose (in μC/cm²) with increasing exposure dose from left to right.

The results of the thickness loss experiments are reported in Figures 4.5 and 4.6. Figure 4.5 does not reproduce error bars, while Figure 4.6 does. Multiple exposures of the same doses were averaged together to produce the data and the error bars. For all data points except two 700 eV and one 250 eV exposure, the error bars fall within the displayed data mark.

At higher electron energies (700 and 2000 eV), the resists were observed to “turn negative” beyond doses of 1000 μC/cm²; for the lower electron energies, exposure doses beyond 2000
µC/cm² were not captured to prevent electron gun filament degradation due to the long (greater than 1 hour) exposure times involved. Resists were observed to clear entirely for electron energies of 2000 and 700 eV, and did not clear in the exposure dose range for the lower energies of 250 and 80 eV. Furthermore, for OS2 the E₀ (energy to complete thickness loss) decreases as electron energy increases from 80 to 2000 eV. This is in line with expectations; electrons with higher energy will deposit more energy in the resist, thus causing the resist to clear at lower exposure doses.

Figure 4.5. (a) Experimental thickness loss for all resists with 80 eV electrons. (b) Experimental thickness loss for all resists with 700 eV electrons.
Figure 4.6. Experimental thickness loss for the OS2 (aromatic polymer, iodonium PAG) resist.

The results of ellipsometry measurements may be erroneous due to some subtle effects of electron exposure. Further work has shown that electron exposure alone can change the optical properties of an ESCAP film, resulting in apparent thickness loss when modeled as one layer. More complex modeling which uses two layers reveals that the exposed top surface has different optical properties, which change from that of bulk ESCAP as a function of dose. Following development, the majority of this region will be developed away, but a thin layer (perhaps < 2 nm thick) that forms the base of the exposed and developed “pit” (Figure 4.4A) may remain. This region is characterized by changes in optical properties as a result of electron exposure whose density of chemical change in insufficient to be dissolved by developer. Additional modeling to account for this may be a focus of future work.
4.3.2 Comparison of Raw LESiS Data with Thickness Loss Results

Figure 4.7 (top) shows the graphed data from the LESiS simulations. Each simulation yielded energy loss event locations which were plotted in a histogram of the number of energy loss events per incident electron per 0.1 nm (referred to as ELE from now on) vs. depth in the resist. Comparison of Figures 4.6 and 4.7 yields some interesting observations. LESiS predicts that the ELE falls to 0 by 5 nm and 15 nm for 80 eV and 250 eV electrons respectively, regardless of dose. This indicates that the maximum thickness loss at these energies should be equal to these corresponding ultimate penetration depths, contrary to experimental data shown in Figure 4.6, where 80 and 250 eV electrons penetrate up to 20 and 30 nm at high doses. Electron penetration depth is a probabilistic process, so it is possible that we have not run enough simulations to truly grasp the statistics of the large experimental exposure doses. One in a million 80 eV electrons (0.0001%) may penetrate greater than 30 nm in the resist, so a simulation of $10^5$ electrons may not result in any electrons penetrating to that depth, whereas a typical exposure of 100 µC/cm$^2$ in a 1 cm$^2$ area in our experiment (approximately $10^{14}$ electrons) will have millions.
Figure 4.7. (A) Number of energy loss events per incident electron vs. depth in resist (in 0.1 nm bins). (B) Number of energy loss events vs. energy calculated from a LESiS simulation of 1000 electrons per energy. (C) The 700 eV ELE curve from (A) subdivided into Ionization and Plasmon components.
4.3.3 Thickness Loss Modeling with LESiS Data

In optical lithography, it is easy to relate dose in mJ/cm$^2$ to $E_0$. In e-beam exposure, however, dose is measured in µC/cm$^2$. This unit convention does not convey any information about electron energies. For example, exposures of 250 and 2000 eV electrons at the same dose will impart differing amounts of energy in the resist. Furthermore, a large amount of energy deposited in one interaction (e.g. a high energy incident electron liberating a tightly bound core electron) will be less efficient in clearing a resist than multiple low energy interactions. If an 80-eV electron liberates an electron with a binding energy of 10 eV, the two electrons will have a total energy of 70 eV; if the binding energy is instead 30 eV, the two electrons will have a total energy equal to 50 eV. The energy lost to binding energies is analogous to friction on the macro-scale.

Thickness loss was then modeled using the following simple procedure (depicted in Figure 4.8): (1) A curve from Figure 4.7 was selected. (2) This curve was multiplied by a scale factor that is analogous to increasing dose in the experimental study. (3) A threshold ELE was set for all energies. (4) The largest depth where each scaled curve meets the threshold is recorded as the thickness loss for a given “dose”. If the scaled curve does not meet the threshold, the thickness loss for that “dose” in 0 nm. (5) A maximum thickness loss was set for this simulation to match the post-dark loss thickness of OS2 used in the experimental study. (6) The threshold ELE was set for all energies such that the resulting simulated data matched the 700-eV experimental thickness-loss results. This was selected because the 700 eV experimental data shows complete thickness loss while also having lower contrast than the 2000 eV data (and thus more data points to match in between zero and complete thickness loss). This procedure was implemented computationally, and the model fit the experimental observations for OS2 with a reduced $\chi^2$ of 0.70.
Figure 4.8. The algorithm used to calculate thickness loss vs. dose explained graphically. Here, the 700eV ELE vs. resist depth curve is scaled by a range of values. The deepest intersection of each curve and the threshold is the recorded thickness loss for each “dose”. If a curve never meets the threshold ELE, the corresponding thickness loss is 0 nm.

This method makes a few assumptions, changes to which may lead to different results. Chiefly, the threshold ELE set for matching the simulation to experimental data reflects a material parameter of the threshold density of solubility changing chemical events that would lead to dissolution in a given development time. To more accurately convert the histogram data from Figure 4.7 into thickness loss prediction, we could apply a function to convert the electron event profiles into chemical gradients. Then, Fick’s Second Law (with the appropriate diffusion
parameters) could be applied to these gradients to determine acid diffusion. Finally, a nonlinear dissolution contrast function could be applied to determine the depth of resist which would dissolve away. This work does not seek to reproduce that work, which may be found in PROLITH, but instead serve as a validation and exploration of the capabilities of LESiS.

Additionally, our model assumes that the chemical reactions induced by each additional electron are not influenced by previous electrons. This work does not take advantage of the dynamic modeling capabilities of LESiS (described in the previous chapter), and thus LESiS considers a “fresh material” for each electron (including secondary electrons). Therefore, this model does not account for potential charging that may have occurred during the experiment. Depending on the secondary electron emission coefficients for the resist and electron energies involved, the resist surface may have built positive (emission coefficient > 1) or negative (emission coefficient < 1) charge, either of which could affect the landing energy of subsequent electrons during exposure. In the simulations described here, LESiS would not accurately simulate the changes in incident electron energy due to charging, and thus might under- or over-predict electron penetration for electrons landing with higher or lower energies than in simulation.

The results of the thickness loss modeling (Figure 4.9) are at the same time promising and indicative of the direction that future work on LESiS should take. These results indicate that low energy electrons penetrate deeper into resists than is predicted by LESiS. The divergence in the data at low electron energies may be accounted for by electron-matter interaction mechanisms not currently incorporated in LESiS.

In reality, low energy electrons (those with less than 10 eV of energy) would elastically scatter indefinitely if not for energy loss mechanisms that dominate this energy range (phonon generation, low energy excitation, etc.). This requires that we set an artificial threshold energy (5 eV in our
simulations) below which we do not track electrons to prevent long computation times. This threshold may exclude some energy loss mechanisms (for example, electron trapping) that contribute to resist exposure chemistry, but are not currently modeled in LESiS. Furthermore, LESiS treats all materials as essentially amorphous and thus cannot account for changes in bound electron energies due to crystalline or molecular effects.

There is evidence\textsuperscript{4,5} to suggest that, especially in molecular materials, there are energy loss mechanisms that could contribute to resist chemistry that occur with electrons below 10 eV or cause energy losses of 8 eV or lower. The likeliness of these possible mechanisms could influence the number of energy loss events per electron and the electron penetration depths.

