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High precision monitoring of outgassing species in model EUV photoresists with a cavity ring-down spectrometer

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ABSTRACT

Background: Extreme ultraviolet (EUV) photoresists play a pivotal role in advancing nanopatterning technologies by balancing image quality and sensitivity. The outgassing behavior of photoresist thin films under EUV and deep ultraviolet (DUV) exposure reveals chemical details relevant to their performance.

Goal: This study focuses on utilizing an analytical technique not previously used in photolithography, the tabletop cavity ring-down spectrometer, to investigate outgassing dynamics in EUV photoresists, enabling precise chemical identification and deeper insights into resist processing.

Approach: The spectrometer's enhanced laser path length (~20 km) and broadband absorption capabilities in the CH overtone region allow for sensitive and temporally resolved detection of outgassed species. Using a model resist comprising a polymer matrix with a photoacid generator and quencher, we analyzed the influence of time delays between exposure and post-exposure bake (PEB) as well as storage under varying environmental conditions.

Results: Suppression of isobutylene outgassing and thickness loss was observed with extended delays between exposure and PEB, potentially linked to water absorption and acid deactivation. The technique proved highly effective in distinguishing subtle chemical differences between processing stages.

Conclusion: Delay times and their environmental conditions, particularly humidity, reduce outgassing and thickness loss of photoresists during PEB, suggesting decreased acid-driven deprotection. This can potentially impact sensitivity, defectivity, and roughness of resist patterns, necessitating precise monitoring and control.

Keywords: EUV photoresists, outgassing, cavity ring down spectroscopy, resist characterization, EUV-induced chemistry

1. INTRODUCTION

The continued scaling of semiconductor devices relies on the development of advanced patterning technologies, where extreme ultraviolet (EUV) lithography has emerged as a key enabler for high-resolution manufacturing. A critical aspect of this process lies in the chemical performance of EUV photoresists, which must meet stringent requirements for sensitivity and resolution. The intricate interplay of electron-induced chemical reactions during exposure and the subsequent post-exposure bake (PEB) governs the efficacy of these materials, making their precise characterization essential [1].

Among the many challenges in optimizing EUV photoresists is understanding how environmental conditions and processing delays influence chemical transformations within the resist film. Time delays between coating, exposure, and PEB, as well as storage conditions, can significantly alter these processes. For example, water absorption during extended delays may deactivate acids within the resist, affecting key reactions and performance outcomes.

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Traditionally, mass spectrometry and gas chromatography have been employed to analyze outgassing behavior [2,3]. However, these methods can lack the sensitivity and temporal precision required for detailed studies of chemical reactions in thin polymer films. In this study, we introduce a tabletop cavity ring-down spectrometer as a novel analytical tool for identifying outgassed species with unprecedented sensitivity and temporal stability. Using a model resist, a polymer matrix with a photoacid generator and quencher, we investigate the role of different exposure types (EUV and DUV) and process delays on the chemical transformations within the resist. Our findings highlight the suppression of isobutylene outgassing after long delay times and explore the underlying mechanisms, offering pathways for enhanced resist design and processing.

2. CHOICE OF MATERIALS

In this work, we systematically investigate the properties of potential EUV resist materials, using a model resist consisting of the fundamental components of a chemically amplified photoresist (CAR), such as polymers, photoacid generators (PAG) and quenchers. This approach will allow for a clearer understanding of the capabilities and function of the novel characterization tool. The polymer chosen for this study is a 6:4 random copolymer of *tert*-butylmethacrylate and 4-hydroxystyrene, referred to as P(tBMA-co-HS). Its detailed chemical structures are depicted in Figure 1. Triphenylsulfonium nonaflate was employed as the PAG, while triphenylsulfonium benzoate served as a photo decomposable quencher (PDQ). For the experiments presented here, the model resist formulation consisted of the pure polymer dissolved at 5.5 mg/mL in a 1:1 mixture of PGME and PGMEA. To this solution, 20 wt% PAG (relative to the polymer) and 100 mol% PDQ (relative to the PAG) were added. The resist was spin-coated on pure 100 mm Si wafers to achieve a homogeneous film thickness of ~17 nm. After spin-coating the samples underwent a post-application bake at 110 C for 60 s.

