

PFOS and PFOA Conversion to Short-Chain PFAS-Containing Materials Used in Semiconductor Manufacturing

Semiconductor PFAS Consortium Photolithography Working Group

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About the Semiconductor PFAS Consortium

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. The consortium includes technical working groups, each focused on the:

- Identification of PFAS uses, why they are used, and the viability of alternatives.
- Application of the pollution prevention hierarchy to (where possible) reduce PFAS consumption or eliminate use, identify alternatives, and minimize and control emissions.
- Development of socioeconomic impact analysis data.
- Identification of research needs.

This data will better inform public policy and legislation regarding the semiconductor industry's use of PFAS and will focus R&D efforts. The Semiconductor PFAS Consortium is organized under the auspices of the Semiconductor Industry Association (SIA). For more information, see www.semiconductors.org.

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Executive Summary

The semiconductor industry has used perfluoroalkyl and polyfluoroalkyl substances (PFAS) in chemical formulations since the 1970s (Buck, Franklin and Berger 2011). In the late 1990s and early 2000s, the scientific community and several regulatory agencies noted that perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) presented significant concerns for persistence, bioaccumulation and toxicity (Yamashita, et al. 2008). After 3M announced and implemented a phaseout of PFOS, photoresist suppliers were forced to either stockpile PFOS or find alternatives for a multitude of photoresist products (United States Environmental Protection Agency 2000).

With an increased understanding of the impact on human health and the environment – and recognizing the longer-term supply gap, regardless of U.S., European Union (EU) and United Nations regulatory exemptions for photolithography in the semiconductor industry – the World Semiconductor Council (WSC) agreed to voluntarily phase out PFOS in May 2006. This resulted in a complete replacement of PFOS by 2016, with primarily short-chain (four or less carbon atoms) PFAS-containing materials used as substitutes. Lithography suppliers transitioned either to shorter-chain PFAS-based surfactants or to non-PFAS surfactants (for example, silicone based), which required significant redevelopment time for chemical suppliers and semiconductor device makers.

Similarly, with photoacid generators (PAGs), photoresist suppliers began looking more urgently for alternatives to PFOS and PFOA in chemically amplified deep ultraviolet (DUV) resists. Non-PFAS-based PAGs do not have the superacidity required for critical lithographic performance. Ultimately, each supplier and customer had to work together to qualify short-chain PFAS PAG replacements of both PFOS and PFOA, although in different timelines (2006 to 2016 for PFOS, and 2018 to 2025 for PFOA).

In photolithography applications, top anti-reflective coatings (TARCs) included PFOS because its long fluorocarbon chain provided a low refractive index, which is key to the operation of these materials. After trying many fluorinated and nonfluorinated variants, success came with a polymer consisting of a perfluorinated main chain connected through a linker unit to a short-chain PFAS-containing material bearing a water-solubilizing substituent. After its introduction in 2004, this type of polymer saw widespread adoption and became the dominant material in the market.

The qualification process for semiconductors is very complex. A particular chemistry is designed to interact with other chemistries at each step of the semiconductor manufacturing process. Today’s modern processes can take up to 1,000 steps and use just as many (or more) chemical formulations to finish manufacturing a semiconductor wafer containing thousands of chips on it. Any PFOS or PFOA surfactant

or PAG component change requires in-depth, multivariable evaluations on both the chemical supplier (verification) and semiconductor device maker (validation) sides to prove that the change will not detrimentally impact the photoresist product. As a result, each product being replaced requires extensive research and development to confirm that critical functional requirements are acceptable. The time and cost of these qualifications to replace all PFOS and PFOA materials thus far has been an average of \$60 million USD per semiconductor device maker.

Based on environmental concerns around PFOS, the semiconductor industry collaboratively evaluated options to mitigate environmental issues, funding extensive university research studies on technologies for removing PFOS and PFAS from wastes and wastewater. Numerous subsequent works have documented the dependency of PFAS removal technologies on the particular wastewater composition and showed the extreme resilience of PFAS-containing materials to destructive methods. Given the issues in finding an effective wastewater treatment, the industry made the more cost-effective choice to substitute out longer-chain PFAS-containing materials, thus mitigating environmental and health risks as well as supply-chain risks.

