Identifying the Occurrence and Sources of Per- and Polyfluoroalkyl Substances in Photolithography Wastewater

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Principal Investigator(s): Damian Helbling, Christopher Kemper Ober

User(s): Paige Jacob

Affiliation(s): Civil and Environmental Engineering, Cornell University
Primary Source(s) of Research Funding: Semiconductor Research Corporation, National Science Foundation
Contact: deh262@cornell.edu, cko3@cornell.edu, pv7@cornell.edu
Website: https://helbling.research.engineering.cornell.edu/
Primary CNF Tools Used: DISCO Dicing Saw, Jelight 144AX UVO-Cleaner, FilMetrics F40

Abstract:

Per- and polyfluoroalkyl substances (PFASs) are contaminants of emerging concern to environmental and human health [1]. PFASs are present in chemical mixtures used during photolithography [2] and might undergo transformation reactions during the steps of photolithography. We acquired five photolithography materials and characterized the occurrence of PFASs in the native materials. We performed photolithography and collected the resulting wastewater samples to evaluate the chemical transformations. The goal of the project is to elucidate the sources of and mechanisms by which PFASs are introduced or generated during photolithography.

Summary of Research:

The occurrence of PFASs in wastewater and fresh water has emerged as a challenge for engineers [1]. A major obstacle for water quality managers and policy makers is that there are thousands of known PFASs, and countless others that may arise from transformation reactions during industrial processing, environmental transport, or water and wastewater treatment [3]. A variety of PFASs are used in photolithography and a recent study demonstrated that photolithography wastewater contains known and previously unknown PFASs [4]. Although it is known that perfluorobutane sulfonate (PFBS) is a widely used constituent of photoacid generators (PAGs) [2], the sources of nearly all of the other PFASs in photolithography wastewater remain unknown.

The complex materials are also subject to transformation reactions induced by the chemical conditions of photolithography. Photolithography requires the application of the photoresist through spin-coating followed by a soft bake, 248 nm exposure, a hard bake, development, and stripping [5]. These steps expose the materials to UV radiation and highly basic conditions. We hypothesize that many PFASs measured in photolithography wastewater are transformation products formed during photolithography.
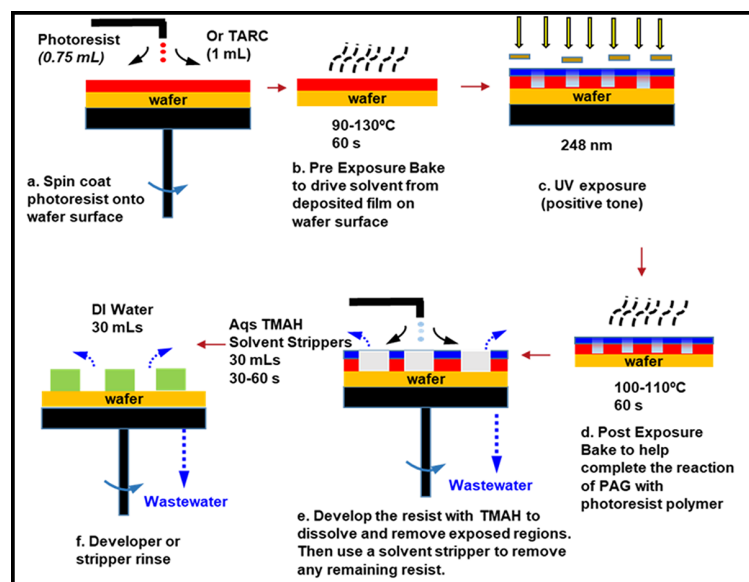

Figure 1: Process diagram of the photolithography workflow conducted at the CNF for each of the five native materials. In this figure, "DI water" = deionized water, and "TMAH" = tetramethylammonium hydroxide.