The results of Chapter 6 elevate the importance of ionization events as a precursor for additional acid production through hole-initiated chemistry. Therefore, it becomes important to understand how the shape of the curves shown in Figure 4.7 are made from the depth-distributions of the modeled energy loss events. LESiS predicts that the number of energy loss events increases linearly with energy (Figure 4.7B).\textsuperscript{6} Furthermore, the numbers of ionization and plasmon events are also linear with energy. Therefore, this work could be repeated when only considering ionization events—such an approach would produce depth-distribution curves such as the one shown in Figure 4.7C. These ionization-only depth-distribution curves are similar in shape to the original curves of Figure 4.7A, and thus, the results of thickness-loss modeling would be similar, with the only change being the threshold required to match the 700 eV data.
Figure 4.9. Comparison between simulated thickness loss and experimental thickness loss for (a) 2000 eV, (b) 700 eV, (c) 250 eV, and (d) 80 eV.
4.4 Improvement in Thickness Loss Modeling

Here, we demonstrate improvements in modeling of electron penetration depth and thickness loss in an open source EUV resist. The previous section,\(^6\) we showed good agreement between modeling of electron penetration depth and e-beam thickness loss data for exposures of 2000 and 700 eV. However, our modeling showed discrepancies between predicted thickness loss at high dose exposures of resist with 250 and 80 eV electrons (Figure 4.9C and 4.9D).

At the time, the thickness loss modeling only accounted for the energy loss mechanisms of ionization and plasmon generation.\(^6\) The model is improved by considering the user-defined electron energy cutoff. In LESiS, electron behavior is simulated until electrons transition below that cutoff (usually 5 eV), which we can consider the “stopping point” of electron travel. We modified the code to track the location of these transitions through the cutoff energy and include this information in our model (Figure 4.10).

This allows us to computationally model an analogue for electron trapping, a low energy electron-PAG interaction shown to contribute to acid production in chemically amplified resists. We performed new simulations and generated new predictions with low-energy electron interactions that contribute to thickness loss.
Figure 4.10. The original thickness loss model presented previously\textsuperscript{10} considers that only ionization and plasmon generation contribute to thickness loss during exposure. The model is improved to include the “stopping point” of the electrons, imposed by the energy cutoff which can be adjusted to stop simulations at different electron energies.
Initially, LESiS was used to calculate photoelectron travel from the site of EUV photon absorption to various cutoff energies (Figure 4.11). The data shows that the first ionization or plasmon events occur within a 0-4 nm distance from electron generation (photon absorption). As the electrons lose energy, they fall below 20, 10, 5, and 3 eV at average distances of roughly 2-6 nm away from the generation site. However, these distributions, especially for the 10, 5 and 3 eV cutoffs, are highly asymmetrical, showing non-zero probability of electrons traveling up to 14+ nm away from generation.

![Distance from Initial Photon Absorption](image)

**Figure 4.11.** Probability densities of distances between photoelectron generation and various electron “interactions”. The first ionization and plasmons events occur 0-4 nm away from the site of EUV absorption. These photoelectrons then fall below 20, 10, 5 and 3 eV cutoffs at 2-6 nm from the generation site.
We modified the thickness-loss model to include these transitions below energy cutoffs, resulting in a change in the profile of energy loss events vs. depth when simulating e-beam exposure (Figure 4.12). The addition of the “stopping point” of the electrons to the model shifts the average and maximum simulated penetration depths deeper into the film (solid to dashed lines in Figure 8). When we apply the thickness-loss calculation algorithm\textsuperscript{10} to the new data, we observe that the model and experimental data begin to match (Figure 4.13). Compared with the original model that does not consider electron energy cutoffs, including transitions below the 5-eV cutoff improves the prediction dramatically. Moving to a 3-eV cutoff results in almost perfect agreement between experiment and simulation for 250 and 80 eV exposures.

**Figure 4.12.** The improvement in the model to track transitions below cutoff energies pushes the energy loss event profiles deeper into the film. When adding these transition events, the curves shift to the right and are more skewed.
Figure 4.13. The modifications to the thickness loss model and algorithm results in better matching between LESiS predictions and experimental data.

4.5 Incorporation of EELS Data in LESiS

4.5.1 EELS Experimentation at Rutgers University (Bartynski Group)

Rutgers University was provided with several PAG and polymer films (Figure 4.2) in addition to the four resists (OS2, OS4, OS12, and OS14) described in Figure 4.1. They used these films in EELS and X-ray Photoelectron Spectroscopy (XPS) studies to investigate the electronic structure of chemically amplified resists and their components. They accompanied this with electronic structure modeling of these resist components to identify features in the data with the underlying physical model. Here is a brief summary of their results.

Rutgers performed these EELS measurements at several energies (30, 50, 70, 90, and 110 eV), but the data shown in the next four figures shows representative examples measured with 110 eV
incident electrons. The data is normalized to the height of the elastic peak; the scale of the axes shows that the features of interest at least two orders of magnitude smaller than the elastic backscattering of the incident electrons. The data shows three main features: (1) ~5 eV energy loss and (2) a 6-7 eV energy loss that both correspond to $\pi-\pi^*$ transitions across the HOMO/LUMO gap in the electronic structure (Figure 4.16), and (3) 10-30 eV energy losses that correspond to plasmonic excitations.

**Figure 4.13.** EELS spectra measured on pure films of the two terpolymers described in Figure 4.1. Reprinted from Ref. 1, produced in collaboration with the Bartynski group at Rutgers University.
**Figure 4.14.** EELS spectra of two films containing 75 wt.% PAG and 25 wt.% 193-polymer (Polymer 2). The 6-7 eV energy loss feature associated with a $\pi-\pi^*$ transition is present, but minor, compared to the broad plasmonic peak. Polymer 2 was chosen due to its relative lack of features compared to ESCAP. Reprinted from Ref. 1, produced in collaboration with the Bartynski group at Rutgers University.
Figure 4.15. EELS spectra of the four open source resists described in Figure 4.1. OS2 and OS4 show the 6-7 eV energy loss feature of ESCAP. The same energy loss feature is present for the PAG molecules (Figure 4.14, 75 wt.% PAG), but at such low intensity as to be negligible for the 15 wt.% PAG films in this figure. Refer to Figures 4.2 and 4.31 for the composition of these open source resists. Reprinted from Ref. 1, produced in collaboration with the Bartynski group at Rutgers University.
Figure 4.16. The 6-7 eV energy loss feature present in the EELS spectra above corresponds to calculated electronic transitions across the HOMO/LUMO gap in the benzene/phenol molecular orbital. Adapted from Ref. 1, produced in collaboration with the Bartynski group at Rutgers University.
4.5.2 Motivation for EELS Incorporation into LESiS

Figure 4.17. LESiS uses probabilistic information based on experiment and calculation for gas-phase atoms. By using data generated from thin-films much like photoresists, we can improve simulation and modeling for resists.

The probabilistic information that LESiS uses to carry out simulations and calculations (Chapter 3) is based primarily on databases of data generated from experiments and calculations of electronic structure of gas-phase single atoms. In order to improve the modeling and predictive simulation capabilities of LESiS, we can incorporate data generated from condensed phase experiments, particularly spectroscopy information from thin-film EELS experiments. To that end, we can take advantage of the data provided by the Bartynski group at Rutgers University, who carried out EELS experiments with various chemically amplified resists and their components (section 4.4.1).
As an example of the discrepancies between the data used by LESiS and real EELS data, Figure 4.18 shows an EELS experiment and a simulated EELS experiment from LESiS. It is clear that LESiS is built on some inaccurate information, particularly with respect to the plasmon and stopping power information. Additionally, LESiS is unable to independently model the electronic structure of materials (or consider vibrational energy losses in the condensed phase), and is thus unable to simulate more complex molecular-orbital dependent energy loss features such as those shown in figure 4.17.

**Figure 4.18.** LESiS lacks accurate stopping power and plasmon information, resulting in the discrepancies shown here. Experimental data produced by the Bartynski Group at Rutgers University.
4.5.3 LESiS Material File Structure Improvements

To incorporate material-specific EELS information, it was necessary to improve the materials database system. Originally, LESiS considered atomic information to compile a material for simulation, and thus drew only upon the atomic composition and density of a user-defined material (Figure 4.19). To incorporate new information that is associated with molecular components, it became important to build a material file system that can call upon particular sub-units that are tagged with specific information so that LESiS could recursively build materials that include both the original ionization and high-energy information and the new low-energy (EELS-based) data (Figures 4.19 and 4.20).

![Original Material Data File](image)

**Figure 4.19.** The original material file system used by LESiS is too simplistic to incorporate the data generated by EELS.
Figure 4.20. An example new material file that tags molecular materials with their appropriate experimental low-energy information, while also translating the overall material composition to include the original ionization and high-energy information.

4.6 EELS Data Processing for LESiS Incorporation

After data collection, the data is processed to transform intensity (electron detector current) into cross-section data for incorporation. The process involves several steps: (1) Scaling the data with respect to the experimental data, (2) converting the data into cross-sections, (3) isolating particular features in the EELS spectra, (4) converting the data to useful probabilistic information, (5) incorporation into LESiS, and (6) data validation via iterative simulation and checking.