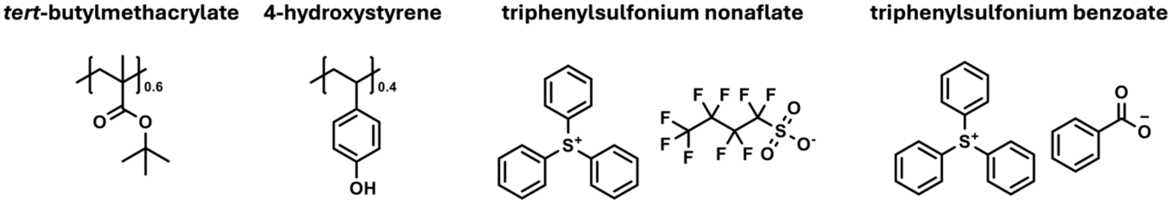

Figure 1. Chemical structures of the investigated polymers, PAG and quencher used to create model resist for evaluation of the characterization technique.

3. EXPERIMENTAL SETUP AND TECHNIQUE

EUV exposures are conducted at beamline 12.0.1.2 of the Advanced Light Source (ALS), which provides tunable wavelengths in the EUV and soft X-ray range. For this study, the exposure wavelength is set to 13.5 nm, corresponding to the industry-standard EUV lithography wavelength. The setup accommodates 100 mm wafers and enables blanket EUV exposure with a spot size of 5 mm x 1 mm, ensuring uniform irradiation across the selected area. Different EUV doses are achieved by scanning the wafer in front of the EUV spot with velocities ranging from 0.01 mm/s to 1.35 mm/s. DUV exposures are performed using an Energetiq laser-driven light source (LDLS), where the broadband emission is filtered to isolate the 193 nm wavelength. This setup is capable of exposing wafers up to 200 mm in diameter, with a homogeneous quadratic exposure spot size of 1 cm x 1 cm. Different DUV doses are ensured by varying the exposure time. The controlled broadband filtering ensures a well-defined irradiation condition comparable to industrial DUV lithography processes.

For the analysis of outgassing during PEB, a cavity ring-down spectrometer (CRDS) from Picarro is employed. CRDS is a highly sensitive and precise technique for detecting molecular absorption, due to the long effective optical path of a laser beam that is resonant with a high-finesse optical cavity [4,5]. When the laser source is abruptly turned off, the intra-cavity optical field decays exponentially with a time constant that is a sensitive, quantitative measure of the cavity loss (see Fig. 2a). Keeping the cavity length fixed and using the periodic cavity resonances as an "optical frequency yardstick" provides a stable, accurate frequency axis for the absorption measurements (see Fig. 2b) [6]. The spectrometer used for this work incorporates a broadly tunable, frequency-agile laser source that emits light between about 1625 nm and 1710 nm, covering most of the first overtone of the C-H stretching vibration. Prior to undertaking the experiments described here, spectra were acquired from samples of pure compounds in known concentrations to build a library of known spectra. Then for real-time sample analysis, least-squares fitting of the frequency-dependent absorption in the vibrational band permits differentiation between absorbing species, even with the same chemical formula, as well as simultaneous quantification of multiple species. This makes the spectrometer particularly well-suited for detecting outgassing compounds at extremely low concentrations, providing critical insights into the chemical processes occurring during PEB.

