What We Don’t Know About EUV Exposure Mechanisms

Amrit Narasimhan1, Liam Wisehart1, Steven Grzeskowiak1, Leonidas E. Ocola2, Greg Denbeaux1, and Robert L. Brainard1*

1 College of Nanoscale Science and Engineering, SUNY Polytechnic Institute, Albany, NY 12203
2 Argonne National Laboratory, Lemont, IL 60439
* RBrainard@SUNYPoly.edu

The lithography community has studied EUV photoresists for nearly thirty years. Yet, some of the most basic details of the interaction of EUV photons with photoresists remain poorly understood. In a typical photochemical reaction using long-wavelength light (\(\lambda = 157-1000\) nm), photons create excited states in photoactive compounds, thereby creating known quantities of intermediates and photoproducts at measurable rates. The photochemical reactions occurring during EUV exposure are much more complex and, as yet, not fully explored. The 92 eV EUV photons ionize molecules in the resist, creating holes and free electrons, however, the numbers of these electrons created, their reaction mechanisms, lifetimes and reaction cross-sections are not well known. Here, we will discuss experimental results and provide insight into these poorly understood aspects of EUV exposure mechanisms.

Keywords: EUV, Secondary Electrons, Mechanisms, Photoresist

1. Introduction

The change in wavelength from 193-nm to 13.5-nm (EUV) light for lithography creates new challenges for resist chemists because the mechanism of EUV exposure is completely different than the mechanisms previously encountered using 193- or 248-nm light. The absorption of EUV photons causes molecular electrons to be ejected with \(\sim 75-82\) eV energy, leaving a radical-cation “hole” in the molecule [1-6]. These liberated electrons have sufficient energy to cause further ionization or other reactions. It is these electrons and their holes that provide the solubility-changing chemistry in photoresists. Understanding the reactivity of electrons and holes is key to optimizing the performance of future EUV photoresists.

At these wavelengths, it is possible to tailor the resist components to minimize photon absorption in the polymer and maximize photon absorption by the PAG [7]. 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% [6].

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 section aims to address some of these topics and provide an overview of research that attempts to answer specific questions, namely: Number of Electrons. Several publications discuss the numbers of electron/hole pairs generated during EUV exposure [2-5]. The methodology varies widely as do the results—numbers of electron/hole pairs span 1.8 to 10 electrons per photon. We will discuss these results as they relate to their implications related to EUV exposure mechanisms and our new interpretation of the data.
Additionally, we will discuss recent research on EUV exposure mechanisms [2,9]. Although most successful EUV resists are chemically amplified, the basic mechanisms by which EUV photons (and the electrons produced by them) react with photoacid generators (PAGs) remain poorly understood. We will compare our new results which quantify the amount of acid generated using in situ dyes and electrochemical studies with the conclusions in the literature.

Finally, secondary-electron blur in EUV resists directly impacts resolution limits. The distances that electrons travel in a variety of materials has been widely studied [10-12]. However, since reaction cross-sections in solid films vs. electron energy, in this energy regime, are not well known, the important question is really, “how far do they go before they react?” The answer to this question is critical to understanding the resolution limits to EUV and all other electron-based imaging technologies, and will be discussed here using a combination of experiment and modeling.

2. Methodology

2.1. Total electron yield in EUV exposure

LESiS (Low energy Electron Scattering in Solids) is a fully stochastic Monte Carlo simulation program that can be used to understand electron behavior in resists [10]. 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 ± 0.8 e/ν 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 (Fig. 1). 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.

2.2. Electron penetration depth

Here, we demonstrate improvements in modeling of electron penetration depth and thickness loss in an open source EUV resist. Originally [10], 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 (Fig. 2).
At the time, the thickness loss modeling only accounted for the energy loss mechanisms of ionization and plasmon generation [10]. 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 (Fig. 3).

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.

3. Results and discussion
3.1. Total electron yield
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 $3.4 \pm 1.0 \text{ e}/\text{hν}$ (Fig. 4). Here, the 22% of energy involved in plasmon generation contributes directly to total electron yield.

| Energy   | %        |
|----------|----------|
| EUV Absorption | 1 e-/p+ pair | 13% |
| Electron Ionization | 1 e-/p+ pair | 16% |
| Plasmons   | 1 e-/p+ pair | 22% |
| CSDA       | 0 electrons | 50% |

Electron Yield: $3.4 \pm 1.0 \text{ e}/\text{per EUV hv}$

Fig. 4. When we include plasmon generation in the tally process to calculate TEY, we find that LESiS predicts at TEY of $3.4 \pm 1.0 \text{ e}/\text{hν}$.