The semiconductor industry and its chemical suppliers have a demonstrated track record of taking action to address the use of chemicals with environmental concerns. The conversion away from long-chain PFAS and PFOS from the semiconductor industry required over 20 years. The industry now relies on short-chain PFAS-containing materials. Despite significant research by chemical suppliers, almost all cases of fluorine-free alternatives are very unlikely to provide the essential properties present in PFAS systems (Ober, Kafer and Deng 2022).

A complicating factor for this technical effort is the lack of a commonly agreed-upon definition for the term PFAS within the multitude of regulatory development activities. Since the noted purpose of this case study is to document the use of all materials that could potentially meet a regulatory definition of PFAS-containing materials, along with the performance requirements necessary to determine the criticality and/or essentiality of the use, the Semiconductor PFAS Consortium defined the scope of materials described in this case study to include all chemistries and materials that contain any chemical with at least one perfluorinated methyl group (-CF₃), at least one perfluorinated methylene group (-CF₂-), or both. Further discussion of the background of the Semiconductor Industry and definition of PFAS can be found in the “[Background on Semiconductor Manufacturing and PFAS](#)” white paper.

1.0 Introduction

Patents show that as early as the late 1970s, companies were using long-chain surfactants (such as 3M’s FC-430) as a part of photoresist formulations (Bratt and Cohen 1980). PFOS-based surfactants were effective at improving the coating uniformity of photoresists. With the introduction of chemically amplified photoresists, the concept of using a PAG for this purpose favored both short- and long-chain PAGs (short chain being C1-C4 PFAS-containing materials, and long chain being C7+ PFAS-containing materials), particularly when the resist design required a strong acid (Fujifilm 1996). Most popular and effective compounds were based on PFOS, PFOA and PFOA-related chemicals (Ito and Wilson 1983).

Giesy et al. demonstrated that PFOS was widely distributed on a global scale and could be persistent and bioaccumulative in various food chains (Giesy and Kannan 2001). As a result, regulatory agencies around the world began proposing and enacting restrictions (see Figure 1) (United States Environmental Protection Agency 2022). The U.S. Environmental Protection Agency (EPA) issued four significant new use rules under the Toxic Substances Control Act between 2002 and 2013, requiring notification to the U.S. EPA before any manufacture, use and/or import of 271 chemically related PFAS-containing materials, which included 88 PFOS-related chemicals. The U.S. EPA provided an exemption for

photolithography, stating that the application used small quantities and that the industry managed the substances responsibly (Hand 2003).

Between 2004 and 2006, the EU and Japan proposed PFOS bans and implemented them – with lithography exemptions – in 2006 and 2010. In parallel, the Stockholm Convention on Persistent Organic Pollutants (POPs) treaty was signed in 2001 to reduce or eliminate the production, use and release of key POPs (United Nations Environmental Protection 2009).

In 2009, Annex B of the Stockholm Convention was amended to include PFOS, again with lithography exemptions (United Nations Environment Program 2009). Similarly, in May 2019, more than 180 countries agreed to ban the production and use of PFOA, its salts and PFOA-related compounds under the International Stockholm Convention on POPs (United Nations Environmental Protection 2019). Semiconductor photolithography exemptions for both PFOS and PFOA gave the industry time to implement replacements.