The goal of the project is to elucidate the sources of and mechanisms by which PFASs are introduced or generated during photolithography. We also aim to study transformation pathways, as improved understanding of transformation pathways will lead to better predictions

Chemical	Measured TOF (g/L)
Photoresist A	1.65±0.14
Photoresist B	0.36±0.03
Photoresist C	1.31±0.04
TARC A	18.1±0.35
TARC B	4.62±0.08

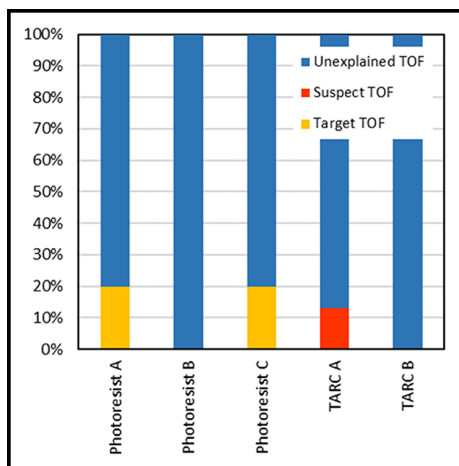*Figure 2: Total organic fluorine measurements of each of the native photolithography mixtures.*

Figure 3: Percentage of total organic fluorine measurements that are accounted for by target or suspect PFASs in the native materials.

step of photolithography. These measurements will allow us to calculate a mass balance of the native materials on the wafer throughout photolithography.

Conclusions and Future Steps:

The results of the target screening of the five materials revealed the presence of only one target PFAS in two of the materials. Photoresists A and C contained PFBS, which is probably used as the PAG anion in these materials, at concentrations of 331 and 268 mg L-1, respectively. The suspect screening results revealed that suspect PFASs were only identified in TARC A. Photoresist B and TARC B did not contain any target or suspect PFASs.

Next, the samples were analyzed by means of CIC for TOF. The TOF measurements of each photolithography material were in the g L-1 range (Figure 2). We also found that TARCs have higher concentrations of TOF, sometimes an order of magnitude higher than photoresists. These measurements display a gap between the TOF accounted for with target and suspect compounds and the total TOF in the materials, leaving a fraction of the TOF unexplained (Figure 3).

After photolithography, we observed that PFBS was still the main target PFAS identified in post- photolithography wastewater samples and was present in the μg L-1 range. We identified a limited number of other target and suspect PFASs in the wastewater samples. We will next analyze the HRMS acquisitions of the wastewater for unexpected PFASs and measure the TOF of the wastewater and wafer samples.

After identifying the PFASs generated during photolithography, we aim to identify transformation reaction pathways for the fluorinated constituents in native materials to identify reactions occurring at each step and link parent chemicals to the products found in the wastewater from that step. Additionally, we are currently in the process of obtaining a 193 nm exposure tool and temporarily installing it within the CNF to perform the same workflow at 193 nm exposures.

of how chemicals transform and inform the development of new photolithography chemicals.

First, we acquired five industrially relevant photolithography materials consisting of three photoresists (Photoresists A, B, and C) and two top antireflective coatings (TARCs A and B). We identified and quantified the PFASs in the materials with multiple analytical techniques, including two high resolution mass spectrometry (HRMS) analyses and a combustion ion chromatography (CIC) analysis. The HRMS analyses consisted of a target screening, where authentic standards of 35 target PFASs and isotope-labelled internal standards were used to quantify PFASs in the materials, and a suspect screening, where HRMS data was mined to gather qualitative information on a list of 171 PFASs that were previously identified in photolithography wastewater samples. The CIC analysis combusts all fluorinated compounds directly into hydrogen fluoride (HF) and the fluoride is then measured with IC to quantify the total organic fluorine (TOF) in the sample [3].

Next, at the CNF we manually performed the steps of photolithography and collected the wastewater from a single material after development and stripping to identify which step may be inducing transformations (Figure 1). We also performed photolithography on clean wafers and collected wastewater samples to characterize the background contamination of PFAS within the CNF and to determine which PFASs are derived from the native materials.

Then we performed target and suspect screenings on the wastewater samples to identify the PFASs present post-photolithography. In addition to collecting wastewater samples, the DISCO dicing saw to was used to cut wafers into pieces that would fit inside the combustion unit to measure the TOF of the wafer after each step of photolithography. Lastly, the FilMetrics F40 was used for thickness measurements of the wafers after each

References:

[1] Z. Wang, et al.; 10.1021/acs.est.6b04806.

[2] C. K. Ober, et al.; 10.1117/1.JMM.21.1.010901.

[3] C. A. McDonough, et al.; 10.1016/j.coesh.2018.08.005 (4) P. Jacob, et al.; 10.1021/acs.est.0c06690.

[4] D. Bratton, et al.; 10.1002/pat.662.