As an example, the EELS data collected for polyhydroxystyrene (Figure 4.21) will be used to demonstrate the data processing methodology that is carried out for each material. The spectra
show three key features: Low Energy 1 (L1), Low Energy 2 (L2), and Plasmon (L3). The experimental information (beam current, detector solid angle, electron energies) are taken into account in the calculations. For each spectra, the equations listed below are used to convert the data to cross-sections.

**Figure 4.21.** EELS spectra for polyhydroxystyrene (PHS) at four different energies. The specific low-energy and plasmon features are indicated. Experimental data produced by the Bartynski Group at Rutgers University.
\[ P(\text{Elastic}) = \frac{I_E}{I_0} = \sigma_E^\Omega k \]  

\[ \frac{I_{LL}}{I_0} = P(E) \cdot P(LL) = \frac{I_E}{I_0} \sigma_{LL} k \]  

\[ \sigma_{LL} = \frac{I_{LL}}{kI_E} = \frac{I_{LL}I_0}{I_E^2} \sigma_E^\Omega \]  

The simplifying assumption is made that each electron detected has undergone at most one inelastic scattering event. The probability of the elastic backscattering \( P(\text{Elastic}) \) is a ratio of the elastically scattered peak \( I_E \) to the total incident beam current \( I_0 \), which is also equal to the detector-geometry-dependent elastic scattering cross section \( \sigma_E^\Omega \) multiplied by a scalar \( k \). Then, the ratio of a particular low-energy loss feature peak \( I_{LL} \) to the total incident beam current \( I_0 \) is equal to the elastic backscattering probability multiplied by the probability of the low-energy loss event \( P_{LL} \). \( P_{LL} \) is equal to the low-energy loss event cross section \( \sigma_{LL} \) multiplied by another scalar. Then, combining these relations, we find that \( \sigma_{LL} \) is equal to the product of \( I_{LL} \), \( I_0 \), and \( \sigma_E^\Omega \) divided by the square of \( I_E \).

First, the elastic scattering cross sections for electrons at each energy for each atomic species were obtained from NIST (these same cross sections are used by LESiS). These cross sections were plotted against scattering angle, and the resulting data were numerically integrated to account for the detector geometry and solid angle. The resulting data (Figure 4.22) for each atomic species shows the expected decreasing trend with increasing electron energy (higher energy electrons backscatter less). Then, the weighted average of this data was constructed for PHS based on the stoichiometric composition for PHS (C₈H₈O). These scattering cross sections were then used to
scale the spectra shown in Figure 4.21 to transform the data into cross-section information (Figure 4.23). The elastic peak for each particular energy is assigned the value of the elastic backscattering cross section (in units of nm$^2$), and the remaining spectral features are scaled accordingly.

**Figure 4.22.** The detector geometry dependent elastic backscattering cross sections for the atomic species and the weighted average constructed from the atomic composition of PHS.
Figure 4.23. The scaled EELS spectra of PHS for four incident electron energies are shown here. Experimental data produced by the Bartynski Group at Rutgers University.

Following the data conversion, the low-energy loss features are isolated from the elastic and plasmon information (and any background). A unique exponential curve is fitted underneath the L1 and L2 features (Figure 4.24), and then this curve is subtracted from the experimental data. The isolated features (Figure 4.25) are then extracted to perform individual processing. Additionally, the plasmon information is similarly processed to convert that data into an energy loss event that serves to replace the original LESiS plasmon data. The L1, L2, and L3 features at each energy are numerically integrated to assign a total cross section that will be used directly in LESiS as described in Chapter 3. Additionally, the cumulative distribution functions (CDFs) for each energy
loss event are constructed \textit{via} numerical integration (Figure 4.26). LESiS uses the CDFs to determine the energy loss of a specific event once the event is triggered.

\textbf{Figure 4.24.} Unique exponential curves are fitted underneath the L1 and L2 features for each spectrum.
Figure 4.25. The isolated energy loss features L1 and L2 following subtraction of the exponential backgrounds from Figure 4.25.
Figure 4.26. The isolated energy loss features are assigned total cross sections via numerical integration with respect to energy (blue). The CDFs are then constructed from this data (red) to be directly imported into LESiS.

The final cross section data for L1, L2, and L3 in PHS are plotted against electron energy (Figure 4.27). Then, when simulating electrons of energies different than the specific energies used in generating the experimental data, LESiS uses a simple three-part algorithm to adjust the cross sections and CDFs as needed (Figure 4.28).
Figure 4.27. The cross sections of the isolated energy loss features L1, L2, and L3 across the experimental incident electron energies.
For $E_{(e^-)} > 110$ eV:

$$\sigma(E) = \sigma(110 \text{ eV}) \quad CDF(E) = CDF(110 \text{ eV})$$

For $E_{(e^-)} < 50$ eV:

$$\sigma(E) = \sigma(50 \text{ eV}) \quad CDF(E) = CDF(50 \text{ eV})$$

For $50 < E_{(e^-)} < 110$ eV, determine closest experimental energies from 50, 70, 90, 110 eV and assign them as $E_{\text{low}}$ and $E_{\text{high}}$:

$$\sigma(E) = \frac{E_{\text{high}} - E}{E_{\text{high}} - E_{\text{low}}} \sigma(E_{\text{low}}) + \frac{E - E_{\text{low}}}{E_{\text{high}} - E_{\text{low}}} \sigma(E_{\text{high}})$$

$$CDF(E) = \frac{E_{\text{high}} - E}{E_{\text{high}} - E_{\text{low}}} CDF(E_{\text{low}}) + \frac{E - E_{\text{low}}}{E_{\text{high}} - E_{\text{low}}} CDF(E_{\text{high}})$$

**Figure 4.28.** LESiS adjusts the cross sections and CDFs as needed when simulating electrons of intermediate energies.

### 4.7 Data Validation in LESiS

Once the data is imported into the LESiS material files, it is necessary to validate the data by comparing the experimental results and simulations of the experiments. This process takes several steps (Figure 4.29): (1) Replicate EELS experiment geometry, and then, in an iterative loop, (2) Run simulations, (3) Analyze data, (4) Compare with experiment, (5) Scale cross sections, and, when comparison with experiment yields a good match, the process is complete. This iterative loop is carried out for each material and each incident electron energy for which data is imported into LESiS.
Figure 4.29. Validation of incorporated EELS data requires an iterative approach that compares simulated EELS results with experimental data, followed by adjustment of the cross sections imported in the materials file system.

The experiment geometry from the Rutgers experiments is replicated by defining the materials, source, and electron beam is LESiS. Then, 50,000 electrons are simulated at a particular incident energy. A *MatLab* script is used to analyze the data and present it in the form of an EELS spectra. Then, by either manual or computational analysis, the total cross sections for each of L1, L2, and L3 (Figure 4.27) are independently adjusted to more closely match the experimental data. The CDFs are not adjusted in this process. After these adjustments, the simulations are carried out again, and the results are compared to experiment. This loop is iterated through until the simulations match the experiment, and then the particular electron energy for the particular
material is considered validated. As an example, Figure 4.30 shows this iterative approach—early iterations with incorrect cross sections are shown in grey, and the final simulation with correct cross sections is shown in red. The final result shows good agreement with the experimental data in blue.

**Figure 4.30.** The validation process requires a iterative approach. Several early iterations for this particular data set (grey) show poor agreement; the final, validated total cross sections are depicted in red. Experimental data produced by the Bartynski Group at Rutgers University.
4.8 Results of EELS Incorporation and Modeling of Complex Resist Materials

After the validation process was completed for the components of the chemically amplified resists shown in Figures 4.1 and 4.2, more predictive simulations were carried out. These components (Figure 4.13 and 4.14) were used to create an EELS basis set (Figure 4.31) from which the more complicated open source resists OS2, OS4, OS12, and OS14 (experimental data in Figure 4.15) could be simulated. The materials were built using the new file system with the appropriate delineation between the original high-energy scattering data and the new low-energy data. After validation, simulations of these more complex materials show good agreement with the experimental results (Figure 4.32).

![Diagram of EELS Data Basis Set, TBPI-PFBS, TPS-PFBS, ESCAP, 193 Polymer, OS2, OS4, OS12, OS14]

*Figure 4.31.* The validation process requires a iterative approach. Several early iterations for this particular data set (grey) show poor agreement; the final, validated total cross sections are depicted in red.
Figure 4.32. After the validations process, the complex open source resists were built using the new file system. The EELS experiments carried out at Rutgers on these four films were then simulated, with the results showing fairly good agreement. Experimental data produced by the Bartynski Group at Rutgers University.

