

Identifying Sources of Per- and Polyfluoroalkyl Substances in Photolithography Wastewater

CNF Project Number: 2938-21

Principal Investigator(s): Damian Helbling

User(s): Vie Villafuerte

Affiliation(s): Civil and Environmental Engineering, Cornell University

Primary Source(s) of Research Funding: Semiconductor Research Corporation

Contact: deh262@cornell.edu, cko3@cornell.edu, vav27@cornell.edu

Research Group Website: <https://helbling.research.engineering.cornell.edu/>

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 health¹. Organofluorine-containing chemicals are widely used in semiconductor manufacturing processes such as lithographic patterning, etching, and stripping, among others²; however, their release from specific fabrication processes are 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 thirty-five 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), fluoride (F⁻), and 29 target PFASs. The goal of this project was to demonstrate if plasma etching processes are a 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,² and 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 etch processes, 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 fluorinated 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, potentially a key source of PFASs measured in fab wastewater effluent.

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. Three key process variables were investigated: (1) wafer coating (bare silicon wafer vs. photoresist-coated silicon wafer), (2) choice of fluorinated etching gas, and (3) plasma etching tool (Figure 1). We coated 4-inch silicon wafers with 500 nm of UVTM 210 Positive DUV photoresist using the Gamma Photoresist Cluster. The ASML DUV Wafer Stepper was used for edge-bead removal.

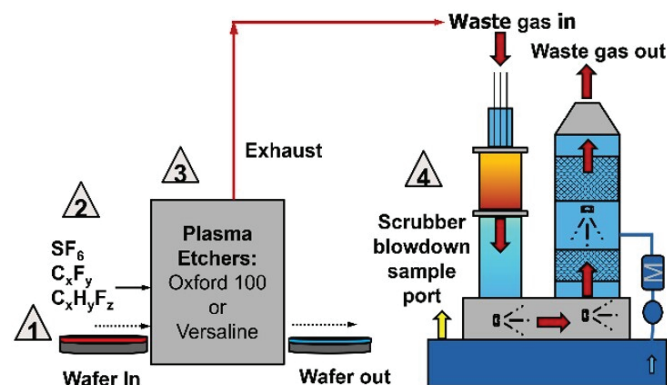


Figure 1: Schematic of the plasma etching and scrubbing process. The resulting exhaust from a plasma etch is routed to a scrubber system. Scrubber blowdown is collected for PFAS analysis.

Etching experiments were conducted for each of the six fluorinated gases studied: CH_2F_2 , CHF_3 , C_4F_8 , C_4F_6 , SF_6 , and $\text{C}_3\text{H}_2\text{F}_4$ (a low global warming potential alternative gas that demonstrated to meet semiconductor manufacturing performance objectives⁵). Each fluorinated gas experiment was conducted on both bare silicon and photoresist-coated wafers using each etching tool: the PlasmaTherm Versaline Deep Silicon Etch, which uses the Bosch process, and the Oxford 100 ICP Dielectric tool. Finally, blowdown samples were collected two hours after the completion of each etching experiment from the GST Durian “plasma-wet” scrubber with its plasma feature deactivated to isolate PFAS contributions of the etching process alone. Additionally, “pre-etch” 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, F-, and target PFASs. The pre-etch TF concentrations for the etching experiments conducted in the Oxford tool (n=28) ranged from 0.17 to 3.16 mg/L, and in the Versaline tool (n=7) from 0.13 to 1.17 mg/L. The post-etch TF concentrations ranged from 0.34 to 9.99 mg/L for the Oxford tool and from 0.17 to 18.2 mg/L for the Versaline tool. Figure 2 shows the distribution of TF concentrations in pre-etch and post-etch scrubber water samples. For both etchers, post-etch samples exhibited higher median TF concentrations and greater variability than pre-etch samples. Fluoride concentrations accounted for 25-95% of TF, with an average of 71%. Summed concentrations of target PFASs ranged from <LOQ to 136 $\mu\text{g/L}$ for the pre-etch samples and from 0.01 to 928 $\mu\text{g/L}$ in the post-etching samples. Perfluorocarboxylic acids (PFCAs), a PFAS class of regulatory concern, dominated the target PFAS profiles in all etching-related scrubber samples, comprising over 50% of the total target PFASs, with trifluoroacetic acid (TFA) being the dominant compound in all cases. Target PFASs accounted for 0.1-77% of the total organic fluorine (TOF) in the samples suggesting the presence of additional unidentified organofluorine compounds. These findings highlight the role of plasma etching processes as a source of organofluorine compound in fab emissions.

