PFAS Release Mapping from Semiconductor Manufacturing Photolithography Processes

Semiconductor PFAS Consortium Photolithography Working Group

September 21, 2023

Acknowledgments: The PFAS Consortium would like to acknowledge the contributions of the Semiconductor PFAS Consortium Photolithography technical working group.

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The Semiconductor PFAS Consortium is an international group of semiconductor industry stakeholders formed to collect the technical data needed to formulate an industry approach to perfluoroalkyl and polyfluoroalkyl substances (PFAS). Consortium membership comprises semiconductor manufacturers and members of the supply chain, including chemical, material and equipment suppliers.

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Date	**Revision Number**	**Revision**
9/21/2023	Rev. 0	Initial Publication

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Abstract
The present report identifies PFAS environmental release pathways from photolithographic processes used in semiconductor manufacturing facilities, providing a template for the development of a release quantification model.

Background
Per- and poly-fluoroalkyl substances (PFAS) are manmade chemicals used in many everyday applications with specific beneficial properties such as chemical stability. Recently, there was suggestion that members of this class of compounds exhibit high environmental persistence (vP), which is combined in some members with bioaccumulation (B) and toxicity (T). It is highly probable that PFAS chemicals will be subject to significant regulatory restrictions in the future. At the same time, PFAS are crucial components of many formulations used in semiconductor manufacturing, such as photolithography, to the extent that manufacture of semiconductor devices is currently not possible without PFAS. "Review of essential use of fluorochemicals in lithographic patterning and semiconductor processing"[1] reports on the use of PFAS-containing chemicals in photo-acid generator (PAG) photoresists used in DUV photography, antireflecting coatings (ARC) and other photolithographic formulations. The paper concludes PFAS alternatives should be investigated, but currently there are no alternatives that match all requirements needed in the critical photolithography steps used in advanced device manufacturing.

The Semiconductor PFAS Consortium (Consortium) has chosen the broadest definition found in recent proposed regulations and includes all chemistries and materials that contain molecules with CF_2 and/or-CF_3 groups. This definition closely aligns with the OECD definition.[2] Not all PFAS within the Consortium's definition are considered bioaccumulative or toxic.

Fluorinated organic molecules possess numerous attributes that provide unique functionality across a wide spectrum of applications. In many situations, it is not just one particular attribute (such as acid strength) that makes a fluorinated organic chemical effective for an application, but the combination of several attributes that enable fluorinated organics to satisfy multiple, overlapping performance requirements.[2]

Given the importance of fluorinated organic chemicals in semiconductor manufacturing, the Consortium has developed seven white papers[3], three case studies, a paper detailing the "Impact of a Potential PFAS Restriction on the Semiconductor Sector"[4] and a socioeconomic analysis[5]. These papers identify PFAS uses in semiconductor manufacturing and assess where their use meets the concept of "essential."[6] In their papers, the authors conclude that for most PFAS use cases, non-PFAS alternatives providing the same performance characteristics are currently unavailable.

Figure 1 is a broad overview of the scope of the Consortium's analysis, showing both front- and back-end semiconductor processing, as well as facility support functions and device assembly, test and packaging operations. The scope of the operations considered by the Consortium starts with a bare silicon wafer entering a manufacturing facility and ends at the packaging of semiconductor devices. It includes the semiconductor and manufacturing related equipment and facility infrastructure required to manufacture semiconductor devices. This report addresses only photolithography formulations and their releases from the photolithography process.