4.9 Conclusions

The previous chapter introduced Monte Carlo modeling and described the underlying physics of the LESiS program. To demonstrate its capabilities, some initial studies of electron yield were demonstrated. In this chapter, we have demonstrated the program’s more advanced capabilities, particularly with respect to modeling of experimentation. While LESiS simulation capabilities
were sufficient for their original, high energy purpose of modeling X-ray and E-Beam (> 50 keV) lithography, it required modification to simulate the low energy electron-matter interactions important in modeling EUV lithography.

To that end, LESiS was used to simulate e-beam thickness loss experiments. As expected, the high-energy e-beam simulations (700, 2000 eV) showed good agreement with experiment. The deficiencies in the low-energy behavior were shown by the mismatch between the 80 and 250 eV exposures and simulations, where thickness loss was under-predicted by the simulations. By incorporating the computational analogue of electron trapping (a low-energy interaction), the thickness loss simulations for the low energies improved significantly, with almost perfect agreement with 3 eV energy cutoffs.

Additionally, EELS experiments carried out by Rutgers university and simulations in LESiS showed poor agreement. By incorporating the EELS data in a methodical manner, we showed improvements in the simulation capabilities of LESiS. Furthermore, it was demonstrated that more complex materials could be simulated in LESiS by relying on the new materials file system which constructed a low-energy data basis set for chemically amplified resist components.

The advent of this implementation could then be used to revisit the thickness loss modeling described earlier in this chapter. The addition of these events, as well as the more accurate stopping power information, may result in more accurate electron penetration depths for low-energy electrons. Furthermore, ionization events may occur deeper in the resist with less energy loss to the CSDA (compare the pre-EELS LESiS simulation with the experimental EELS data in Figure 4.18). However, more energy would be consumed by the 6-7 and 4-5 eV energy loss features in the experimental EELS spectrum for OS2 (Figure 4.32). All LESiS work should be revisited in light of this improvement in simulation capabilities.
4.10 References


Chapter 5: Studying Electron-PAG Interactions using Electron-Induced Fluorescence

5.1 Introduction

As discussed in Chapter 2, three primary mechanisms have been proposed for electron-matter interactions that produce chemical reactions within the resists: (1) electron trapping and (2) hole-initiated chemistry, and (3) internal excitation. The first mechanism, also known as dissociative electron attachment (DEA), is well known in gas-phase electron reaction literature.\textsuperscript{1,2} In this mechanism, free electrons may be captured by a molecule, destabilizing the bond structure and causing decomposition. In the second mechanism, the holes created during ionization create acid.\textsuperscript{3} Mechanisms (1) and (2) are discussed further in Chapter 6.

Here, we propose and evaluate the third mechanism, called \textit{internal excitation} (also known as dissociative electron excitation), that may contribute to resist chemistry. In this method, shown schematically in Figure 5.1, a temporary electromagnetic coupling between a ballistic and a bound electron causes an energy transfer from the free electron to the bound electron, promoting this electron to a higher energy level. This excited state may result in (a) the decomposition of the molecule, (b) the emission of a photon (fluorescence), or (c) the loss of energy as heat. Experiments using electron energy loss spectroscopy (EELS) show evidence of internal excitation,\textsuperscript{4,5} also known as electrical excitation\textsuperscript{6} or dissociative electron excitation.\textsuperscript{7}

Previous work by Brainard\textsuperscript{8} and Kozawa\textsuperscript{3} (Figure 5.2) indicates that chemically amplified resists can show maximum quantum yields of 5-6 acids produced per absorbed photon at very high PAG concentrations. Resists with higher quantum yield have lower Z-parameters,\textsuperscript{9,10} so improving
quantum yields should improve resist performance. Electron-capture and hole-initiated chemistry rely directly on preceding ionization events to produce the free electrons or holes that are consumed in these mechanisms, and are thus limited by the secondary electron yield and the binding energies of the resist. In contrast, internal excitation does not consume a free electron and may only require 2-3 eV of a free electron’s energy; the potential for much higher quantum yields exists for PAGs that can take advantage of internal excitation to react to produce acid. In order to determine the quantum yield of internal excitation, we have studied internal excitation using the analogous process of electron-induced fluorescence.

**Figure 5.1.** A schematic of the internal excitation mechanism occurring between a ballistic electron and a molecule. The energetic electron loses some energy to a bound electron in a molecular orbital, resulting in the promotion of the molecule to an excited state. This excited state can then (a) react (a PAG may react to generate an acid), (b) emit a photon (fluorescence), or (c) lose energy as heat (non-radiative relaxation).
Figure 5.2. Three similar PAGs used by two groups show a maximum of 5-6 acids per photon, even at extremely high PAG loading. (Data from Refs. 3 and 8 used with permission from SPIE and The Japan Society of Applied Physics, respectively.)

5.2 Methodology

With internal excitation, the small energy gained by a bound electron results in the decomposition of a molecule. Here, F is the fluorophore in its ground state, F* is the fluorophore in the excited state, and A+ and B- are the byproducts of the fluorophore decomposition.

\[ F + e^- \rightarrow F^* + e^- \rightarrow A^+ + B^- + e^- \] (5.1)

Directly measuring the ionic products of internal excitation is difficult in the solid phase; it is unlikely for ions to outgas from resist films. Fluorescence is a suitable analog to internal excitation,
and provides a more feasible approach to measurement. Electron-induced fluorescence allows the study of the transient excited state by monitoring the photons emitted as the excited state relaxes.

\[ F + e^- \rightarrow F^* + e^- \rightarrow F + e^- + \text{hv} \]  \hspace{1cm} (5.2)

With this framework in mind, it is possible to evaluate fluorophores with respect to their fluorescent quantum yield (fluorophores emitted per incident electron). Fluorophores that perform poorly decompose rather than emit photons, and those that perform well emit photons rather than decompose. While it is important to study the latter group to investigate internal excitation, poorly performing fluorophores may provide insights in the chemical nature of PAGs that fall apart as intended.

### 5.2.1 Materials

In this study, we subjected fluorophores (Figure 5.4A) in several polymers (Figure 5.4B) to electron beam exposure to study electron-induced fluorescence. Fluorophores were obtained from Sigma Aldrich with greater than 95% purity, except where noted (Table 5.1). Figure 5.3 shows the distribution of these fluorophores with respect to optical absorption and emission wavelengths.\(^{11}\) Fluorophores were formulated at 4 wt. % solids (polymer and fluorophore) in the necessary solvent, with the solids consisting of 25 wt. % fluorophore and 75 wt. % polymer. Each formulation was spin-coated on 100 mm silicon wafers at 2000 RPM. The thickness of each film was measured using profilometry (Table 5.1).
Figure 5.3. Fluorophores considered for this study plotted with respect to maximum absorption and emission wavelengths.\textsuperscript{11}
Figure 5.4. (a) Fluorophore structures. (b) Polymer chemical structures.
Table 5.1. The fluorophore-polymer formulations evaluated in this study, with accompanying optical characterization.

* Described in Sec. 2.4, ** From profilometry, †DCE is 1,2-Dichloroethane, ‡PM is 1-Methoxy 2-Propanol, °90% purity

<table>
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<th>Fluorophore</th>
<th>Polymer Matrix (Solvent)</th>
<th>Optical Absorbance $\lambda_{\text{max}}$(nm)*</th>
<th>Optical Emission $\lambda_{\text{max}}$(nm)*</th>
<th>Film Thickness (nm)**</th>
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<td>270</td>
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<td>130</td>
</tr>
<tr>
<td></td>
<td>ESCAP (PM)</td>
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<td>102</td>
</tr>
<tr>
<td>Tris(2,2′-bipyridyl)dichlororuthenium(II) hexahydrate (TBR)</td>
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5.2.2 Experimental Design

The experiments were performed in a vacuum chamber equipped with a Kimball physics EFG-7 electron gun, capable of electron energies from 80 to 5000 eV, with a working distance of 25 cm. Inside this chamber, called ERIC (Electron Resist Interaction Chamber), a sample is exposed with a normal incident electron beam at selected energies and doses. Beam current is measured using a copper Faraday plate biased at +90 V in a grounded metal container covered with a 90% open area grounded nickel mesh over a 1 cm² aperture. We estimate that the beam current measured is within 10% of the true value based on backscattering and secondary electron generation within the mesh and plate.

The instrumentation for these experiments was constructed by our lab (Figure 5.5). A fluorophore-polymer sample coated on a silicon wafer is exposed to an electron beam. A portion of the photons emitted by the film via electron-induced fluorescence are captured by a lens-photodiode system and converted into a current that can be measured by any picoammeter.