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 (Fig. 5). 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 $3.7 \pm 0.7$ (if plasmons do not produce electrons) and $4.7 \pm 0.8 \text{ e}/\text{hν}$ (if plasmons do produce electrons).

Work carried out by several groups [2-4] suggests that the total electron yield (or TEY) from EUV absorption is $\sim 2-4 \text{ electrons per absorbed photon (e}/\text{hν})$. 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 et al. and used with PROLITH by De Schepper et al. predicts $3.69 \pm 0.08$ eV/\(\text{hv}\) \cite{4,13}. Additionally, Kozawa and Tagawa, using assumptions from higher energy radiation physics, predict 4.2 eV/\(\text{hv}\) \cite{2}. 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.

### 3.2. Reaction mechanisms in chemically amplified resists

Researchers \cite{2,3,6,8,10,14-19} 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 6). In electron trapping, a low energy electron (perhaps 0-5 eV \cite{17}) 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 \cite{2,10,15}. (2) Holes left in ionized atomic species within the resist may also contribute to resist chemistry \cite{2,14}. 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 \cite{14}.

Kozawa and Tagawa have arrived at a proposed mechanism for acid production in chemically amplified EUV resists that is built upon electron trapping and hole-initiated chemistry. Their proposal is best summarized by Thackeray et al \cite{14}. 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 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.”

In this proposed mechanism, hole-initiated chemistry and electron trapping are both required in order to produce acid. In other words, acid production is a function of 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 using Coumarin-6 in two different polymers with the same PAG have shown acid production even when the hole-initiated pathway is suppressed, such as in the polymer poly-4-methoxystyrene (PMS). Exposures of films of PMS and PAG to 75 keV e-beam and EUV show acid production through protonation of Coumarin-6 via absorbance spectroscopy [9, 20].

The production of acid in PMS-based films lends support to the independent operation of electron-PAG reactions to produce acid. Deprotonation of PMS has been shown, through pulse radiolysis [2] and calculation [20], 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. [14], Goldfarb et al. [18], and Tarutani et al. [19] 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. Bulk electrolysis of PAGs at their reduction potentials has shown a 1:1 correlation between electrons injected and acid produced, demonstrating acid production through direct electron-PAG interactions at the low energies involved in electrolysis [9]. Furthermore, 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. 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 [2-4].

Additionally, the mechanism proposed by Kozawa and Tagawa requires that an acid anion is released near 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 instead operate independently, this confinement of electron range is no longer required. Therefore, it is important to understand how electrons can cause chemistry within resists far away from EUV absorption.

3.3. Electron penetration depth in EUV resists

Initially, LESiS was used to calculate photoelectron travel from the site of EUV photon absorption to various cutoff energies (Fig. 7). 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-

![Fig. 6. A short summary of three chemical mechanisms involved in acid production in chemically amplified resists.](image)
zero probability of electrons traveling up to 14+ nm away from generation.

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 (Fig. 8). 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 Fig. 8). When we apply the thickness-loss calculation algorithm [10] to the new data, we observe that the model and experimental data begin to match (Fig. 9).

Fig. 8. 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.

Fig. 9. The modifications to the thickness loss model and algorithm results in better matching between LESiS predictions and experimental data.
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.

4. Conclusions

The basic physical interactions involved in EUV photochemistry are well known, but their impact on EUV photochemistry remains an active area of research. While predictions of total electron yield have been narrowed to a range of 2-4 e⁻/hν, we have demonstrated that simple changes in electron-resist models may have a dramatic impact on these numbers. Additionally, some of the underlying chemical mechanisms involved in EUV exposure are still not well understood. Experimental evidence supports mechanisms in which direct electron-trapping by PAGs produce acid, and that polymers are also involved in acid production mechanisms. Simulation and thickness-loss results shown earlier indicate that electrons involved in EUV exposure can cause chemistry up to 14+ nm away from the holes left behind. Combined with direct electron-PAG acid production demonstrated through electrolysis, these results suggest that hole-chemistry may not be required to generate acid. However, comparisons of acid yield in different polymer films containing PAG do show increased acid production in polymers where the hole-initiated pathway is possible. Future work should also be directed to applying mechanistic analysis and experimentation to the development of more exotic metal-based or nanoparticle resist systems.

Acknowledgements

The authors would like to thank D. Frank Ogletree for useful discussions concerning plasmon contributions to electron generation, and group members Michael Murphy, Jodi Hotalen, and Bill Earley for valuable feedback. This work was supported, in part, by the Center for Nanoscale Materials, a U.S. Department of Energy Office of Science User Facility under contract no. DE-AC02-06CH11357.

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