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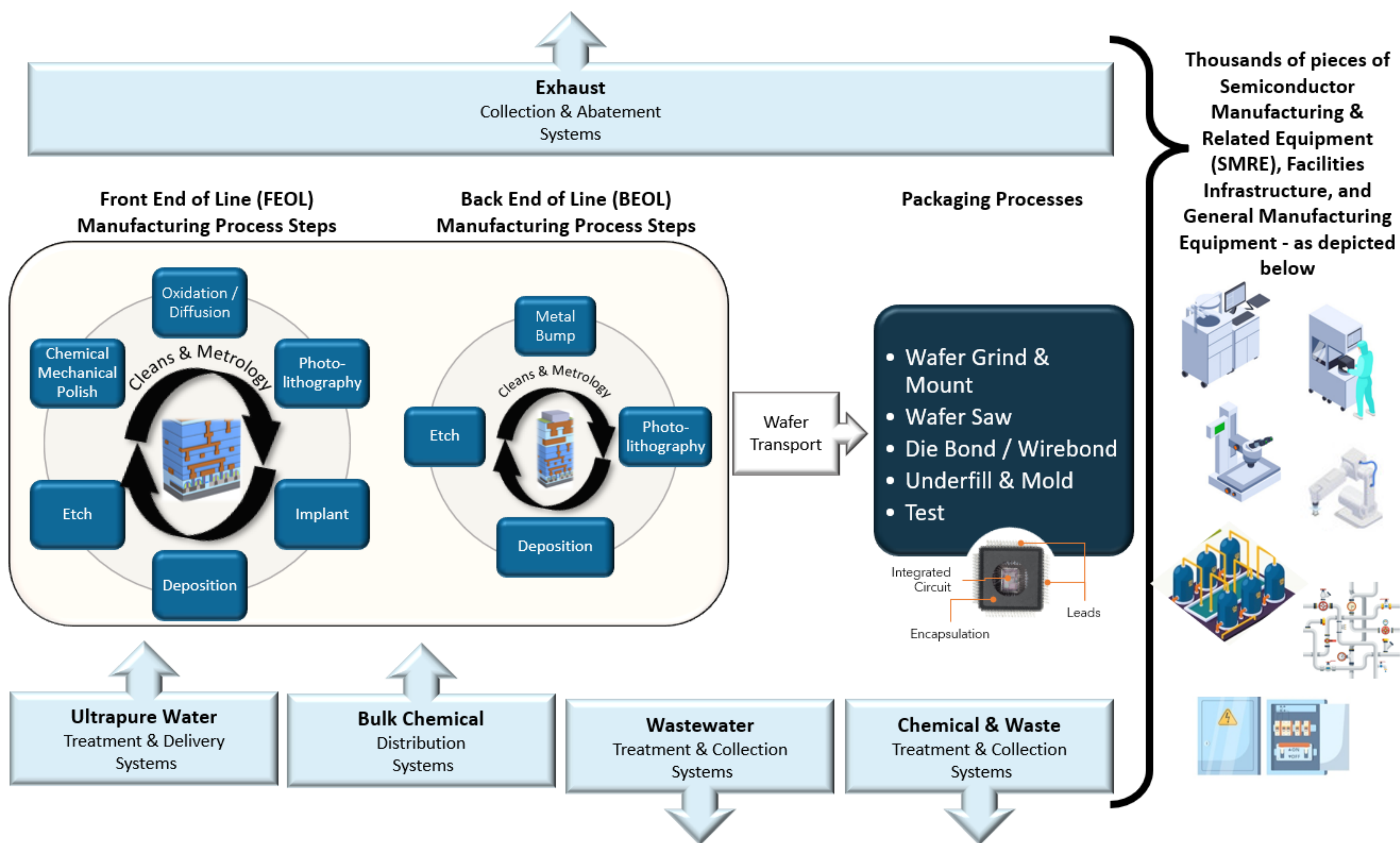

Figure 1: General overview of semiconductor manufacturing process steps, operations and systems evaluated by the Semiconductor PFAS Consortium.

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PFAS have been an enabling technology in the development of ever smaller and more advanced semiconductors over the last 30 years through cutting edge lithographic developments. PFAS materials have been designed, developed, and optimized as dedicated substances to satisfy many functions and performance needs in lithographic imaging products. Thus, replacement with a new non-PFAS material would likely require multiple solutions depending on the application, which has a significant impact on the estimated timelines.

Objective

The objective of this paper is to identify the principal, potential PFAS environmental release pathways from semiconductor manufacturing facility photolithography operations and provide a generalized template for the development of specific PFAS release quantification models for semiconductor manufacturing.

Lifecycle of Lithography Formulations

The lifecycle of a lithography formulation is summarized schematically in Figure 2 for the example of one key raw material, photoacid generators (PAGs). Working from the right side of the diagram, semiconductor manufacturers purchase photolithography chemicals from photolithography chemical suppliers. Photolithography chemical suppliers formulate lithography chemical mixtures using an array of chemicals that they may either synthesize themselves, or purchase from a raw chemical supplier. The focus of the following discussion is the use of photolithography formulations containing PFAS by semiconductor manufacturers.