A picoammeter is not sufficient in this case, due to the large background glow of the electron gun filament in the chamber. To account for this, the electron beam is pulsed by a 5 V TTL (Transistor-Transistor Logic) square wave with a 50% duty cycle generated by a GW Instek GFG-8215A function generator. Thus, the sample also produces a fluorescent emission at the same frequency as the electron gun pulses. The current generated by the photodiode – the large background due to the filament and the small pulsed response due to the sample fluorescence – is measured by a Model 7270 DSP (Digital Signal Processing) Lock-In Amplifier, manufactured by Signal Recovery, a division of AMETEK. The lock-in amplifier uses the TTL signal as an external reference to “lock-in” on the small, pulsed increase in photodiode current and eliminates the large DC from background glow of the filament. This allows a relatively high signal-to-noise ratio in a
system otherwise dominated by a large DC offset. The lock-in amplifier is operated in wide bandwidth current input mode with AC coupling, a 10 ms time constant, and 20 nA sensitivity. The input device is a FET, with an AC gain of 24 dB.

The lens-photodiode system contains two aspheric lenses\textsuperscript{12} purchased from Edmund Optics. The lenses each have a focal length of 18 mm, and combined, reproduce the roughly 1 cm\textsuperscript{2} sample exposure area on the 10x10 mm working area of the photodiode with a magnification of 0.25. The lens system has a 20 mm aperture and is positioned 45 mm away from the exposure area on the sample, resulting in a solid angle $\Omega = 0.150 \pm 10\%$ sr captured by the lens (and ultimately, the photodiode). An AXUV100G photodiode is used, with responsivity determined by NIST.\textsuperscript{13}

---

**Figure 5.5.** (a) A fluorophore-polymer film coated on a silicon wafer was exposed to a pulsed electron beam. The emitted photons were captured by a lens-photodiode system which converts emitted photons into a measurable current. (b) A more detailed schematic of the lens-photodiode system: **A:** AXUV100G photodiode, 10x10 mm active area, $\lambda = 10$-1100 nm, **B:** Two aspheric 18 mm focal length lenses, $\lambda = 350$-2500 nm, **C:** 20 mm aperture
In a typical experiment, the sample is loaded in the vacuum chamber. For a given electron energy, the focus is adjusted to produce a 1 cm\(^2\) exposure area. The electron energy of interest is 80 eV, roughly the energy of photoelectrons generated by EUV in chemically amplified resists. However, not all fluorophores produce a measurable photodiode current for 80 eV exposures, so exposures are carried out with electrons of energies at 80 to 5000 eV.

The electron beam current is measured in a non-pulsed state with the detector described previously. Therefore, the measured current was not the time average of the pulse electron gun current, but instead the amplitude of the beam current. The onset of “full current” is specified by the manufacturer to be on the order of microseconds, far shorter than the pulse frequencies used. Additionally, the beam current is independent of changes in the duty cycle. Beam currents are set between 0.7 to 1.0 \(\mu\)A. The pulse frequency of the electron beam is selected by measuring the photodiode current at the lock-in amplifier and varying the frequency at the function generator until this signal is minimized—typical frequencies are between 500 and 700 Hz. These frequencies minimize interference from other instrumentation in the lab that may operate at lower or higher frequencies. The lock-in amplifier automatically adjusts the phase to improve the signal-to-noise ratio.

Figure 5.6 shows a typical photodiode current measured with this process. Data was recorded for some time with the electron gun off to establish a background, and then the gun was pulsed at 635 Hz. The photodiode current due to fluorescent emission in the sample was measured for an additional 20-60 s, before the gun was turned off to verify the background signal. For each sample, the test shown above was repeated at least 4 times, allowing an estimation of the associated error.
Figure 5.6. The photodiode signal recorded during a typical exposure – in this case, a 2000 eV exposure of TBR.

5.2.3 Data Processing

Data is recorded from the lock-in amplifier via a programmed LabVIEW interface. This data is then processed to subtract a selected background and output half-life and maximum signal information. The maximum signal recorded (Figure 5.6) as the gun is turned on is used to calculate the number of photons emitted per incident electron.

\[
\frac{\text{Photons Emitted}}{\text{Incident } e^-} = \frac{4\pi I_P}{R I_G \Omega E_Y} \quad (5.3)
\]
Here, $I_P = \text{photodiode current (A)}$, $R = \text{photodiode responsivity (A/W)}$, $I_G = \text{electron beam current amplitude (A)}$, $\Omega = \text{solid angle collected}$, and $E_\gamma = \text{energy of emitted photon}$. The energy of the emitted photon and the photodiode responsivity are determined using the optical characterization (Sec. 5.2.4) and the NIST responsivity measurements (Figure 5.7).

![Image of emission spectrum and photodiode responsivity](image)

**Figure 5.7.** The responsivity of the AXUV100G photodiode as reported by NIST$^{16}$ and the emission spectrum of Eosin Y.

For each sample, the fluorescent emission spectrum (Figure 5.7) taken by optical characterization is converted into a probability density function with respect to photon energy ($E = \frac{hc}{\lambda}$), and the emitted photon energy $E_\gamma$ is computed by

$$E_\gamma = \int_{-\infty}^{\infty} E \cdot I(E) \, dE \quad (5.4)$$

where $I(E)$ is the probability density function of the emission spectrum. Then, the photodiode responsivity is plotted with respect to photon energy, and $R$ is determined by
\[ R = \int_{-\infty}^{\infty} R(E) \cdot I(E) \, dE \] (5.5)

where \( R(E) \) is the responsivity of the photodiode from the NIST data.

To eliminate the effects of film thickness on the collected data, the film thicknesses measured by profilometry (Section 5.2.1), along with the known concentration of the fluorophore, are used. This allows the calculation of the effective cross section of internal excitation – the cross section of the internal excitation mechanism for an incident electron of a given energy, along with all of its daughter electrons. However, for low energy electrons (< 1000 eV), there is some threshold energy for which film thickness exceeds penetration depth.\(^{14}\) Prior work in the group is used to calculate penetration depths at these energies.\(^{15}\)

### 5.2.4 Optical Characterization of Polymer Films

The same formulations exposed under e-beam are aliquoted in 1-2 mL portions into Corning Costar® 24-Well Flat Bottom Multiple Well Plates made of polystyrene. Macro-scale (~5 mm) films are then grown in each well by applying a vacuum of less than 0.1 torr. This is done under vacuum as opposed to air to expedite solvent evaporation and film growth. As a secondary benefit, the increased solvent evaporation speed prevents well plate degradation due to the solubility of the well plates in the formulation solvents. Formulations in PM were well behaved, with well plate degradation due to solubility occurring only after 4-6 hours at STP. Dichloroethane (DCE) proved more aggressive, with full well plate degradation in under a few minutes. Therefore, fluorophore-polymer samples originally formulated in DCE were re-formulated in anisole (for Coumarin 6) or PM (for Rhodamine B) and then aliquoted in the well plates.
After one to two hours, the well plates with films are removed from vacuum and evaluated in a TECAN Infinite® 200 plate reader. Absorption spectra are taken for each formulation from 350 nm to 850 nm in 5 nm steps, with a bandwidth of 2 nm. Then, the fluorescent emission spectrum is taken at the maximum absorption wavelength for each formulation. The maximum absorption and emission wavelengths for each formulation are reported in Table 5.1.

5.3 Results and Discussion

5.3.1 Effective Cross Sections of Internal Excitation

In this study, we set out to compare the performance (i.e. the number of photons emitted per incident electron) of a variety of fluorophores. The first aim is to determine the validity of these comparisons, so the effects of the polymer matrix must be analyzed. Figures 5.8 and 5.9 show that both Rhodamine B and Crystal Violet perform differently in different polymers, with both performing best in PHS.

It is clear from this data that comparisons between fluorophores in different polymers are not very useful in drawing conclusions. Furthermore, by referring to Table 5.1, we can see that each film has a different amount of fluorophore due to differing film thicknesses and different molar masses. It is then best to analyze the cross sections (calculated using a previously developed methodology\(^{15}\)) of internal excitation within the same polymer environment whenever possible. Figure 5.10 compares the cross section of internal excitation for 7 fluorophores in PMMA.
Figure 5.8. The number of photons emitted per incident electron by Rhodamine B in three polymers.

Figure 5.9. The number of photons emitted per incident electron by Crystal Violet in three polymers at various incident electron energies.
Figure 5.10. The cross sections of internal excitation for 7 fluorophores in PMMA across a large range of incident electron energies.

Coumarin 6 has the highest cross section at 80 eV (the energy of photoelectrons generated by EUV) of the fluorophores in PMMA, while 4-Methylumbelliferone has the lowest cross section of the fluorophores that produced a signal at 80 eV. Many fluorophores did not produce a signal distinguishable from background at electron energies below 700 eV—only four fluorophores (TBR, Coumarin 6, Rhodamine B, and Crystal Violet) did.