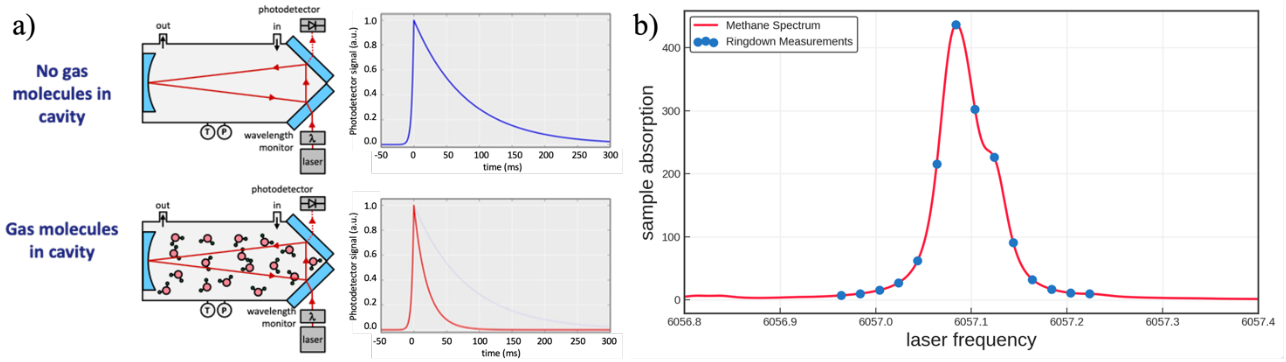

Figure 2. Working principle of the cavity ring-down spectrometer (a) and exemplary measurement spectrum for methane (b).

To ensure efficient capture of all outgassing products, a sampling adaptor is affixed to the wafer, enclosing the resist surface and guiding the emitted species toward the CRDS detection system during the PEB. A controlled gas flow of 40 sccm is maintained within the setup to facilitate consistent sample transport and measurement conditions. The PEB process is simulated by placing the wafer on a programmable hotplate. First, the baseline (zero signal) of the system is recorded by purging it with pure nitrogen for 10 minutes. Subsequently, the gas flow is directed through the adaptor at ambient temperature for an additional 5 minutes to establish a baseline measurement under practical conditions. Following this step, the hotplate temperature is linearly increased to 110 °C over 10 minutes and then held at 110 °C for 20 minutes. Finally, the hotplate is turned off to initiate the cool-down phase.

4. RESULTS AND DISCUSSION

In an initial study, we examined the generation of isobutylene during the PEB of the model resist after EUV exposure. The sample was irradiated with an EUV dose of 30 mJ/cm² over an area of 15 cm². Figure 3 compares the detected isobutylene outgassing for both unexposed and exposed films during the PEB. The red trace shows the temperature profile, while the black trace plots the isobutylene signal in parts per billion (ppb). No isobutylene signal is observed for the unexposed sample, whereas a strong outgassing signal is recorded for the exposed sample. The data clearly demonstrate that the detection tool is highly sensitive to isobutylene released from the exposed regions of the film. Isobutylene formation occurs via bond cleavage of the tBMA monomers, promoted by acid generated during EUV exposure [7]. Notably, the outgassing signal increases rapidly once the temperature exceeds 40 °C and reaches a maximum near 80 °C. After this point, the signal briefly decreases, then rises sharply again upon reaching 110 °C. Subsequently, the signal drops dramatically to below 10% of its maximum value. Once the hotplate is turned off, the signal promptly returns to zero.

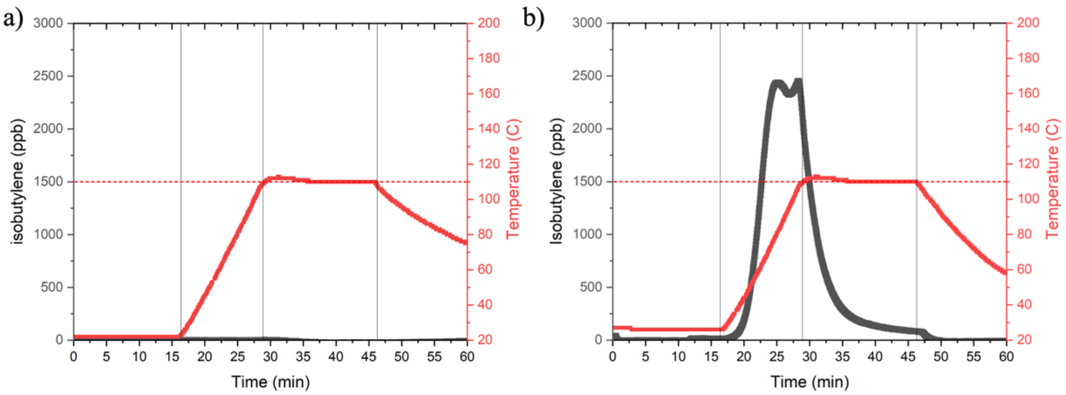

Figure 3. Comparison of isobutylene signal during PEB as a function of time for two identical model resists with (b) and without (a) EUV exposure.