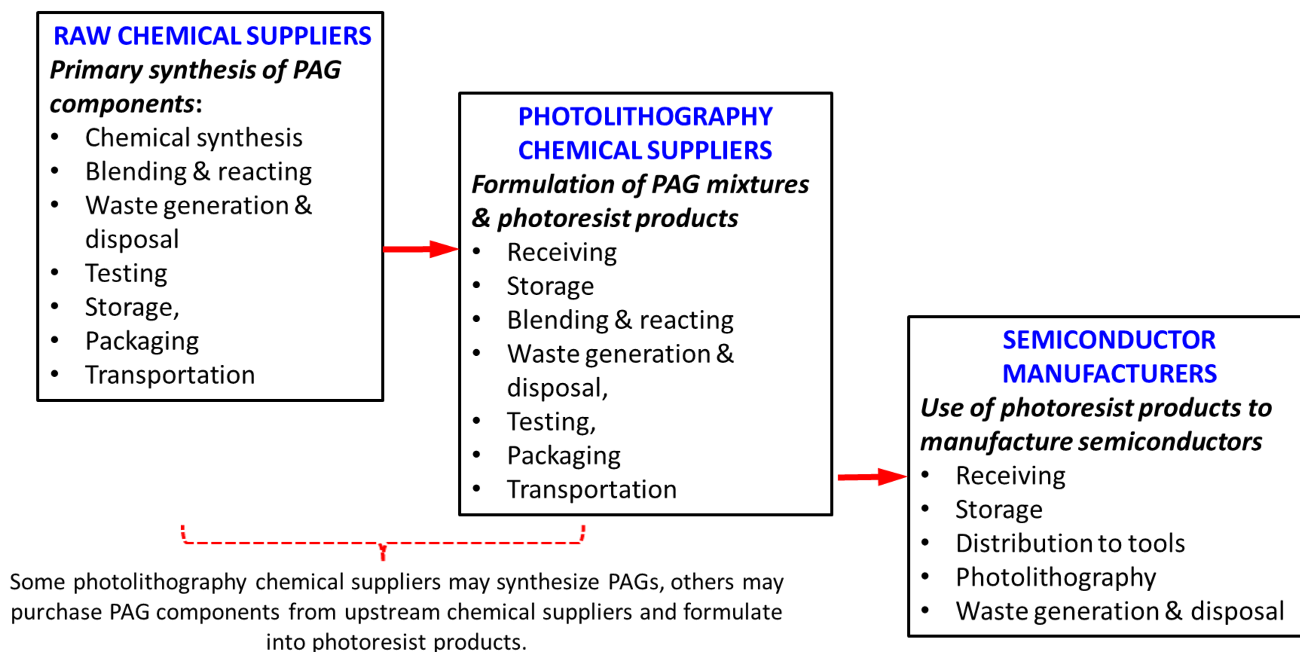

Figure 2. Example supply chain for photoacid generator photolithography chemical products.

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PFAS use applications in Photolithography

There are seven key use applications in which PFAS chemicals are used in semiconductor photolithography (see also Table 1 for a summary):[4]

- **Photoacid generators** (PAGs) are key components of the Chemically Amplified Resists (CARs), certain chemically amplified polybenzoxazoles (PBO) and polyimides (PI), and Bottom Anti-Reflective Coatings (BARCs) that are used in advanced lithography. They generate strong acids on exposure to actinic radiation, *e.g.*, UV light. The predominant PAG chemicals are organic salts consisting of sulfonium or iodonium-cations and PFAS super-acid anions, although non-ionic PAGs that generate PFAS super-acids are also used in some niche applications. The high acidity of the super-acids arises from the strong electronegativity of the fluorine atoms, which makes them capable of causing the solubility change of the photoresist. All successfully demonstrated PAGs for high performance resists are fluorinated, some down to a single CF_2 unit, and presently no universally applicable viable fluorine-free alternatives exist for a vast array of lithographic materials. The reasons for the use of PFAS PAGs and the prospects for replacements have been discussed in detail in an SIA whitepaper.[7] Current photoacid generators have been in development for 25 years, and alternatives are expected to take from 15 to more than 20 years to reach production. For an alternative to be successful it would have to show acidity comparable to perfluoro sulfonic acids, show similar lack of side reactions, lack volatility, and show minimum diffusivity for high resolution patterns. These chemicals are spin coated onto the wafer.

- o **Photoresist polymers**, especially in EUV applications, control pattern profile. PFAS polymers increase EUV absorbance, improve dissolution properties and increase resolution.

- o **Top antireflective coatings (TARCs)** require a very low refractive index, low surface energy and excellent barrier properties, all of which are provided by fluorinated polymers. Currently, no viable alternative materials exist for the 365 nm and 248 nm TARC applications. For 193 nm TARCs, which are only a small fraction of the market, dyed TARCs with lower PFAS levels have been described; however, these have the disadvantage of leading to a productivity loss of 25-30% due to exposure energy being lost to absorption in the TARC.[8] Development of dyed TARCs for 248 nm and 365 nm is more challenging because at these wavelengths, chromophores are less absorbing. TARCs are water-based materials applied in a spin coater.

- o **EUV anti-collapse rinses** are used to prevent pattern collapse of fine lines due to capillary forces. Anti-collapse rinses are also used sometimes in optical lithography. However, for EUV lithography the capillary forces leading to pattern collapse are much larger and it is essentially impossible to use aqueous developed CARs without them. The first generation of EUV rinses uses PFAS surfactants, but efforts are underway to develop PFAS-free substitutes. These materials are water-based and are applied in the last phase of the development step.

- o **Immersion top coatings** require very low surface energy (resulting in very high, water contact angles), excellent barrier properties, water insolubility but solubility in aqueous developers, and a lack of intermixing with the photoresist. Typical immersion top coat chemistries have been described in the literature.[2,9] Currently, no viable PFAS-free alternatives exist and there are not even any concepts for PFAS replacement for this application. Fluorine-free systems have resulted in patterning failure in immersion processes.

- o **PFAS Surfactants** have unique properties, such as very low surface tension and a combination of hydrophobic and oleophobic behavior, that have been utilized in various types of photolithographic materials. Applications include photoresists (248nm, 193nm, immersion, thick film, etc.), PBO/PIs,

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BARCs, TARCs, color filter photoresists for imaging, and rinse solutions. The surfactants are used to improve film quality by suppressing Bénard cells, altering surface interaction, wetting characteristics, and component mixing, all of which help to minimize defects in the lithographic process and thus increase lithographic yield. Prospects and timelines for replacements have been discussed in a Consortium white paper.[9] Siloxane-based surfactants have been demonstrated as non-PFAS alternatives for many applications, and replacement efforts at materials suppliers are under way. However, for some advanced applications, use of these alternatives has led to compromised performance, and more development is still required.