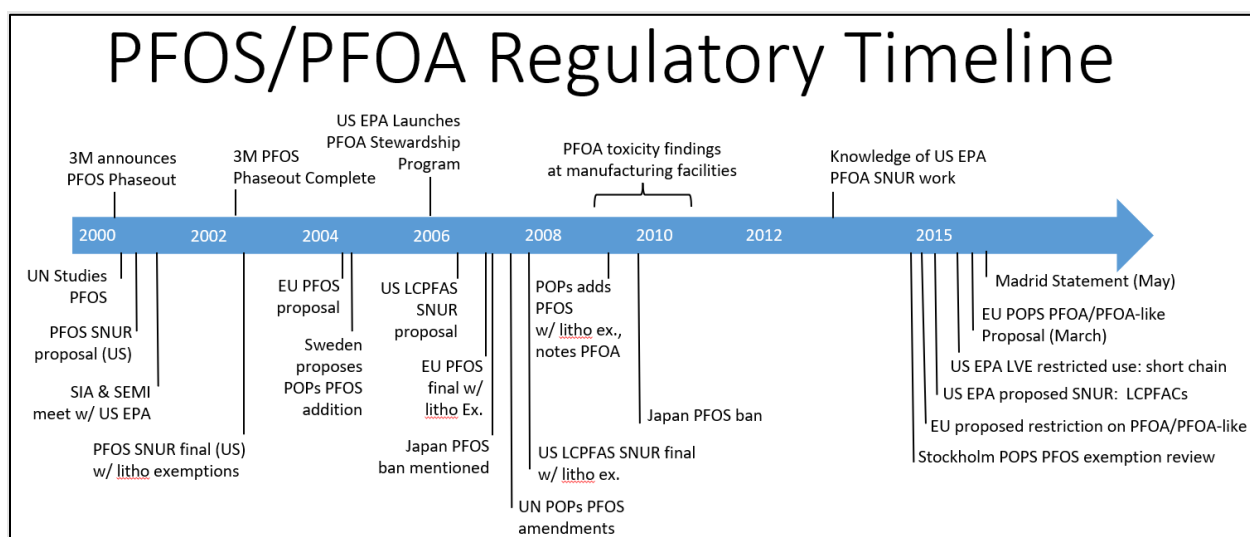


Figure 1: PFOS/PFOA regulatory timeline (circa 2000-2016) (Source: Semiconductor Industry Association).

With an increased understanding of the impact on human health and the environment, and regardless of the exemption, the WSC agreed to voluntarily phase out the use of PFOS-based chemicals in May 2006. (World Semiconductor Council 2006); (World Semiconductor Council 2011) The global semiconductor industry began working on identifying replacement materials and implementing them. As result of the close partnership between the industry and the entire supply chain, PFOS use decreased significantly between 2006 and 2016 (see Figure 2). The WSC announced the phaseout of critical PFOS-based chemicals in 2017 (World Semiconductor Council 2017). With the success of the PFOS reduction, and with a similar framework, the WSC committed to transition away from the use of PFOA and PFOA-related substances in 2018, with the intention to complete it by 2025 (World Semiconductor Council 2017).

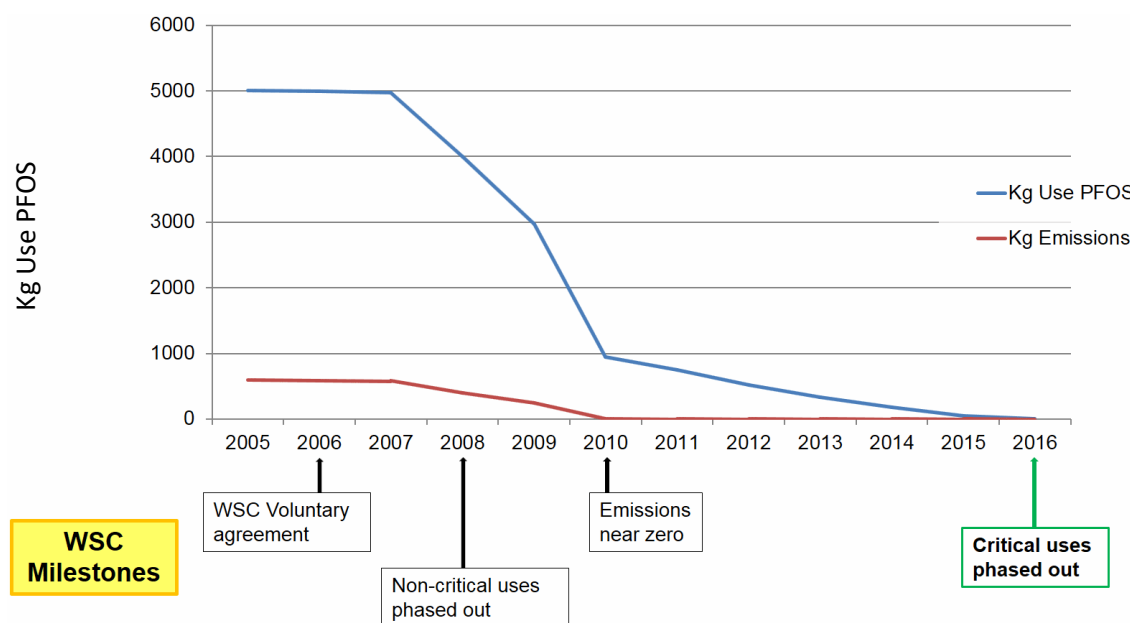


Figure 2: Global semiconductor PFOS elimination.

