Identifying Sources of Per- and Polyfluoroalkyl Substances in Photolithography Wastewater

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Primary CNF Tools Used: Suss Gamma Resist Cluster, ASML DUV Stepper, Oxford 100 ICP Dielectric, PlasmaTherm Versaline Deep Silicon Etch

Abstract:

Per- and polyfluoroalkyl substances (PFASs) are contaminants of concern to environmental and human health.1 Organofluorine-containing chemicals are widely used in semiconductor manufacturing processes such as lithographic patterning, etching, and stripping, among others; 2however, their release from specific fabrication processes is not well understood. While previous work focused on PFASs in wastewater and photolithography materials, putative sources such as plasma etching processes and scrubber blowdown have been underexplored. This study investigated PFAS formation during plasma etching of silicon wafers using various fluorinated etch gases. We performed nine plasma etch experiments and collected aqueous blowdown samples from a plasma-wet scrubber connected to two plasma etch tools. The samples were analyzed for total fluorine (TF), adsorbable organic fluorine (AOF), and 24 target PFASs. The goal of this project was to demonstrate if plasma etching processes are a significant source of PFASs and other organofluorine compounds in semiconductor fabrication facilities (fabs) emissions.

Summary of Research:

A variety of PFASs and other organofluorine-containing compounds are used during semiconductor manufacturing, 2and emissions of PFASs from fabs are of emerging concern. While most previous studies have focused on PFASs in fab wastewater samples or specific materials used during photolithography,[3,4]other potential PFAS sources, such as plasma etching processes and air scrubber blowdown, remain underexplored.

Fluorine inputs to plasma etch processes include both organofluorine-containing materials coated on the wafers (e.g., photoresists) and fluorinated gases. Hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs), commonly used for silicon wafer etching, introduce fluorine into the system. The exhaust gas from these processes is treated with wet scrubbers, where PFASs can partition into aqueous scrubber blowdown. We hypothesize that fluorine-containing gases used in plasma etch processes generate fluorine radicals that react with organic chemicals deposited on the wafer surface to form PFASs, which are then released in the exhaust, likely a key source of PFASs measured in fab effluent.

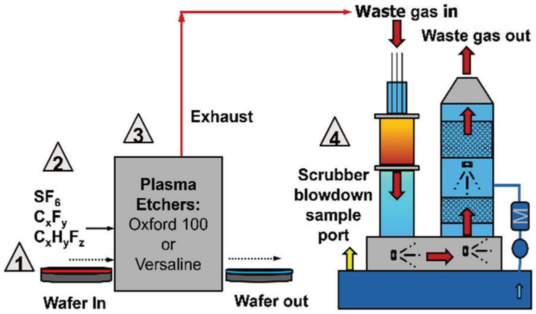

Figure 1: Schematic of the plasma etching and scrubbing process. The resulting exhaust from a plasma etch is routed to a scrubber system. Scrubber blowdown is collected for PFAS analysis.

We designed experiments to (1) demonstrate the formation of PFASs during plasma etching and transport to aqueous scrubber blowdown; and (2) identify the specific process conditions influencing PFAS formation. Four key process variables were investigated: (1) photoresist type, (2) choice of fluorinated etch gas, (3) plasma etching tool, and (4) use of plasma-enabled vs. non-plasma scrubber (Figure 1). We coated 4-inch silicon wafers with 500 nm of UV^{TM} 210 Positive DUV photoresist using the Gamma Photoresist Cluster. The ASML DUV Wafer Stepper was used for edge-bead removal. Etching experiments used six fluorinated gases including CH_2F_2, CHF_3, C_4F_8, C_4F_6, SF_6, and $C_3H_2F_4$ (a low global warming potential alternative gas that demonstrated to meet semiconductor manufacturing performance objectives). [5]The etching experiments were conducted on both bare silicon and photoresist-coated wafers in each etching tool: the PlasmaTherm Versaline Deep Silicon Etch, which uses the Bosch process, and the Oxford 100 ICP Dielectric tool, with each listed gas. Finally, duplicate blowdown samples were collected immediately after the completion of each etching experiment from the GST Durian "plasma-wet" scrubber with the plasma feature deactivated, to isolate PFAS contributions of the etching process alone. The plasma scrubber feature was activated only during the first Versaline experiment. Additionally, duplicate baseline samples were collected from the scrubber water tank before any etching to account for background PFAS concentrations.

We analyzed the scrubber blowdown and baseline samples for TF, AOF, and 24 target PFASs. The baseline-corrected TF concentrations ranged from below the limit of quantification (<LOQ) to 506 mg/L, while the AOF concentrations from 0.3 to 91 µg F/L. Summed concentrations of target PFASs ranged from 0.02 to 3.4 µg/L for the baseline samples and from 0.2 to 12.8 µg/L in the post-etching samples (Figure 2). Perfluorocarboxylic acids (PFCAs), a PFAS class of regulatory concern, dominated the target PFAS profiles in all etching-related scrubber samples, comprising over 94% of the total target PFASs. Target PFASs accounted for 8-32% of the total AOF in the samples, suggesting the presence of additional unidentified organofluorine compounds (Table 1). These findings highlight the role of plasma etching processes as a source of organofluorine compound in fab emissions.

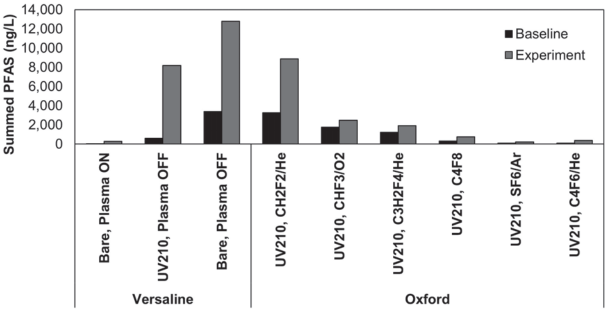

Figure 2: Summed PFAS concentrations for each etching experiment. "Baseline" refers to the sample before etching and "experiment" to the samples collected after etching experiments.

Sample Name	Etcher	PR, Plasma, Gas	AOF (µgF/L)	ΣPFAS (µgF/L)	ΣF in target PFAS (µg F-/L)	% Unexplained	% Explained
3a	Versaline	Bare, Plasma ON	<LOQ	0.27	0.18		
7a		UV210, Plasma OFF	61.97	7.57	5.17	92%	8%
9a		Bare, Plasma OFF	91.07	90.93	9.44	90%	10%
11a	Oxford	UV210, CH2F2/He	13.74	5.62	3.86	72%	28%
13a		UV210, CHF3/O2	2.19	0.70	0.48	78%	22%
16a		UV210, C3H2F4/He	1.79	0.70	0.47	74%	26%
18a		UV210, C4F8	1.32	0.44	0.29	78%	22%
20a		UV210, SF6/Ar	0.27	0.13	0.09	68%	32%
22a		UV210, C4F6/He	1.96	0.29	0.20	90%	10%

Table 1: Summary results for AOF and target PFASs in scrubber blowdown samples from the CNF.

Conclusions and Future Steps:

We conclude that (1) PFASs are formed during plasma etching processes and are captured in the scrubber blowdown from exhaust gases; and (2) target PFASs quantified in these samples can only explain up to 32% of the total AOF. Future steps will focus on: (1) conducting nontarget PFAS analysis in an effort to identify other PFASs that explain the remaining portion of the total AOF; (2) determining a more stable baseline between etching experiments; (3) conducting more etching experiments while modifying process variables such as testing other photoresist formulations and utilizing the new Oxford Cobra etcher.

References:

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