

Thin EUV photoresist layers for microelectronic devices: pivotal benefits of the Orbitrap™ mass analyzer for accurate analysis

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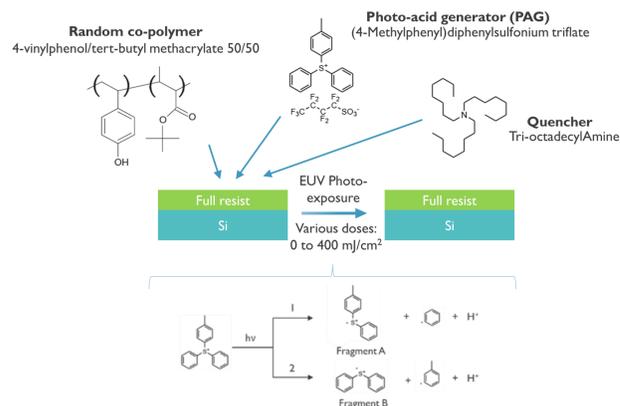
INTRODUCTION

- Photolithography is a well-established process used to pattern microelectronic devices. However, a deep understanding of the chemistry of all the photoresist components (polymer, photoacid generator (PAG) and quencher) is needed to allow to optimize and improve the process for future devices of smaller dimensions (nm), following the Moore's law. One of the important aspects to investigate is the 3D distribution within thin chemically amplified photoresist (CAR) used for fine patterning in extreme ultraviolet lithography (EUVL).
- This study reports on the application of secondary ion mass spectrometry (SIMS) for examining thin CAR films on silicon. SIMS depth profiling was carried out using a gas cluster ion beam (GCIB) to preserve the molecular information of the different organic components in the layer, i.e. to minimize sputter induced damage. Specific attention concerned the distribution of the PAG molecule within these films, along with the photo-induced fragmentation occurring on EUV photo exposure.

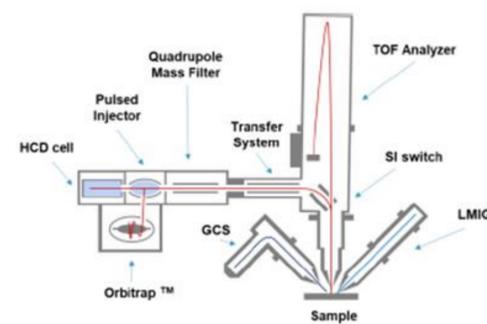
EXPERIMENTAL DETAILS

- 35nm thick model CAR material (composed of a polymer with protection groups, a PAG and a quencher) was spin-coated onto Si wafers, baked at 90°C for 60s and exposed in an ASML's EUV scanner NXE3300 at various doses up to 400mJ/cm². To amplify the catalytic deprotection reaction, the samples were exposed to a post bake (PEB) at 90°C for 60s.

- During EUV photo exposure, the PAG cation decomposes in the PR layer, activating the acid formation (H⁺) following two possible routes. During the PEB, the PAG is expected to diffuse and catalyze chemical reactions, such as the deprotection of the protective group in the polymer. The quencher acts as a pattern resolution enhancer.



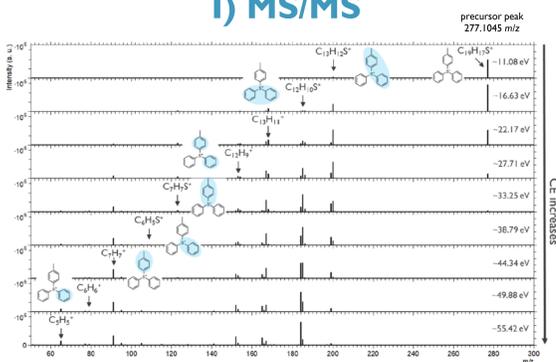
Schematic representation of the molecular structures for random co-polymer, PAG, quencher, and of the reactions involved during EUV photo exposure and post-photo exposure bake (PEB) for PAG cation.



Schematic representation of M6 Hybrid SIMS instrument.

- ToF-SIMS analysis was performed with a ToF-SIMS NCS instrument (IONTOF, Germany) operated in dual beam mode using Bi₁⁺ species at 15keV as analysis beam (in spectrometry mode for high mass resolution, i.e. >7000 @ m/z 29) and GCIB using Ar₂₀₀₀⁺ at 5keV as sputter beam.
- The Orbitrap™-SIMS analysis was performed on a M6 Hybrid SIMS instrument (IONTOF, Germany) operated in single beam mode, using the GCIB as primary ion gun with the same conditions as used in the ToF-SIMS experiment. The mass resolution was set to 240000 @ m/z 200.
- Both ToF- and Orbitrap™-SIMS experiments were acquired in the positive ion detection mode.