Next, we compared outgassing signals for films exposed to varying EUV doses, ranging from 15 to 30 mJ/cm². Figure 4 presents both the contrast curve of the model resist and the corresponding isobutylene outgassing signals measured during PEB. The contrast curve exhibits a strong dose response around 17.5 mJ/cm², with a dose-to-clear determined to be 20 mJ/cm². The outgassing signal is negligible for 15 mJ/cm², but increases markedly with dose thereafter. Even at 30 mJ/cm², the signal remains significantly higher than at 20 mJ/cm². Consequently, for all subsequent experiments, an exposure dose of 30 mJ/cm²—50% above the dose-to-clear—was chosen to ensure a robust outgassing signal. It can also be seen that there is a thickness loss for lower doses, where no outgassing during the PEB can be measured. This thickness loss could be attributed to thickness loss during the exposure or outgassing of other components than isobutylene.

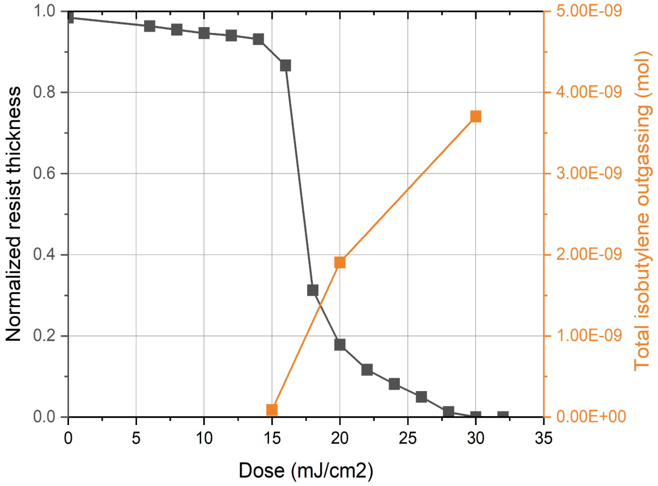

Figure 4. Comparison of total isobutylene signal during PEB and the remaining film thickness after development for the EUV model resist as a function of exposure dose.

When comparing EUV-exposed model resists with different delay times between exposure and PEB, a pronounced influence of the delay on the outgassing behavior is observed. After a 36-hour delay, the outgassing from the EUV-exposed sample is dramatically reduced, and it only commences at higher temperatures (>80 °C). This behavior suggests that two distinct mechanisms lead to deprotection of the tBMA monomers, resulting in isobutylene outgassing at low (<80 °C) and high (>80 °C) temperatures. As the delay time increases, the low-temperature outgassing fraction is not observed, whereas the second mechanism remains relatively unaffected. This could also account for the second high-temperature outgassing peak seen in the sample with a shorter (~3-hour) delay between exposure and PEB.