Figure 5.11 compares fluorophores in the Xanthene chemical family. Rhodamine B has the highest cross section below 2000 eV, and has roughly the same cross section as Eosin Y at 2000 eV and above. Fluorescein 5(6)-isothiocyanate had the lowest cross sections in this family.

Figure 5.12 shows the effective cross sections of internal excitation of Coumarin 6 (in PS and PMMA) and Tris(2,2’-bipyridyl) dichlororuthenium(II) hexahydrate (TBR), the best performing fluorophores in the study. TBR, the only metal-containing fluorophore evaluated, had the highest
internal excitation effective cross section of any fluorophore studied. Furthermore, it’s cross section increases at lower incident electron energies, which is unusual amongst the fluorophores in this study.

**Figure 5.11.** The cross sections of internal excitation for the four fluorophores in the Xanthene family in this study.
Figure 5.12. The cross sections of internal excitation for the best performing samples in this study.

Finally, the maximum internal excitation quantum yield (QY), or maximum number of photons emitted per incident electron, is plotted on top of the absorption and emission wavelengths in Figure 5.13. From this, it seems that the best performing fluorophores in this study absorb at 450 nm (or 2.8 eV). At the moment, this seems coincidental – further study of fluorophores is required to determine if this is a trend.

The QY measurements made here are justified by Kasha’s rule, which states that “the same fluorescence emission spectrum is generally observed irrespective of excitation wavelength”\cite{24}. The electronic excitation transitions that are allowed may differ slightly due to transitions forbidden by angular momentum considerations, but photon emission is a result of relaxation from the lowest excited state in a given multiplicity, so as long as internal excitation excites the fluorophores, they will produce the same emission spectrum. Furthermore, then, the photon
emission is a direct function of the number of electrons “absorbed”—i.e. less electron interactions will produce proportionally less emission. This is further supported by the Vavilov corollary which states that the number of photons emitted per photons absorbed (or, in this case, interacting electrons) is independent of excitation wavelength (or deposited electron energy).

Figure 5.13. Maximum internal excitation quantum yield (E-Beam QY) plotted on top of the absorption and emission wavelengths for the fluorophores in this study.

5.3.2 Fluorophore-polymer Reactions

While determining the background signals produced by pure polymer films, it was noticed that polystyrene without added fluorophore began to glow at substantial electron exposure doses (Figure 8). Radiolysis literature\textsuperscript{16-19} suggests that radiation damage of polystyrene eliminates H\textsubscript{2} from the polymer backbone, resulting in conjugation. At higher doses, the backbone conjugates to
such an extent that electrons can be promoted to excited states that can result in photon emission (300 to 500 nm) upon relaxation.

Figure 5.14 also shows that polymer-fluorophore interactions and reactions can play a large role in electron beam exposures. The curve in red is the number of photons emitted per incident electron with 25 wt.% Coumarin 6 in polystyrene. At a dose of about 0.1 μC/cm², this sample emits the fluorescence induced by exposure. This signal decays with time, indicating that Coumarin 6 is reacting upon exposure to produce a molecule that is no longer fluorescent, at least, in the regime that can be captured by our optics (> 350 nm). At even larger doses, there is a lack of fluorescence of the polystyrene itself, indicating that the radiation damaged Coumarin 6 and polystyrene are reacting with each other, and that this reaction inhibits long-range backbone conjugation that yields the fluorescence of the polymer itself.

**Figure 5.14.** E-beam exposure of pure polystyrene results in photon emission at high doses (blue). The addition of Coumarin 6 yields fluorescent emission at lower doses, but no secondary emission from the polystyrene itself, indicating fluorophore-polymer reactions can inhibit this process.
5.3.3 Fluorophore Reaction Kinetics

We can also analyze the data to study the kinetics of the reactions involved in these experiments. It is evident that in addition to electron-induced fluorescence, e-beam exposure also causes side reactions (and possibly internal excitation) that deplete the original fluorophore (Figure 5.9). This results in a decrease in fluorescent signal over time. Prior photobleaching kinetics literature\textsuperscript{20-23} indicates that this decay process is not a simple first order or second order reaction, but instead can be modeled by a sum of exponential terms:

\[
I_P \propto \left[ h\nu \right] \propto \sum_{i=1}^{n} A_i \cdot \exp \left( -\frac{t}{\tau_i} \right) \tag{5.6}
\]

where \( I_P \) is the photodiode current, \( \left[ h\nu \right] \) is the “concentration” or number of photons produced. Each \( A_i \) and \( \tau_i \) are an amplitude and decay constant associated with a specific reaction process. The data in Figure 5.15 is best fit by four separate exponential terms (with diminishing returns at \( n > 4 \)). The decay constants and amplitudes for the four terms are listed in Table 5.2. It is also possible to calculate a rough half-life for this process for qualitative comparisons, though this has no deeper connection to reaction mechanisms.

With this simple modeling of the reaction kinetics, it is possible to evaluate different fluorophores for possible structures for novel PAGs that may take advantage of internal excitation. It would be best to further study fluorophores with high internal excitation cross sections at 80 eV (primary EUV photoelectron energy), as well as those that decay quickly, indicating that internal excitation leads to fluorophore reactions that are analogous to acid production by PAGs.
**Figure 5.15.** Fluorescent emission kinetics of TBR in ESCAP. The decay in signal is likely due to e-beam induced side reactions that deplete the amount of original TBR over time.

**Table 5.2.** The amplitude and decay times associated with an $n = 4$ fit of the data.

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<tr>
<th>Amplitude (nA)</th>
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5.4 Summary and Conclusions

EUV resist chemistry is believed to be dominated by the reactions of energetic (2-80 eV) electrons generated by photoionization and successive electron ionization. Prior work indicates that hole-initiated chemistry and electron trapping mechanisms contribute to resist chemistry. In this study, we propose that a third mechanism, internal excitation, is a viable pathway for electron reactions. Instrumentation was built and evaluated to measure electron-induced fluorescence, a process analogous to internal excitation. We observed polymer-fluorophore reactions and were able to model the reaction kinetics that lead to fluorescent emission signal decay.

Furthermore, it has been demonstrated that electron induced fluorescence occurs in these films and it is possible to quantify this process. A variety of fluorophores were studied, spanning different chemical families and absorption wavelengths from 415 to 590 nm. Two fluorophores, Coumarin 6 and Tris(2,2’-bipyridyl)dichlororuthenium(II) hexahydrate performed significantly better than the other fluorophores, and both absorb at 450 nm (2.8 eV). Further study is required to determine if other fluorophores that absorb at this wavelength will also perform similarly.

However, despite detecting measurable signals, the maximum quantum yield for this process is 0.45 photons emitted per incident electron amongst the fluorophores studied, and for many others, QY was less than 0.02. For 80 eV electrons, all measured QYs were < 1%, indicating that current models of resist and PAG reactions need not take internal excitation into account. It may be possible to design new PAGs to take advantage of internal excitation, but a broader study of fluorophores of many different structures is required.
5.5 References


Chapter 6: Mechanisms of EUV Exposure: Electrons and Holes

6.1 Introduction

Three primary mechanisms have been proposed for electron-matter interactions that cause chemistry within chemically amplified resists (CARs). In a mechanism proposed by Kozawa (Figure 6.1A), the holes left behind by liberated electrons can cause subsequent chemistry that is useful for photoresists. In a second mechanism, liberated electrons (that have lost a majority of their energy) may be captured by a molecule, destabilizing the bond structure and causing decomposition. This mechanism (Figure 6.1B), known as electron trapping or dissociative electron attachment (DEA), is well known in gas-phase electron reaction literature. This chapter will explore these two mechanisms.
In Chapter 5, we proposed and evaluated the possibility of a third mechanism called internal excitation (also known as electrical excitation or dissociative electron excitation\(^4\)), whereby one electron could potentially interact to produce multiple acids (Figure 6.1C). In internal excitation, a temporary electromagnetic coupling between a ballistic and a bound electron causes an energy transfer from the free electron to the bound electron, promoting this electron to a higher energy level. If this higher energy level results in an unstable state, it is possible that this internal excitation results in the decomposition of the excited molecule. It is possible for this to occur even when the ballistic electron loses as little as 2-3 eV, so the initial high energy electron is not consumed in this process and may proceed to react further. However, we observed that the yields of these interactions were low, on the order of 1% for the best performing systems, indicating that this is not a viable mechanism for significant acid production.\(^2\)
Figure 6.2. A mechanism for the generation of acid in chemically amplified resists, proposed by Kozawa and Tagawa, and summarized by Thackeray et al.