- **Barrier Layer Polymers (polybenzoxazole (PBO), polyimide (PI))** are critical for advanced patterning. They typically contain CF_3 groups in the polymer backbone that provide solubility in environmentally friendly casting solvents and can even enable aqueous development. PBO/PI polymers contribute electrical, thermal, and mechanical protection for the semiconductor device and isolate the device components from the impact of moisture. This application differs from all of the above in that part of the PFAS material used remains in the final device.

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Table 1: Examples of key PFAS use applications in semiconductor photolithography modified from "The Impact of a Potential PFAS Restriction on the Semiconductor Sector"[4]

PFAS use application	Function	Example types of compounds used	PFAS criticality
Photoacid Generators (PAGs)	Precursor for the photoacid catalyst needed for CARs, PBO/PI, BARCs, and color filter resists.	Perfluoroalkylsulfonates C4 or lower and C4 or lower substituted superacid anions such as C1. For some advanced resists, these are bound to polymers.	PFAS component of PAGs generates strong acids that do not show side reactions that interfere with the chemical amplification process.
Photoresists – polymers	Control pattern profile in EUV.	C1 PFAS polymer.	Increases absorbance, improves the dissolution properties, increases resolution.
EUV anti-collapse rinses	Prevent pattern collapse	Fluorinated surfactants	Lower surface tension and rinse liquid higher contact angle to reduce capillary forces.
TARCs	Control of thin film interference effects in resists.	Fluorinated water and developer soluble polymers.	High fluorine content is needed to achieve the low refractive index needed to effectively suppress film interference effects.
Immersion barriers (immersion topcoats)	Protection of the resist from immersion liquid and of the exposure process equipment from contamination. Prevent water film pulling and resist component leaching in immersion topcoats.	Spin-on barriers: Water insoluble and developer soluble polymers with fluorinated side chains. Embedded barriers (in situ top coats): oligomeric or low molecular weight polymeric highly fluorinated compounds. Fluoroalcohol methacrylate polymers with high water contact angles ($>90^{o}$).	Barriers that are soluble in casting solvents, insoluble in water but soluble in developer, and that show no intermixing with photoresists. Hydrophobicity and control of contact angle, inert under 193nm radiation, and transparency.
Surfactants	Improved coating uniformity in photoresists, PBO/PI, BARCs, and color filter resists	Longer chain PFAS (C6-C8) and telomer alcohols pending form polymer backbones. Now mostly replaced by C4 pendant chains.	Low surface tension, control of contact angle.

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PFAS use application	Function	Example types of compounds used	PFAS criticality
Barrier Layer Polymers (PBO/PI)	Provide electrical, thermal, and mechanical protection for semiconductor devices. Also protects the device components from the impact of moisture.	Water-insoluble C1 PFAS polymers.	C1 PFAS groups attached to the polymer backbone provide solubility in environmentally friendly casting solvents and enable aqueous development.

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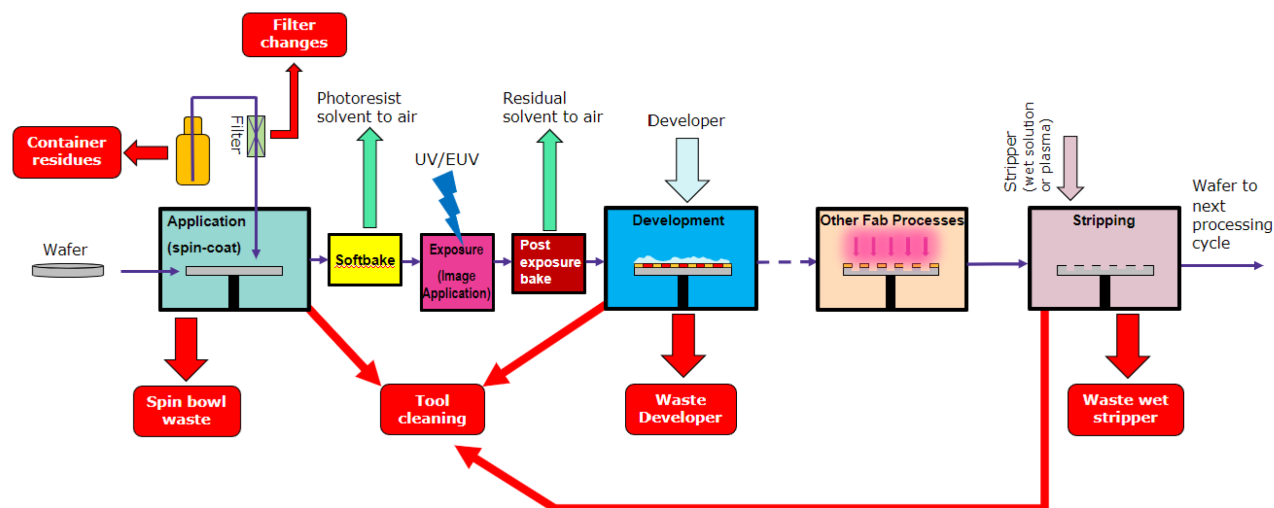
Photolithography Unit Operations

Semiconductor photolithography occurs in a series of unit operations summarized in Figure 3.



