Characterization of PFAS Free PAGs in Photoresist

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Abstract:

The reduction of PFAS 'forever chemicals' has been of recent focus for the semiconductor industry for both legislative and environmental concerns. These chemicals, containing -CF2- or -CF3 bonds1, are difficult to break down due to high bond energy and thermal stability. PFASs are of concern to the environment due to this property, building up in the biosphere and interfering with biological systems. Recent legislation is pushing for the removal of PFASs in the semiconductor industry leading to the need for PFAS free photoresists2. This project focuses on the performance of PFAS-free PAGs in photosensitive resists, which may match or outperform their PFAS counterparts and factors that influence it.

Summary of Research:

Photosensitive resists generally have four steps: pre-bake, exposure, post exposure bake (PEB), and development. In the baking stages, temperature and time affect the results and properties. Exposure is influenced by dosage, mJ or uC/cm^2, given to the photoresist and correlates with resist thickness. Overexposure also poses a concern with cross-linking, causing the photoresist to become insoluble and harder to remove than an adequately exposed area. Proper development ensures that the exposed or unexposed sections, depending on whether a positive or negative resist is utilized, dissolve completely.

One of the tests uses a PFAS free PAG-bound ESCAP resist with an array of resolution tests that varied the dose using the ASML 5500 DUV stepper. The stepper is capable of resolution down to 200 nm, setting the best possible result. The criteria for a good resist are development through the thickness of the resist and smooth edges that follow the original pattern. However, due to effects such as corner rounding, optical diffusion, acid diffusion, and optical proximity effects, small features will have more pronounced rounding and imperfections when compared to the original mask.

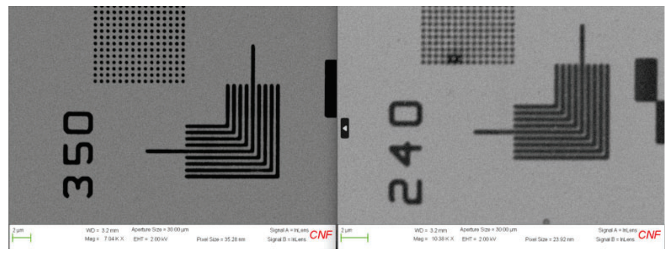

Figure 1: DUV resolution comparison at 350 nm and 240 nm.

Figure 1 compares a good result in a DUV in the bulk of the feature at 350 nm, compared to expanded lines on 240 nm. The rounded corners and ends of the lines test show the optical and chemical effects of photolithography. Figure 2 has good features at 300 nm and continually decreases in quality down to 250 nm. 300 nm has clear edges with some variations, overall a good result. 280 nm has noticeably less quality, with more jagged edges and some sections bridging on the sides. Under 280 nm is unviable, having too much inconsistency.

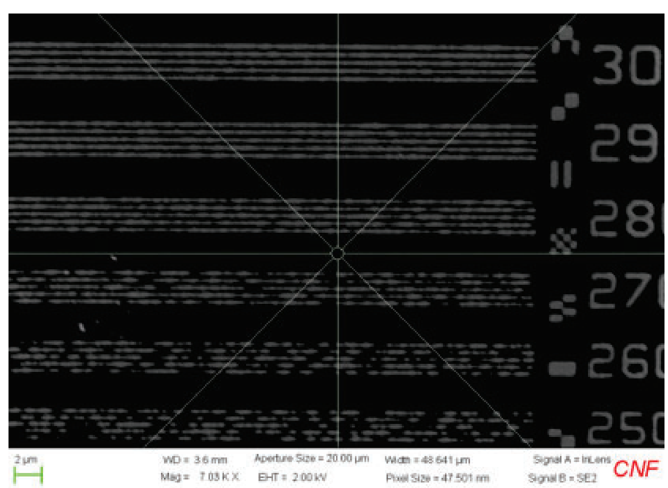

Figure 2: DUV resolution test at approximately 115.5 mJ/cm^2 with good results at the top starting at 300 nm and getting worse as you go down to 250 nm..

E-beam photoresists were tested in lieu of EUV due to the mechanism of how EUV PAG resists work. They rely on secondary electrons to create an acid that allows for the photomask to become more soluble. Using the Nabity NPGS and Zeiss Supra SEM, the electron beam skips to the secondary electron state, bypassing the need for EUV radiation to generate secondary electrons. This was used to test resolution and how thorough the thickness the photoresist exposures are. Using AFM, each dose's height map is recorded then digitally processed. Using Gwyddion, the major steps are background slope removal, averaging the depth of the exposure development, and normalizing using the thickness of the resist (fig. 3). This gives us the exposure thickness of the resist. The P3 PAG (fig. 4) was tested, with the best resolution of the set at 500 nm (fig. 3).

Conclusions and Future Steps:

This research shows room for improvement for using PFAS-free PAGs, with up to 90 nm of improvement potential for DUV on the ASML 5500. The main limitation with testing is how fast the PAGs can be synthesized, with only enough being made for one or two samples per week. These characterizations show a significant step in moving toward PFAS-free photoresists by utilizing PFAS-free PAGs. However, more testing and improvements to the process are needed before they can be applied and reduce PFASs in the environment.

References:

[1] OECD (2021), Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance, OECD Series on Risk Management of Chemicals, OECD Publishing, Paris, https://doi.org/10.178

[2]. Environmental Protection Agency. (2019). EPA PFAS action plan (EPA 823-R-18-004). U.S. Environmental Protection Agency. epa.gov

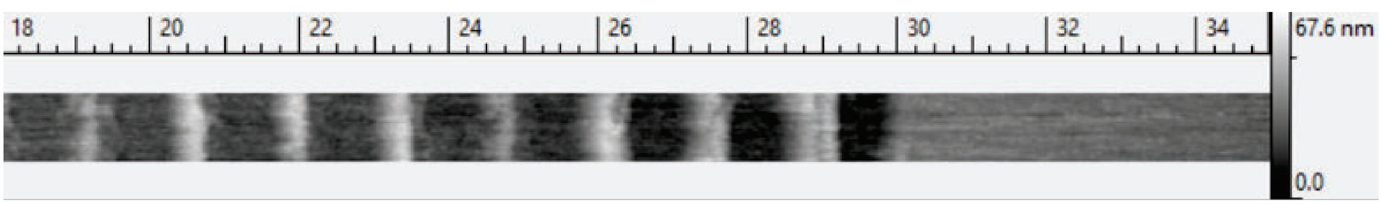

Figure 3: Ebeam resolution test with 500 nm line distance and width. Dose of 125 uC/cm^2 for the tested setup of 110°C for 240s.

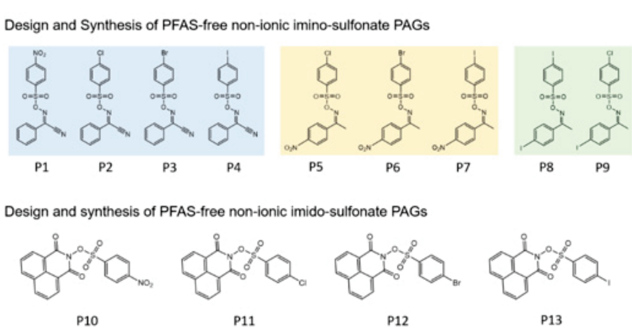

Figure 4: PFAS free PAG chemicals. Report on identification of PFAS-free non-ionic PAGs as solubility switch groups in photoresists. Task #: 3244.001. Christopher K. Ober, Yu Zhong.

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