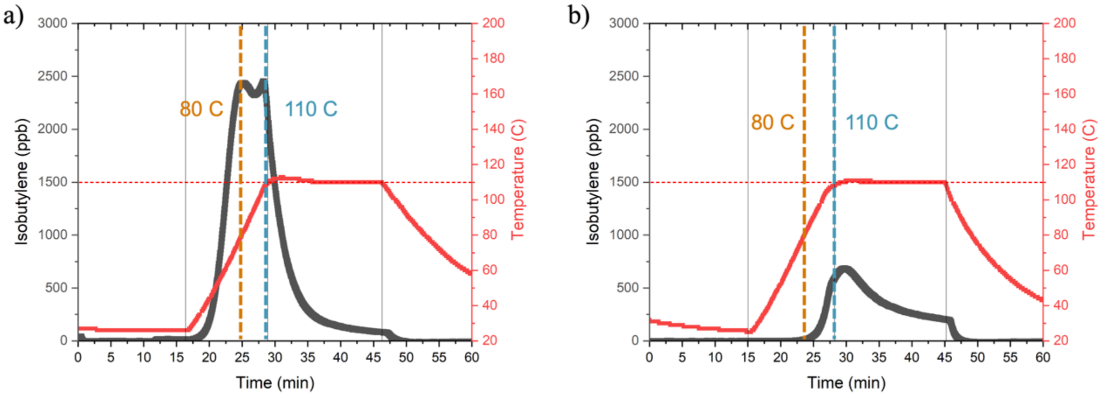

Figure 5. Comparison of isobutylene signal during PEB as a function of time for two identical model resists with identical exposure conditions and delay times of 3h (a) and 36h (b) after exposure.

To investigate this shift in outgassing behavior and its potential link to the deprotection mechanism of the polymer, we conducted a more comprehensive study of the delay time using DUV exposure at a wavelength of 193 nm. Using DUV exposure is an effective way to examine the process conditions and especially the effect on the PAG. Moreover, it offers better control over delay times by circumventing the logistical constraints of synchrotron-based EUV sources. Using the same model resist, we exposed samples to 20 mJ/cm² over an area of 15 cm². Figure 6 shows the resulting outgassing signals for samples processed immediately (upper left) and samples with a 24-hour delay under three storage conditions: nitrogen flow (upper right), ambient (lower left), and humid (lower right). Humid conditions were achieved by placing the exposed wafer in a sealed box containing an open water container to saturate the internal humidity. The results clearly indicate that a 24-hour delay between exposure and PEB leads to a substantial reduction in the outgassing signal. Under ambient and humid conditions, the outgassing decreases by more than 90% compared to samples processed without delay. Even under continuous nitrogen flow, the signal is reduced by approximately 40%, although trace humidity may still be present within the sample storage enclosure. Notably, the temperature at which the outgassing signal peaks also increases. In the absence of delay, the outgassing signal reaches a maximum at around 65 °C and diminishes close to zero by 110 °C. By contrast, the samples undergoing 24-hour delay time under ambient (~60% RH) and humid conditions (~100% RH) exhibit minimal outgassing until the temperature exceeds ~85 °C, with the peak outgassing occurring shortly after reaching 110 °C.

We may therefore conclude that exposure to humidity or other chemical components of the ambient air (e.g. NH_3, oxygen) during storage leads to a deactivation of the generated acid within the film, which in turn inhibits or reduces the efficiency of deprotection during the PEB. The absorption of water into photoresists and its impact on the dose-to-clear has been investigated in several model systems, including tBOC-protected PHS [9]. With the CRDS tool employed in this study, it is now possible to directly quantify the effect of environmental conditions during storage time on the PEB step and the related deprotection mechanisms.