Red boxes indicate waste streams that may contain PFAS.
Note: Optional BARC/photoresist/optional TARC or immersion topcoat spin-coating operations occur in sequence, with the wafer returning to the spin-coating step between operations.

Figure 3: Process flow diagram for photolithography unit operations.

Process equipment exhaust and abatement: Every photolithography process step has an associated piece of process equipment with exhaust flow and likely an air emissions control component, as indicated in Figure 3. Most PFAS used in photolithography are ionic or polymeric, and therefore not expected to have significant vapor pressures, or emissions components at ambient temperatures. No published information is presently available regarding the potential behavior of photolithography PFAS chemicals in exhaust or abatement systems. Future studies may be necessary in order to determine whether exhaust systems should be included in the release mapping.

The unit operations are:

- **Resist (including PBO/PI) application (spin-coat):** Photoresist (consisting of polymer, PAG and organic solvent) is spin coated on the wafer surface in an enclosed photolithographic track tool. Spin-coat is used to ensure the resist film is thin and uniform and applied at a specific thickness. Often, the wafer surface is pre-wet with a solvent to help spread the photoresist atop the wafer surface and reduce the amount of photoresist that is needed to achieve a uniform film.
- **BARC:** Before resist is applied, a BARC (which may contain PAG) may also be applied to the wafer surface to mitigate reflection from the wafer surface and maintain the accuracy of the pattern. This layer may use edge bead removal and is typically pre-baked prior to resist application.
- **Pre-exposure bake (soft bake):** A pre-exposure bake step is used to heat the applied photoresist and drive off excess solvent in a manner that helps produce a uniform coating of the resist on the wafer.

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- **Edge Bead Removal:** In some applications, a thin region of the photoresist is removed from the periphery of the wafer as an aid to wafer handling. This process would occur in the spin-bowl after the spin-coat operation. The photoresist removed during this step typically is released to a solvent waste system for off-site destruction. Edge bead removal, if used, reduces the quantity of photoresist going to the development and resist strip steps, and thus reduce the quantity of photoresist that would potentially go to an aqueous waste discharge.
- **Spin-coat with TARC:** In certain situations, the photoresist is coated with a thin layer of material to reduce the reflection of light during the imaging step. The TARC material does not contain PAG but is highly fluorinated due to the need for a low refractive index.
- **Immersion top coatings**, used in 193 immersion lithography, are very low surface energy (resulting in a hydrophobic surface that affords a high contact angle with water), have excellent barrier properties, water insolubility but solubility in aqueous developers, and a lack of intermixing with the photoresist. Their purpose is to prevent leaching of photoresist components such as PAGs or photoacids into the immersion medium (water) and to prevent water droplet defects resulting from meniscus pulling.
- **Exposure (image application):** The exposure step involves beaming a UV light source through a photomask to create a patterned image of the desired device structure within the photoresist. The light initiates photolysis of the PAG, which in turn releases an acid from the PAG anion and creates an acidified image in the resist film. The fraction of the wafer surface that is exposed to light varies depending on the step, but on average half of the resist on the wafer surface is exposed. Industry experts have estimated that on the order of one-half of the onium compounds are converted to daughter products during the exposure step. Less data is available regarding the behavior of the PAG fluorinated acid anion during exposure, but it is expected to retain its structure during 248 and 193 nm exposure. Experiments would be necessary to confirm the actual conversion rate and the variables that may be important.
- **Post exposure bake (PEB):** A PEB step, sometimes referred to as “hard bake”, is used to heat the resist and promote the imaging reactions that are initiated by the exposure step. PEB finalizes chemical changes in the photoresist and hardens the resist image so it withstands the subsequent implant, deposition and etch steps required to transfer the pattern to the wafer surface.
- **Development:** In development, unwanted photoresist is removed from the wafer. This step typically uses the strong base, 2.38% tetramethylammonium hydroxide (TMAH), to dissolve the “deprotected” polymer and leave a three-dimensional relief pattern. The pattern serves as the locus of subsequent etch or deposition steps that are used in fabricating the integrated circuit. Most photoresists are "positive tone" in which the exposed region is made base soluble and removed from the wafer surface using aqueous TMAH type developer. In some photoresists, known as "negative tone photoresists" the exposed regions are made less soluble, and the typically solvent-based developer removes the un-exposed regions from the wafer surface. Aqueous developer typically drains to wastewater. Solvent developer is collected in a separate solvent drain and collection system.
- **Postbake** (not shown on the diagram)**:** The postbake finalizes chemical changes in the PBO/PI and some photoresists and is designed to provide required thermal stability and mechanical properties and hardens the patterned image so it withstands the subsequent implant, deposition and etch steps required to transfer the pattern to the wafer surface.
- **Photoresist Strip:** Component material is either deposited or removed from the patterned surface and then the remaining resist is stripped off using either a wet strip (aqueous or organic solvent) or plasma strip/ash.

