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

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Principal Investigator(s): Damian Helbling[1], Christopher Kemper Ober[2]
User(s): Paige Jacob[1]

Affiliation(s): 1. Civil and Environmental Engineering, 2. Materials Science & Engineering; Cornell University
Primary Source(s) of Research Funding: Semiconductor Research Corporation and National Science Foundation
Contact: deh262@cornell.edu, cko3@cornell.edu, pvj7@cornell.edu
Website(s): https://helbling.research.engineering.cornell.edu/
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Abstract:

Per- and polyfluoroalkyl substances (PFASs) are contaminants of concern to environmental and human health [1]. PFASs are present in photolithography materials [2] and might undergo transformation reactions during photolithography. We acquired five photolithography materials and characterized the occurrence of organic fluorine and PFASs in the materials. We performed photolithography experiments, collected the wastewater samples for subsequent analyses, and used a mass balance approach to assess the extent of transformations. The goal of the project was to evaluate the evolution of fluorinated materials during photolithography to gain an improved understanding of whether photolithography is a major source PFASs in fabrication (fab) wastewater.

Chemical	Measured TF	Measured AOF	% of Solid Components as TF	% TF captured by AOF
Photoresist A	1.65±0.14	0.37±0.04	1.65±0.14	22.3±1.93
Photoresist B	0.36±0.03	0.18±0.00	0.55±0.04	51.8±3.67
Photoresist C	1.31±0.04	0.68±0.08	0.65±0.02	52.0±7.25
TARC A	18.1±0.35	2.38±0.27	60.2±1.12	13.2±1.70
TARC B	4.62±0.08	0.62±0.06	15.4±0.27	13.4±1.19

Table 1: Average and standard deviation of total fluorine (TF) and adsorbable organic fluorine (AOF) concentrations (g L-1) conducted by means of combustion ion chromatography (CIC) in the five photolithography materials prior to photolithography.

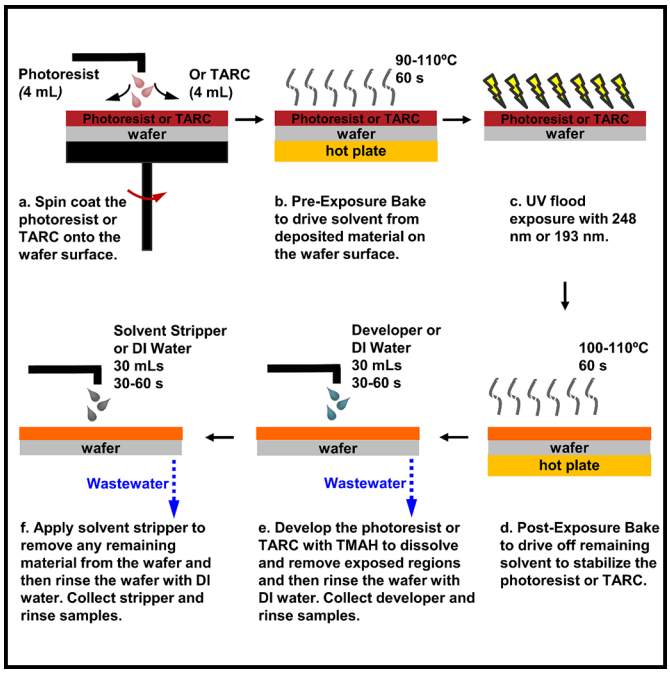
Summary of Research:

A variety of PFASs and fluoropolymers are used in photolithography materials and a recent study demonstrated that fab wastewater contains 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 other PFASs in fab wastewater remain unknown.

Constituents of photolithography materials are also subject to transformation reactions induced by the conditions of photolithography, which expose the materials to UV radiation and highly basic conditions [5]. We hypothesize that a major source of PFASs in fab wastewater are PFASs used or generated during photolithography. We acquired five photolithography materials and designed experiments to: (1) characterize the organic fluorine and PFAS in the materials; and (2) assess the formation or destruction of PFASs during photolithography.

We acquired three photoresists (Photoresists A, B, and C) and two top antireflective coatings (TARCs A and B). We measured the total fluorine (TF) of the materials, which ranged between 0.36 - 18.1 g L-1 (Table 1). We also measured the adsorbable organic fluorine (AOF) of the materials, which ranged from 0.18 - 2.38 g L-1 (Table 1), confirming that the materials have organofluorine-containing constituents.