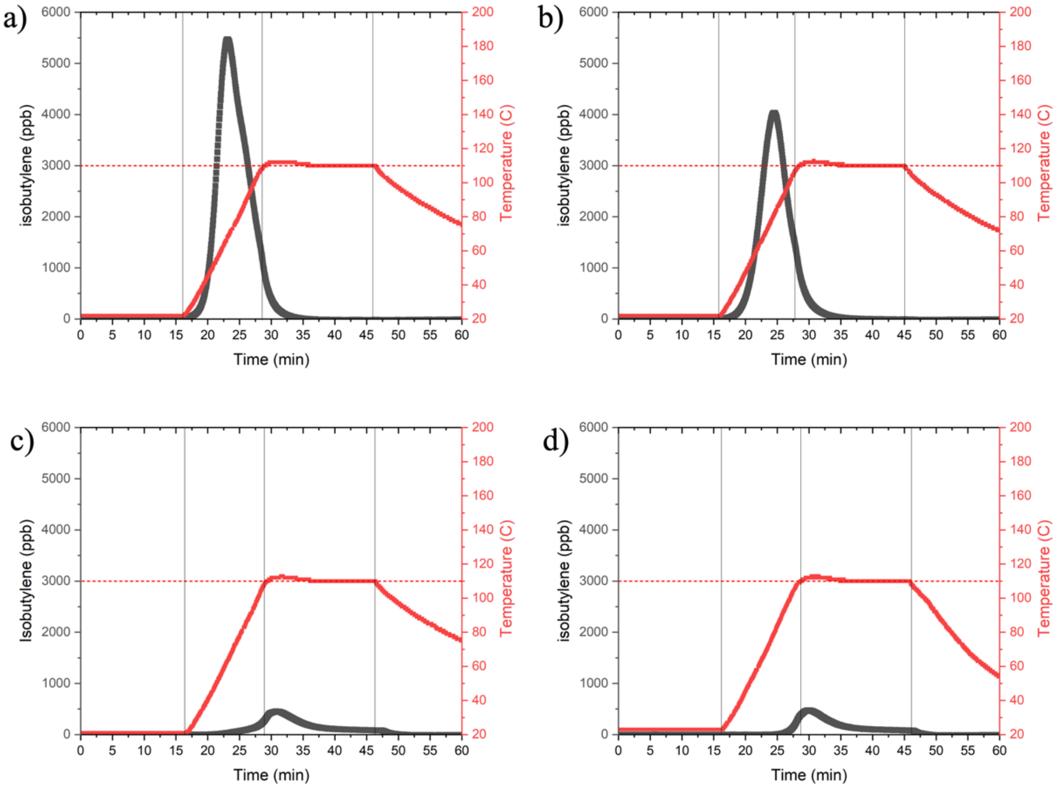

Figure 6. Comparison of isobutylene signal during PEB as a function of time for identical DUV-exposed model resists with identical exposure conditions with delay times of ~3min (a) and 24h under constant nitrogen flow (b), ambient conditions (c) and increased humidity (d).

Figure 7 provides an overview of the total isobutylene outgassing (in moles) measured during PEB for DUV-exposed samples stored under various conditions. Delay times ranged from 3 minutes to 24 hours under ambient conditions, and additional 24-hour delays were carried out under humid, vacuum, and nitrogen environments. Vacuum conditions were achieved by placing the wafer in a vacuum chamber at an average pressure of 5×10^{-7} Torr. The data reveal a progressive decline in outgassing with longer ambient storage times, with reductions of approximately 10% after one hour and as much as 90% after 24 hours. Storing samples under vacuum or nitrogen flow substantially reduces these effects, resulting in a 60% decrease in outgassing after 24 hours of vacuum storage and a 40% decrease under nitrogen. Notably, the vacuum-storage protocol includes a 20-minute transfer in a nitrogen-filled bag. Although the modest drop in outgassing within the first hour likely does not markedly affect the dose-to-clear of the samples, it could alter the deprotection behavior of the tBMA segments in P(tBMA-co-HS) within the film and potentially cause pattern defects. Additional in-depth studies will be necessary to fully understand these effects.

The CRDS tool also enables the quantification of the total outgassing volume by integrating over the outgassing signal in ppb and multiplying it with the total gas flow inside the tool (40 sccm). By assuming an ideal gas, one can then calculate the total number of outgassing isobutylene molecules in moles. Comparing these values to the estimated number of tBMA segments in P(tBMA-co-HS) in the exposed film volume—calculated to be approximately 7.3×10^{-8} moles (for an area of 15 cm² and thickness of 17 nm)—shows that, in the absence of a storage delay, around 25% of the total isobutylene in the film is released during PEB.

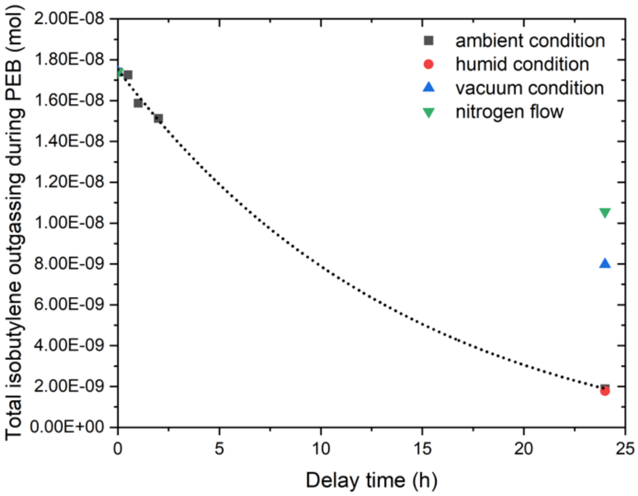

Figure 7. Comparison of the absolute isobutylene outgassing during PEB in moles for different delay times between DUV-exposure and PEB under different storage conditions. The black dotted line is inserted to guide the eye.