Conclusions and Future Steps:

We conclude that (1) plasma etching processes generate fluorinated compounds that are captured in scrubber blowdown water, as demonstrated by elevated TF, F- and PFAS concentrations in post-etch samples; and (2) observed variability in TF, F-, and PFAS concentrations suggests that process conditions influence organofluorine emissions. Future steps will focus on: (1) increasing the number of replicates for each experimental condition to improve statistical power and better characterize experimental variability; (2) performing statistical analyses to identify patterns in the data and determine which process variables best explain the variability; and (3) conducting additional etching experiments while including more low global warming potential etching gases and different photoresist formulations to further evaluate their influence on organofluorine emissions.

References:

- [1] Wang, Z.; DeWitt, J. C.; Higgins, C. P.; Cousins, I. T. A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)? *Environ Sci Technol* 2017, 51 (5), 2508–2518. <https://doi.org/10.1021/acs.est.6b04806>.
- [2] Ober, C. K.; Käfer, F.; Deng, J. Review of Essential Use of Fluorochemicals in Lithographic Patterning and Semiconductor Processing. *Journal of Micro/Nanopatterning, Materials, and Metrology* 2022, 21 (01). <https://doi.org/10.1117/1.JMM.21.1.010901>.
- [3] Jacob, P.; Barzen-Hanson, K. A.; Helbling, D. E. Target and Nontarget Analysis of Per- and Polyfluoroalkyl Substances in Wastewater from Electronics Fabrication Facilities. *Environmental Science & Technology* 2021, 55 (4), 2346–2356. <https://doi.org/10.1021/acs.est.0c06690>.
- [4] Jacob, P.; Helbling, D. E. Exploring the Evolution of Organofluorine-Containing Compounds during Simulated Photolithography Experiments. *Environmental Science & Technology* 2023, 57 (34), 12819–12828. <https://doi.org/10.1021/acs.est.3c03410>.
- [5] Windsor, A. J.; Clark, J. C.; McMurdy, G.; Joseph, E. A.; Syvret, R. G.; Olson, R. J.; Cha, J. J. Viability of HFO-1234ze(E) (Trans -1,3,3,3-Tetrafluoropropene) as a Low Global Warming Potential Silicon Dioxide Etch Gas. *Journal of Vacuum Science & Technology B* 2025, 43 (2). <https://doi.org/10.1116/6.0004194>.

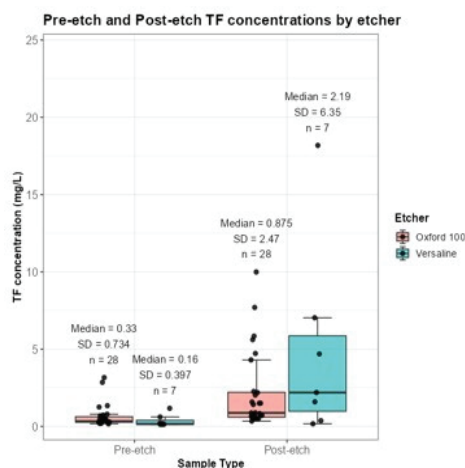


Figure 2: Boxplots showing TF concentrations in pre-etch and post-etch scrubber blowdown samples collected from the Oxford and Versaline etching systems.