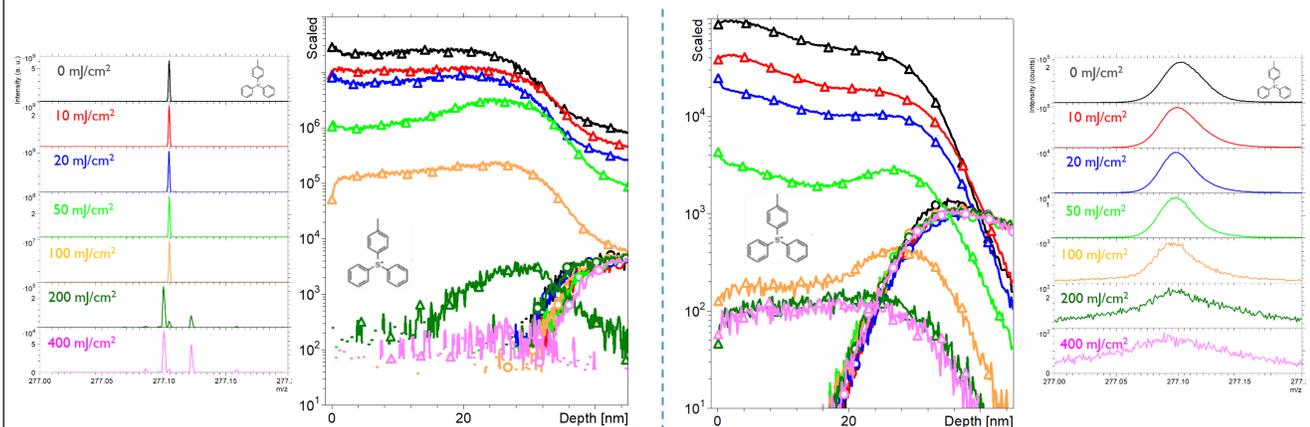
I) MS/MS



MS/MS spectra (in the Orbitrap™ mass analyzer) overlay at different collisional energies (CE) of unexposed sample. The most relevant fragments are indicated by an arrow and their molecular formula. The fragment structures are indicated on the molecular structure signified as shaded.

- The precursor ion (at 277.1045 m/z) becomes barely visible after ~33.25eV, (→ near complete fragmentation). The intensity of smaller fragments increases for higher CE. A clear assignment is done thanks to the exceptional mass resolution and accuracy of the Orbitrap™ analyzer.
- The observed fragmentation trends support the peak assignment at 277.1045 m/z to the PAG molecular ion as opposed to some other isomer (a molecule with formula C₁₃H₁₂S, but with a different molecular structure).

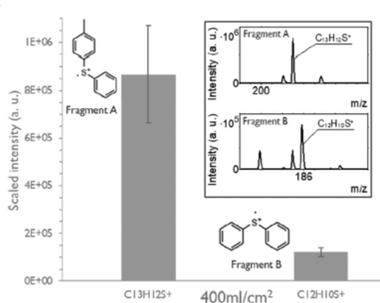
II) Orbitrap™-SIMS vs ToF-SIMS



(Left) Orbitrap™-SIMS & (Right) ToF-SIMS depth profile overlays showing the PAG molecular 277.1045 m/z signal (▲) and the Si signal (○) in scaled intensity (scaled to the Si signal in the substrate) and depth (in nm) as a function of photon irradiation dose and the spectra overlays of the molecular PAG mass peak integrated over the whole PR thickness for increasing doses.

- A gradual decrease of the PAG molecular peak is observed with increasing exposure dose in agreement with expected PAG decomposition.
- A drastic drop of the PAG molecular peak is observed with Orbitrap™-SIMS after 100mJ/cm², reaching intensities close to the background level for the exposure at 400mJ/cm².
- A signal is still observed for exposure doses higher than 100mJ/cm² in the ToF-SIMS profiles and the highest applied dose (400 mJ/cm²) seems not to be sufficient to completely decompose the PAG.
- The Orbitrap™-SIMS spectra of the 200 and 400mJ/cm² samples show the presence of multiple peaks at 277.1045 m/z (most likely related to the polymer matrix, e.g. C_xH_yO_z structure) which will result in the misleading assignment of the peak in ToF-SIMS due to the limited mass resolution (a minimum mass resolution of ~63000 is required to avoid such mass interference).

III) PAG FRAGMENTATION PATHWAY



- Fragment A displays ~7x greater intensity than fragment B, which would indicate what is the most likely PAG fragmentation pathway during EUV photo exposure.

Orbitrap™-SIMS intensity plot of fragments A and B integrated over the film thickness of the sample exposed at 400mJ/cm². The insets show the mass spectra (integrated over the entire layer) of the two fragments and the related assignments.

SUMMARY

- We demonstrated that GCIB-SIMS experiments run with an Orbitrap™ mass analyzer can reveal important modifications in the chemical composition of PR films during EUV photo exposure. These modifications could not be highlighted with a conventional ToF-SIMS, due to severe mass interference between the PAG molecular ion and some neighboring signals related to the polymeric matrix.
- The MS/MS performed in the Orbitrap™ mass analyzer allows to unambiguously assign the 277.1045 m/z peak to the PAG molecular ion.
- Thanks to the high mass resolution and mass accuracy of the Orbitrap™ analyzer, it was possible to identify the most probable fragmentation pathway of the PAG molecule during EUV photo exposure.