To further elucidate the effect of storage conditions, we measured the film thickness of selected samples following coating, DUV exposure, and PEB. These samples were either processed with minimal storage time (less than three minutes) or stored for 24 hours under ambient, humid, or vacuum conditions. Immediately after the exposure step the film thickness was consistently reduced by 2 nm. By contrast, the thickness changes attributable to PEB depended strongly on the storage conditions. For minimal storage times, the additional thickness loss during PEB was about 3.5 nm, nearly double the reduction observed during exposure. Under vacuum conditions, the PEB-related thickness loss was around 3 nm, despite notably lower outgassing measured during PEB.

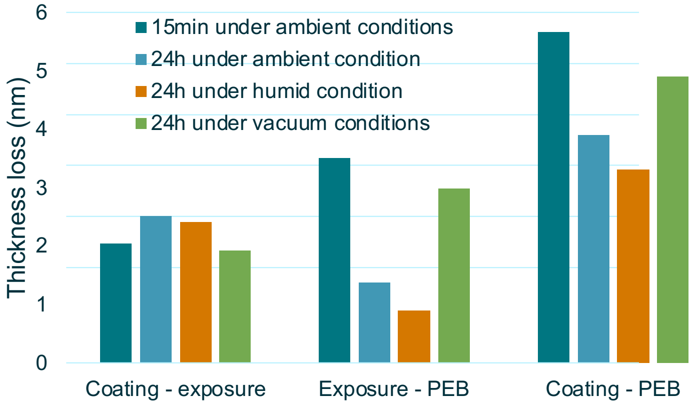

Figure 8. Comparison of absolute and relative thickness loss during different process steps for identical model resists with identical exposure conditions and different delay times under different conditions between exposure and PEB.

This finding suggests that, due to Le Chatelier's principle [10], the continuous removal of isobutylene during vacuum storage may have driven additional deprotection reactions to restore equilibrium. As a result, despite the significant difference in isobutylene outgassing levels during PEB, the overall thickness change remains comparable. Meanwhile, for samples stored for 24 hours under ambient and humid conditions, the film thickness loss was approximately 1.3 nm and 0.9 nm, respectively. These results indicate that the observed reduction in outgassing during PEB is primarily due to partial deactivation of the deprotection mechanism, rather than to any prior outgassing during storage.

5. CONCLUSION AND OUTLOOK

In summary, our investigation demonstrates that both humidity and storage conditions have a profound impact on acid activity within the film, the subsequent acid-catalyzed deprotection of tBMA segments in P(tBMA-co-HS), and overall outgassing behavior during the post-exposure bake. Using CRDS as a real-time detection tool, we established that delaying the PEB for several hours can significantly suppress isobutylene release, particularly under ambient and humid conditions. This suppression likely arises from acid deactivation by moisture and translates into reduced deprotection of the polymer during PEB, as confirmed by lower outgassing signals and smaller final thickness losses.

In contrast, storage in vacuum and nitrogen preserve a portion of the generated acid, reducing the extent of outgassing decay over time. Although these storage conditions still produce a measurable decrease in outgassing, the effect is less pronounced than under ambient or humid environments. Film thickness measurements reveal that storage in vacuum, despite lower outgassing, can still lead to substantial thickness changes, suggesting that multiple processes—ranging from acid loss to structural rearrangements—govern the overall deprotection chemistry.

Taken together, these results emphasize the need to carefully control environmental conditions and delay between exposure and PEB to ensure repeatable process performance. The ability to quantitatively detect and compare outgassing products under varying storage conditions provides critical insights into the deprotection mechanisms of EUV and DUV resists, ultimately guiding strategies for improved lithographic pattern fidelity and process stability.

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