We performed a target analysis for 39 PFASs in the materials. In Photoresist A and Photoresist C, we identified PFBS at 581±50 mg L-1 and 470±104 mg L-1, respectively, and the fluorine from PFBS accounts for 20% of the TF in both materials. PFBS was the only target PFAS that can explain a significant portion of the TF in these two materials. In an effort to identify other PFASs that could contribute to the TF, we performed suspect and nontarget analyses. We identified 20 suspect PFASs in TARC A and found that these PFASs explained 17.0±13.8% of the TF in TARC A. No other suspect or nontarget PFASs were found in the other materials. After applying target, suspect, and nontarget screenings, 80% of the TF in Photoresist A and C, 92% of the TF in TARC A, and approximately 99% of the TF in Photoresist B and TARC B remains uncharacterized. We suspect that the remaining TF can be attributed to fluorine present in polymeric form.



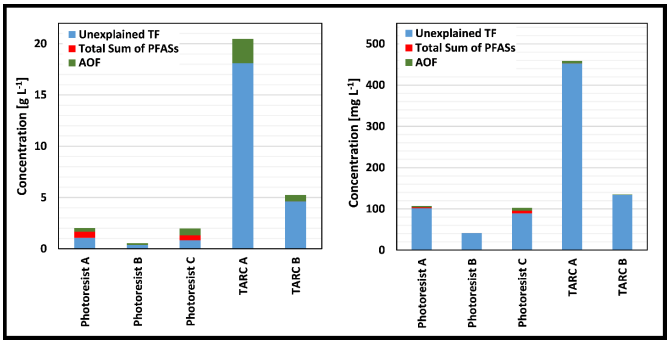


Figure 1, top: Photolithography process diagram detailing specific experimental parameters of each step. The exact parameters applied at different steps (i.e., spin coating and baking) were adjusted for each material according to the specifications provided by the manufacturers.

Figure 2, below: (a) Concentrations in g L-1 of unexplained total fluorine (TF), measured adsorbable organic fluorine (AOF), and the amount of TF that is attributed to the total sum of target PFASs measured in the materials. (b) Concentrations in mg L-1 of unexplained total fluorine (TF), measured adsorbable organic fluorine (AOF), and the amount of TF that is attributed to the total sum of target PFASs measured in the 248 nm wastewater samples. We note the different units used on the y-axis in (a) and (b) that reflect dilution of each material during the photolithography experiments.

We performed photolithography experiments and collected the wastewater from each material after development and stripping (Figure 1). We performed TF and AOF analyses and target, suspect, and nontarget screenings on the wastewater samples to identify the PFASs present post-photolithography. These measurements allowed us to track the mass of the materials throughout photolithography.

The wastewater samples generated contained no measurable TF. We surmise that a combination of TF loss during spin coating and subsequent dilution in the wastewater samples resulted in concentrations that were below the method limit of quantification. Next, we measured the AOF of the wastewater samples which ranged from 126.7 - 6976.7 ug L-1.

We performed a target screening on the wastewater samples and determined the extent of formation or destruction of the target PFASs by implementing a mass balance approach. These mass balance analyses indicate that target PFASs were being created or destroyed to some extent during photolithography, but that the changes in masses fail to explain more than 1% of the TF of each material. Over 75% of the TF of each material remains unexplained after these mass balance analyses indicating the stability of the organofluorine-containing constituents (e.g., fluoropolymers) of these materials during photolithography [2]. We also applied the suspect and nontarget screening workflows on the samples.

We discovered 13 suspect or nontarget PFASs unique to the wastewater of each material and exposure but expect that none of these compounds would contribute greater than 1% to the measured TF.

Conclusions and Future Steps:

We conclude that: (1) the selected photoresists and TARCs have organofluorine-containing compounds at similar levels of other industrial and commercial products and formulations; (2) target PFASs present in these materials can only explain up to 20% of the TF in a material; and (3) the simulated photolithography experiments did not induce significant transformations. This study highlights the complexity of tracking the source of PFASs in a fab, as the simulated photolithography experiments did not yield the expected results.

Future steps will focus on evaluating the fate and transformation of fluoropolymers during photolithography and wastewater treatment.

References:

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