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Kozawa and Tagawa have arrived at a proposed mechanism for acid production in chemically amplified EUV resists based on hole-initiated chemistry and electron trapping.\(^1\) Their proposal is best summarized by Thackeray et al. in four steps (Figure 6.2).\(^7\) In this mechanism, (1) an EUV photon is directly absorbed by the polymer matrix, liberating a photoelectron and leaving a charged radical on the polymer side group. (2) The radical cation polymer undergoes a disproportionation reaction with a nearby unexposed polymer unit, creating a neutral radical and a cationic polymer group. (3) The electron liberated in the first step, or any other secondary liberated along the way, interacts with a PAG through electron trapping (dissociative electron attachment) to release the

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acid anion. (4) The acid anion reacts with the radical polymer group created in step 2, and the acid is “released.” In their proposal, hole-initiated chemistry and electron trapping are co-dependent mechanisms that are both required for the production of a single acid.

Here, we have carried out experiments which seek to directly investigate the proposed mechanisms involved in EUV exposures of chemically amplified photoresists. In these experiments, we measure acid production due to PAG electrolysis and EUV exposure using an acid-sensitive dye. Our experiments directly target the contributions of electron trapping and hole-chemistry to overall acid production, and specifically focus on understanding the independent or dependent acid production of these reaction pathways.

### 6.2 Methodology

#### 6.2.1 Materials

Photoacid generators used in this work (triphenyl sulfonium and t-butyldiphenyliodonium triflate) were obtained from Tokyo Ohka Kogyo. Nonafluorobutane sulfonic acid (or perfluoro-1-butane sulfonic acid) was obtained from Sigma Aldrich. The polymer polyhydroxystyrene (PHS), 15,000 MW, was obtained from Nippon Soda Co., Ltd. The polymer polymethoxystyrene (PMS) was synthesized from 4-vinylanisole (obtained from Sigma Aldrich) in the following preparation.

The monomer 4-vinylanisol, solvent 1-methoxy-2-propanol (PM), and initiator azobisisobutyronitrile (AIBN) were mixed in a round-bottom flask, with AIBN amounting to 3% mole ratio to 4-vinylanisole. The solution was refluxed under low pressure N₂ at 132 °C overnight. The product was crashed out of solution by addition to cold methanol, then vacuum filtered. The precipitate was further washed with cold methanol, before drying under vacuum. ¹H-NMR
confirmed that the product was of high purity and PMS, although molecular weight was not determined.

### 6.2.2 Experimental Design

Experiments were designed to directly match investigation of the Kozawa mechanism (dependent electron trapping and hole-chemistry) and direct production of acid through electron trapping (Figure 6.1). Solid-phase acid quantum yield measurements were made to determine acid production with phenolic (PHS) and non-phenolic (PMS) polymers, where it is proposed that the non-phenolic polymer cannot undergo a disproportionation reaction to produce the hydrogen from a hole (Figure 6.3, A1). In this case, the Kozawa mechanisms proposes that acid production in PMS should be suppressed. To test independent acid production via electron trapping, PAGs were electrolyzed in acetonitrile at their reduction potentials over time, and acid production was measured by extracting aliquots periodically and determining acid content. In this case, an independent acid production mechanism should result in an acid yield of 1 H⁺/e⁻.
Figure 6.3. The dependent and independent mechanism proposals were simplified into two separate approaches, 1A and 1B, which were experimentally investigated via 2A, 2B, and 2C. In experimental 2A and 2B, the acid yield of phenolic and non-phenolic polymers was compared. In method 2C, bulk electrolysis of PAGs was used to investigate acid production without polymer.

The acid-sensitive dye Coumarin 6 (C6) was used to measure acid content in both solid- and solution-phase experiments. Upon protonation to C6H⁺, the absorption wavelength of C6 changes from 460 to 530 nm. This shift in absorption allows a direct measurement of acid production using UV/Vis absorbance spectroscopy, of either solid films or solutions. This method has been used extensively in prior literature to measure FQYs of various PAGs in resist films.
6.2.3 Electrolysis of PAGs

Cyclic voltammetry was carried out using a Bas-i Epsilon cyclic voltameter (CV), according to the procedure described in Grzeskowiak et al.,\textsuperscript{8} where methodology for bulk electrolysis is also described. In brief, the standard 3-mm platinum disk electrode is replaced with an unfurled braided copper wire to increase the surface area with which to electrolyze the PAG. The potential is maintained at the PAG reduction potential for a period of 2-3 hours, during which 200 μL aliquots are extracted every 30 minutes. These aliquots are added to individual 1.8 mL portions of 37.4 μM solution of C6 in acetonitrile and loaded into quartz cuvettes, and the absorbance is measured in a Cary 50 UV/Vis spectrometer from 400 to 600 nm (Δ = 0.5 nm). The data produced by the Bas-i Epsilon instrument (current vs. time) during each 30-minute electrolysis run was numerically integrated to calculate the charge transferred. A standard curve is developed where known amounts of nonafllic acid are added to 1.8 mL portions of C6 solution and similarly measured via UV/Vis absorbance spectroscopy. The absorbance data for the electrolysis samples is converted to acid yield using this standard curve. The acid yield is plotted against cumulative charge in Figure 6.5B.
Figure 6.4. Using a cyclic voltammetry cell, the reduction potentials of various PAGs can be measured by observing the locations of peaks in positive current as the voltage is swept from 0 mV to +2000 mV, then to -2000 mV, and back to 0 mV. Here, the reduction potential for triphenylsulfonium triflate is shown to be -1420 mV. We adapted the use of this cell for bulk electrolysis measurements.

6.2.4 Acid Yield Measurements

Research by Higgins et al.\textsuperscript{9,10} and Hirose, Kozawa, and Tagawa\textsuperscript{11} determined film quantum yields (FQYs) of acid production during EUV exposure by formulating chemically amplified resists with Coumarin 6 to measure the concentration of acid in a film with UV/Vis absorbance spectroscopy. These researchers determined FQYs for resists containing three different PAGs at concentrations ranging from 0-1000 mM. Ultimately, the film quantum yields of these resists were shown to plateau at PAG concentrations greater than 600 mM, with iodonium PAGs producing more acid
than sulfonium or nonionic PAGs at all concentrations. More importantly, this work demonstrated a maximum FQY of 4.9-5.9 acid per photon (H⁺/hν) for the iodonium PAGs.⁹-¹¹

The method for acid quantum yield measurements has been adapted from Higgins et al.⁹ A resist is formulated with the appropriate PAG and polymer at 8-12 wt.%. Chemically amplified resists studied in the rest of this work are formulated in polyethylene glycol monomethyl ether acetate (PGMEA or PMA). Any acid quencher (base) is left out so that the acid production of the PAG is not suppressed. The appropriate acid is added to the formulation to make a standard curve. Once the general resist has been formulated, enough 2 wt.% Coumarin 6 in dichloroethane is added such that Coumarin 6 is 2.5 wt.% of the solids in solution. The absorbance (at λ = 530 nm) of the standard curve films is measured using a Cary 500 UV/Vis absorbance spectrometer, and the absorbance of a 0 wt.% acid is subtracted from all resulting data.

After the standard curve has been measured, the resist-C6 formulation (without added acid) is spin-coated on a quartz wafer and exposed to EUV. The EUV source power is measured before and after a set of exposures. The resist is exposed to the EUV beam at a 45° angle, creating elliptical exposure spots. A series of eight exposures is carried out, spanning 0.1-60 mJ/cm², to create eight exposure regions. The absorbance of these exposed regions is then measured. The absorbance of the unexposed region is subtracted, and then, using the standard curve, these absorbances are converted into acid concentrations using the standard curve. Finally, this data is plotted against the exposure dose in units of absorbed photons per nm³, calculated using the CXRO database¹⁵ for EUV absorbance measurements. The film quantum yield, or FQY, is measured by taking the slope of the linear regime of this data.
6.3 Results

6.3.1 Bulk Electrolysis of PAGs

Prior electrolysis of PAGs by Thackeray et al., Goldfarb et al., and Tarutani et al. showed that PAG reduction potential correlates well with EUV photospeed ($E_0$) and acid yield, indicating that PAG electron affinity directly relates to acid production in EUV exposure. However, this work did not show that electrolysis of PAGs yields acid.

Direct electrolysis of PAGs (Section 2.3) shows an increase in the absorbance of C6H+ at 530 nm, indicating acid production (Figure 6.5A, for Ph3S+ Nf). When this data is converted using the calculated standard calibration curves, the data is plotted in Acid (moles) vs. Electrons (moles) (Figure 6.5B). The data, for an iodonium PAG and a sulfonium PAG, shows acid production via direct bulk electrolysis of PAGs. Furthermore, the slopes of the two curves, both approximately unity, indicates that the acid yield of electrolysis is 1:1, i.e. one electron produces one acid. Electrolysis injects low energy (< 2 eV) electrons into the analyte, so acid yield in this case is directly due to low energy electron-PAG interactions, which we posit is electron trapping.
Figure 6.5. (a) UV/Vis absorbance curves for bulk electrolysis of triphenylsulfonium nonaflate shows an increase in absorbance of 530 nm, corresponding to an increase C6H^+, and thus acid production through increased electrolysis. After application of the standard calibration curve, these results are plotted to the right. (b) Acid vs. Electrons for the iodonium and sulfionium PAGs, showing ~1:1 acid production per electron.