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- **Solvent strip**: In a solvent strip, an organic solvent is used to dissolve and remove the residual photoresist. The waste from a solvent strip operation goes to a solvent drain, which is containerized (often in a bulk waste tank) and shipped offsite for destruction (typically via incineration or fuel blending). A small percentage of solvent stripper may remain and subsequently be rinsed off the wafer surface by an aqueous rinse step and released to the facility's industrial wastewater drain.
- **Wet etch strip:** In a wet etch strip, an aqueous mixture consisting of acid and oxidizer or similar aqueous mixture is used to remove the residual photoresist. The waste from a wet etch strip would typically go to an industrial wastewater drain.
- **Plasma strip/ash:** In a plasma strip or ash, the photoresist is converted to gaseous combustion products. Because wet strip tends to leave residue on the wafer, plasma strip has become the standard strip process.
- **Barrier Layer Polymers** (polybenzoxazole (PBO), polyimide (PI)) are critical for advanced patterning. Barrier layers are spin coated onto wafers but differ from all of the above in that part of the PFAS material used remains in the final device.

Conceptual Release Map

The release map presented in this report follows the general methodology of the 2010 Organisation for Economic Co-operation and Development (OECD) Emissions Scenario Document (ESD) No. 9[10] and the Semiconductor Onium PAG Consortium release models[11] with some modifications. This release map is more comprehensive because it covers not only photoresists but all types of PFAS-containing formulations used in semiconductor photolithography, including aqueous materials and dielectrics that remain in the final device. Any of the photolithographic unit operations can be described by its associated set of parameters.

Figure 4 provides a conceptual flow and release map for PFAS-containing formulations used in semiconductor photolithographic processing with parameters defined in Table 2.

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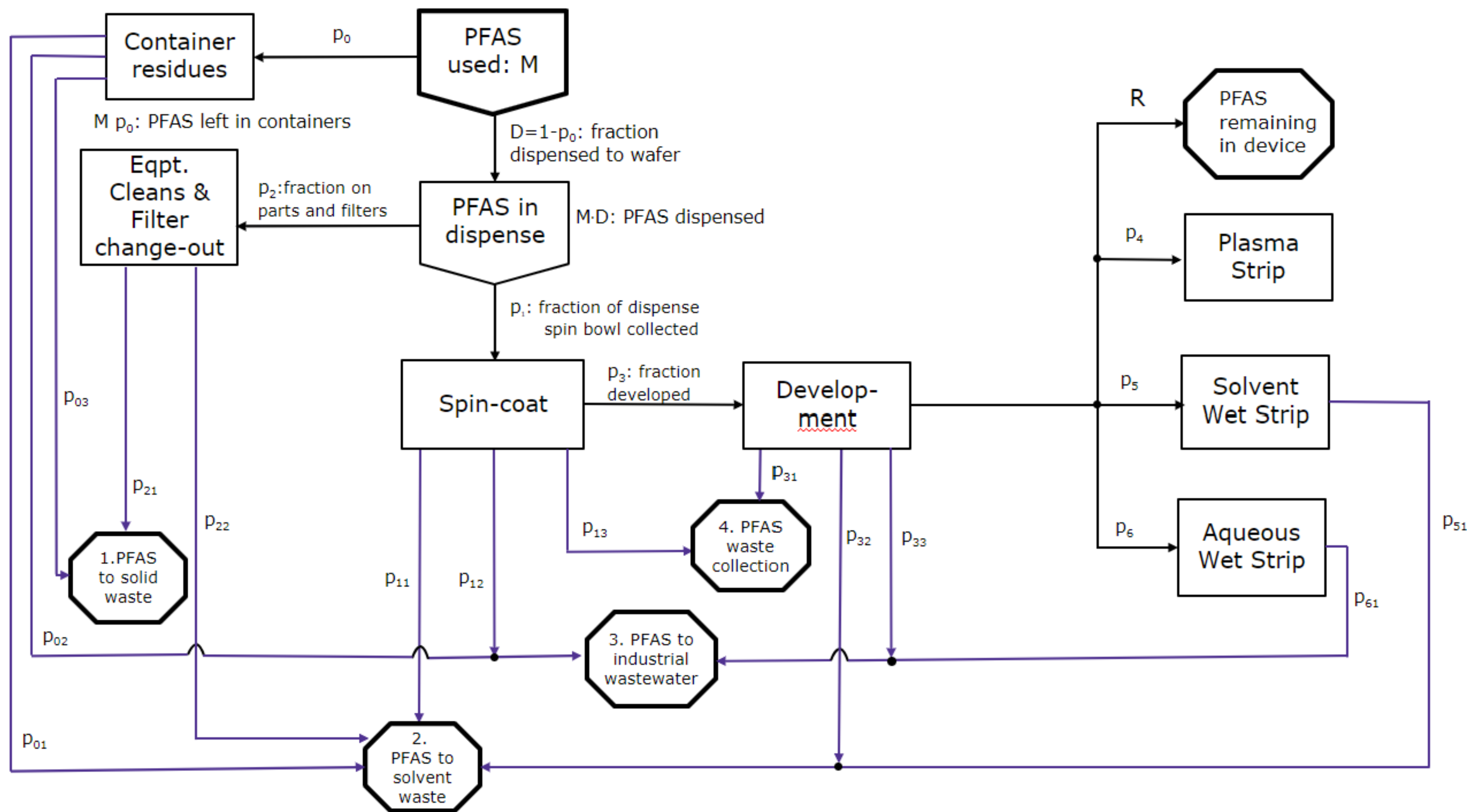

Figure 4: Potential PFAS release map for photolithography unit operations.

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Table 2: Definition of parameters used in Figure 4.

Parameter	Description
M	Total mass of PFAS used for the application
p_0	Fraction of PFAS material in container that is dispensed to wafer
p_{01}	Fraction of residual material in container going to solvent waste
p_{02}	Fraction of residual material in container going to industrial wastewater
p_{03}	Fraction of residual material in container going to solid waste
p_1	Fraction of dispensed PFAS material that is collected as spin bowl waste
p_{11}	Fraction of spin bowl waste that goes to solvent waste
p_{12}	Fraction of spin bowl waste that goes to industrial wastewater
p_{13}	Fraction of spin bowl waste that goes to PFAS waste collection
p_2	Fraction of dispensed PFAS material that remains in process equipment and is removed during equipment cleans
p_{21}	Fraction of material equipment cleans that is solid waste
p_{22}	Fraction of equipment cleans material that is solvent waste
p_3	Fraction of PFAS in coating that is dissolved in developer
p_{31}	Fraction of PFAS in spent aqueous developer and rinses that goes to wastewater
p_{32}	Fraction of PFAS in spent solvent developer and rinses that goes to solvent waste
p_{33}	Fraction of aqueous developer waste that goes to PFAS waste collection
p_4	Fraction of PFAS in coating that goes to plasma strip processes
p_5	Fraction of PFAS in coating that goes to solvent wet strip processes
p_{51}	Fraction of solvent wet strip waste that goes to solvent waste
p_6	Fraction of PFAS in coating that goes to aqueous wet strip processes
p_{61}	Fraction of aqueous wet strip waste that goes to industrial wastewater

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Table 3: Waste streams from the processes described in Figure 4.

Waste Stream #	Description	Source(s)
1	Solid waste	Container liners, filters, wipes and other contaminated solids from equipment cleans
2	Solvent waste	Container residue, organic solvents from equipment cleans, organic spin bowl waste, organic development, organic wet strip
3	Industrial wastewater	Container residues, aqueous spin bowl waste, aqueous developer waste, aqueous wet strip
4	PFAS waste collection	Aqueous spin bowl waste, aqueous developer waste, aqueous wet strip

Photolithography formulations are packaged in a variety of containers including glass bottles and plastic containers with a collapsible polytetrafluoroethylene (PTFE) liner. A residual amount of the formulation remains in the container (**Container residues (p_0)**). Heels from organic solvent-containing containers (p_{01}) are drained to solvent waste, frequently after rinsing with a solvent, resulting in no release to wastewater.[10] Heels of aqueous products (p_{02}) are discharged to industrial wastewater, frequently after rinsing with water. Some facilities collect and containerize heels and rinsate and send that material offsite for incineration. Some formulations are packaged in special plastic containers with a collapsible inner PTFE liner, liners (p_{03}) are removed and sent to hazardous waste incineration as solid waste, whereas empty glass and plastic bottles are recycled, incinerated or landfilled.[10]

Equipment cleaning and routine maintenance including supply line filter change-out (**Eqpt. Cleans and Filter Change-out (p_2)**) result in the generation of contaminated solids that are released to incineration or landfill (p_{21}). If organic solvents are used during cleaning, waste is collected as solvent waste (p_{22}). No photolithographic solvent-based material is released to wastewater or aqueous waste.
BARCs, resist, immersion top coats and TARCs are applied via **spin coat**. During the coating application, the majority of the formulation is spun off the wafer. BARCs and resist are organic formulations and excess spin bowl residue goes to solvent waste ($p_{11} = 1$, $p_{12} = 0$). Coated wafers undergo patterning and development where a fraction of the PFAS-containing coating is removed. The OECD and SIA studies[9,10] assume an average fraction of resist removed during development of 50% ($p_3 = 0.5$). Most photoresists are developed using aqueous developers, with the removed PFAS material going to wastewater ($p_{31} = 0$, $p_{32} = 0$, $p_{33} = 1$) while a few new facilities are installing PFAS collection and waste treatment ($p_{31} = 1$, $p_{32} = 0$, $p_{33} = 0$). A small fraction corresponding to negative tone development of 193 nm photoresists goes to solvent waste ($p_{31} = 0$, $p_{32} = 1$, $p_{33} = 0$).