6.3.2 Acid Film-Quantum-Yield measurements

EUV exposures of films composed of only polymer (PHS or PMS) and 2.5 wt.% Coumarin 6 showed no measurable acid production, even at exposures of up to 360 mJ/cm^2 (Figure 6.6). Under these exposure doses, the normal striking visible color changes of the film on the quartz wafer were not observed. Further UV/Vis absorbance spectroscopy showed no appreciable change (variations of less than 1%) in absorbance intensity at either 460 nm (neutral C6) or at 530 nm.
(C6H+). This indicates that hole-initiated chemistry cannot independently produce acid, even in the case of phenolic polymers such as PHS, in which the disproportionation reaction is possible.

Figure 6.6. Solid films containing only polymer (A: PHS, or B: PMS) and C6 showed no measurable acid production in EUV exposure, even at doses of 360 mJ/cm².

EUV exposures of these films containing PAG showed different results (Figure 6.7). Both PMS and PHS films, composed of 15 wt.% PAG (triphenylsulfonium triflate) and 2.5 wt.% showed acid production. The non-phenolic PMS film showed a FQY of 3.1 ± 0.1 H+/hv, whereas the phenolic PHS film exhibited an FQY of 5.1 ± 0.1 H+/hv. Based on direct electrolysis of PAGs and the previous results where films with no PAG showed no acid production, we posit that the 3.1 H+/hv in the PMS film are entirely due to the electron-trapping reaction. Then, the PHS film shows a 65% increase in acid production, likely due to the Kozawa proposal of dependent mechanisms which is possible in the phenolic polymer.
These results are supported by prior work, where Nakano et al.\textsuperscript{14} demonstrated acid production in solutions containing PAG and PMS. Additionally, a similar solution of PHS and PAG showed roughly double the acid yield. Calculations by Endo et al.\textsuperscript{15} show that PMS has a high energetic barrier to deprotonation, effectively “knocking out” the hole-initiated disproportionation pathway that results in acid production. Therefore, we conclude that the acid yield we observe in our PMS/PAG film (Figure 6.7, red) is entirely due to direct electron-PAG reactions.

This data indicates that the Kozawa proposal of dependent mechanisms does contribute (~40%) to acid production in chemically amplified resists consisting of phenolic polymers. In this case, additional acid is produced when the disproportionation reaction is possible, but only in the presence of PAG (or perhaps an electron trap), indicating that the release of an anion to produce acid is necessary for this pathway. However, this data suggests that roughly 60% of acid production in phenolic-polymer CARs is due to independent acid production from direct low-energy electron trapping by PAG.
Figure 6.7. EUV exposures of PHS (phenolic) and PMS (non-phenolic) films containing 15 wt.% triphenylsulfonium triflate and 2.5 wt.% C6 showed acid production, with FQYs of 3.1 ± 0.1 and 5.1 ± 0.1 H+/hν, respectively. This indicates that acid production in phenolic CARs is due to a 60% contribution of electron trapping, and a 40% contribution of dependent hole-chemistry and anion release.

6.4 Summary and Conclusions

Here, we have shown that experiments focused on mechanistic analysis can result in insight the fundamental processes involved in EUV exposure. Specifically, we have narrowed down on the possible mechanisms of acid production in organic chemically amplified photoresists. Previous
work, from our group and others, has shown that 5-6 H⁺/hv are possible in CARs, which naïve analysis may suggest requires 6-10 e⁻/hv. However, a combination of experimentation and modeling predicts 2-4 e⁻/hv, indicating that there must be acid production mechanisms that account for this discrepancy. Prior work from our group has ruled out internal excitation (or dissociative electron excitation) as a viable pathway for significant acid production in CARs. Acid production mechanisms focusing on electron trapping and hole-initiated chemistry differ in their understanding of the independence of these reaction pathways to produce acid.

In this work, we have shown that direct acid production through electron trapping is possible—i.e. polymer is not needed to produce acid from electron-PAG interactions. However, the Kozawa mechanism is correct in that there exists an additional acid production pathway that is a result of a disproportionation reaction in phenol polymers that requires an anion to produce acid. Additionally, the first pathway (independent electron trapping) contributes roughly 60% of the acid, with the remaining 40% from the dependent hole-chemistry. Future work should focus on evaluating electron trapping through electrolysis of systems that contain resists components in addition to PAG, perhaps oxidation of resist polymers in the presence of PAG, or additional solid-phase EUV exposures of PHS and PMS films with varying PAG loading to tease out kinetic information, or the ultimate limits of acid production in chemically amplified EUV resists.
6.5 References


Chapter 7: Future Work and Conclusions

7.1 Conclusions

EUV photochemistry is complex and poses many challenges for resist chemists in the future. The results presented in this thesis should demonstrate that there is much work to be done in both academia and resist companies to better understand this active field of research. The objective of this work was to investigate the mechanisms involved in acid generation in chemically amplified photoresists and determine their contribution to resist chemistry. To this end, we developed computational and experimental techniques to evaluate and study those mechanisms.

In order to pursue these goals, we asked specific questions to guide our research:

1. **Can simulations of EUV exposures be improved by modifying the underlying physical and chemical models to incorporate low-energy electron-resist interactions?** We have demonstrated (Chapters 3 and 4) that improvements in simulation capability can be made by modifying the framework of LESiS. We showed that total electron yield can be adjusted via the simple scaling of the CSDA. We showed that improvements in thickness-loss modeling can be made when incorporating the computational analogue of electron-trapping, and we demonstrated improvements in EELS simulation of low-energy electron behavior in resist materials by incorporating the low-energy loss events.

2. **Can the contribution of internal excitation to acid generation be determined experimentally?** We determined through analogous e-beam induced fluorescence studies that internal excitation plays a small role (< 1% yield) in electron-resist interactions. For the best performing fluorophores, internal excitation showed almost negligible photon
yield under the e-beam exposure of (high concentration) fluorophore containing films. Thus, internal excitation could not explain the discrepancy between $6^+ H^+/hv$ observed experimentally.

3. **Can the relationship between and relative contributions of electron-trapping and hole-initiated chemistry towards acid production in resists be determined?** We determined through bulk electrolysis that PAGs held at the reduction potential exhibit a 1:1 relationship of electrons to acid. Furthermore, this demonstrates that hole-chemistry is not needed to create acid from electron-PAG interactions. Using acid quantum yield determination using an acid-sensitive dye, we determined that pure polymer do not produce acid, even from exposure to high doses of EUV ($> 10X E_{size}$), and that acid production only occurs in films containing PAGs (or other potential electron traps). In addition, we determined that in typical chemically amplified resists, direct electron-PAG reactions are responsible for about 60% of acid production, while the remaining 40% is generated through a hole-initiated pathway that relies on disproportionation reactions of radical cations on the polymer backbone.

In conclusion, this thesis presents several studies of electron-resist interactions using both computational and experimental approaches. We have provided a brief overview of the role of photoresists in IC manufacturing and the challenges that the implementation of EUV poses to resist designers. We provided an in-depth mechanistic overview that guided the remainder of the work: the incorporation of chemical mechanisms and molecular interactions served to improve computational modeling of resists, and experimental investigations of the contributions of internal excitation, electron trapping, and hole-initiated chemistry determined the roles that each play in
acid production in chemically amplified photoresists. We hope that the techniques developed and the results presented here will serve to inform photoresist research and eventually yield EUV resists viable in future IC manufacturing.

7.2 Future Work

The work outlined in this thesis can serve as the framework of future investigation of EUV mechanisms. In particular, some of these techniques may be applied to directly evaluate organic chemically amplified resists developed in industry. Future work should include:

- Acid quantum yield measurements should be paired with resist outgassing measurements to determine the relationship between outgassing and acid production.

- By continuing acid quantum yield measurements for PAG-containing PHS and PMS films at different PAG concentrations, it may be possible to derive kinetic or energetic information about electron trapping and hole-chemistry.

- The LESiS backend should continue to be modified and developed for use under the guidance of Leo Ocola.

- In order for LESiS to be used to simulate metal-based resists, the remaining elements (Z = 1-100) should be added to the materials database.

- Improvements to LESiS must be made with users in mind, including GUI improvements for LESiS for ease-of-use and a revised users’ manual.