TARC is applied in the form of an aqueous solution that is spun onto the resist coating. To achieve a high coating quality, TARC spin-on generally uses larger dispense volumes than photoresists or other coatings, while resulting in a thinner film. TARC spin bowl residue disposal is handled in one of three ways (p_{11}, p_{12} and p_{13}):

- Some users have installed a separate drain ($p_{11} = 0$, $p_{12} = 0$, $p_{13} = 1$) to a PFAS waste collection system (4. PFAS waste collection) for treatment or offsite disposal.
- Some users are able to send their TARC waste down the solvent waste drain ($p_{11} = 1$, $p_{12} = 0$, $p_{13} = 0$) which feeds to a solvent waste tank (2. PFAS to solvent waste), contents of which are sent offsite for

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destruction in a hazardous waste incinerator or burned as a fuel in a cement kiln. This method cannot be used at all facilities because water and photoresist are known to react and create a gel that clogs the drain line and waste collection vessel.

- Some users discharge TARC to the industrial wastewater drain ($p_{11} = 0$, $p_{12} = 1$, $p_{13} = 0$) which goes to industrial wastewater treatment (3. PFAS to industrial wastewater) before merging into the combined facility effluent.

All TARC on the wafer is removed in the development step ($p_3 = 1$). In most facilities, development waste drains to wastewater ($p_{31} = 0$, $p_{32} = 0$, $p_{33} = 1$) while a few facilities are installing PFAS collection and waste treatment ($p_{31} = 1$, $p_{32} = 0$, $p_{33} = 0$). All parameters for subsequent steps are zero.
Immersion top coats are solvent-based materials applied via spin-coat, with the bulk of the material ending up in the spin bowl and being disposed of as solvent waste. All material on the wafer is removed in the development step and discharged to wastewater ($p_3 = 1$, $p_{31} =0$, $p_{32} = 0$, $p_{33} = 1$). No material remains after development, so the parameters for subsequent processes are all zero.
Aqueous-based rinse formulation is dispensed during the development cycle ($p_3 = 1$). There is no way to separate out the waste from developer and rinsewater. None of the material remains on the wafer. For most facilities, therefore, a single release pathway exists for dispensed material, all of which is discharged to wastewater ($p_{31} = 0$, $p_{32} = 0$, $p_{33} = 1$).

Resist remaining on the wafer after development is removed in a strip process. The three different types of strip processes used are solvent strip, aqueous strip, and plasma strip. Material removed in solvent strip is routed to solvent waste ($p_{51}=1$), while material removed in aqueous strip is directed to wastewater ($p_{61}=1$). Plasma stripping generates gaseous waste which is passed through exhaust scrubbers. The efficacy of PFAS removal destruction in the overall process is described by parameter p_7, with assumed complete destruction of all PFAS during plasma dry stripping corresponding to $p_7 = 0$. No resist remains on the wafer after stripping ($R=0$).

Solvent-developed polyimides/polybenzoxazoles (PI/PBO) are spun on from and developed with solvents. There is limited data on the fraction remaining on the wafer but is currently assumed to be greater than 75%. All spin bowl residues go to solvent waste ($p_{11} =1$, $p_{12}=0$). However, the space filling of structures patterned in PI/PBO is generally much higher, and a lower percentage of material removed during development than for photoresists. All spin bowl waste goes to solvent waste ($p_{31} = 0$, $p_{32} = 1$, $p_{33} = 0$). There is a significant fraction of material on the wafer after development that is not stripped but remains in the final chip ($p_4 = p_5 = p_6 = p_7 = 0$, $R > 0$).

Aqueous-developed polyimides/polybenzoxazoles (PI/PBO) are spun on from solvent and developed with aqueous developers. All parameters are the same as for solvent-developed PI/PBO except that now $p_{31} = 0$, $p_{32} = 0$, $p_{33} = 1$ since all developed material will likely go to wastewater.
The industry uses a number of methods for disposal of solid, solvent, and aqueous wastes, including high temperature incineration, fuel blending, and solvent recycling – in compliance with local regulations. With respect to wastewater, some release to the environment is currently predicted.
There is a need for more efficient analysis techniques. The current standard method, LC-MS/MS, is slow and has less than complete finding rates for PFAS targets and is incapable of detecting polymeric PFAS.

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Conclusions and Next Steps

This release map provides the known routes for PFAS releases from semiconductor photolithography processes. For each step identified in the release map, establishing release factors would enable an assessment of the quantities of PFAS-containing materials that move through the semiconductor manufacturing process and their environmental fate.

Quantification of PFAS releases will require additional data collection, likely through surveys and perhaps studies. A need exists to investigate a number of release parameters. While previous studies[9,10] and estimates by lithography experts have provided somewhat consistent estimates, these parameters should be updated by surveying users on current and proposed practices with respect to uses, releases and disposal methods. The Semiconductor PFAS Consortium plans to carry out surveys of semiconductor manufacturers to obtain reliable values for the associated release parameters in preparation for developing a photolithography PFAS mass balance model.

The semiconductor industry continues to actively identify, test and implement improved process controls that minimize releases to the environment, including PFAS-containing materials. The industry is also researching prospective PFAS substitutes, which is an expensive and time-consuming endeavor. The research and validation of alternatives is a lengthy process that entails identifying potential substitutes, evaluating their potential human and environmental risks, conducting laboratory and pilot tests, designing and retooling equipment, conducting verification tests, and finally implementing a substitution.

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