The success of this work was largely because there was a known replacement: short-chain PFAS-containing materials. There was already research suggesting that short-chain PFAS-containing materials were an “easy” drop-in replacement, since data showed that they could produce a strong acid (a key ingredient that would provide similar performance and functionality to long-chain PFAS-containing materials) (Kim, Ayothi and Ober 2005). In addition, the industry, as well as regulatory agencies, believed that short-chain PFAS-containing materials were safer than long-chain chemicals. According to Hand, unlike PFOS, a short-chain PFAS such as perfluorobutane sulfonic acid (PFBS) had been classified as an insignificant hazard by the U.S. National Institute of Occupational Safety and Health and required no label warning by the EU in 2003 (Hand 2003). There was not concern regarding PFBS in the early 2000s like there is now (United States Environmental Protection Agency 2021).

After identifying replacements, material qualification and integration occurred across several chemical suppliers and multiple semiconductor device makers. This case study focuses on the technical challenges that both parties encountered during the replacement. Chemical suppliers did a significant amount of work before introducing the replacement to semiconductor device makers, including proving that these replacements provided performance equal to the original product.

Subsequently, semiconductor device makers executed these replacements in high-volume manufacturing fabrication plants across multiple chronological technology processes. The efforts were wide scale, since replacements per node took six months to two years to execute. A failed replacement required the investigation of other samples through an iterative process. It was not an easy task, and results varied by technology node and customer.

2.0 Chemical Supplier Impacts

In the early 2000s, PFOS-based components used in photoresists were mainly surfactants, TARCs and PAGs. PAGs were almost exclusively a part of DUV photoresists. PFOS-based surfactants were widely used in g-line, i-line and DUV photoresists. TARCs were used in combination with photoresists. In all cases, the amount of PFOS-based components in photoresists was small: surfactants typically at <1 wt%, TARCs at ~2 wt% and PAGs typically at <2 wt%. Nonetheless, in response to regulatory actions by the

U.S. EPA and the 3M PFOS phaseout mentioned above, material suppliers began to transition away from PFOS-based formulary components.

2.1 Surfactant Replacement

Even with the U.S. EPA's PFOS exemption for photolithography applications, once 3M announced and implemented a phaseout of PFOS-based components (especially surfactants), photoresist suppliers were forced to find alternative surfactants for the multitude of photoresist products that used 3M PFOS surfactants or similar PFOS-based surfactants.

At the time, 3M offered replacement surfactants based on shorter-chain PFAS-containing materials that were deemed technically capable and acceptable from an environmental, health and safety perspective compared to PFOS-based versions. Thus, suppliers transitioned either to shorter-chain PFAS-based surfactants or non-PFAS surfactants (for example, silicone based). Either transition required significant research and development, commercial resources, and time. These efforts competed with and hindered new product invention and development until the identification, qualification and implementation of PFOS alternatives.

2.2 PFOS PAG Replacement

Similarly, with PAGs, once 3M announced and implemented a phaseout of PFOS-based materials, photoresist suppliers began looking more urgently for alternatives to PFOS-based PAGs (United States Environmental Protection Agency 2000), which were used almost exclusively in chemically amplified DUV resists. Even though suppliers could still supply photoresist formulations with PFOS-based PAGs under the U.S. EPA's PFOS exemption for photolithography applications, they began efforts to eliminate them in both current formulations and from consideration for future formulation development and commercialization. Because the superacidity characteristic of PFOS-based PAGs was critical to the performance of chemically amplified DUV formulations, suppliers transitioned to shorter-chain PFAS-based PAGs.

With very few exceptions, non-PFAS based PAGs have been unable to meet critical lithographic performance requirements. An example material, camphorsulfonate, worked for 248-nm photoresists but was completely ineffective in 193-nm photoresists relative to triflate (C1)- and nonaflate (C4)-based PAGs. As with surfactant replacements, each formulation transition required significant research and development, commercial resources, and time.

Component replacement in a photoresist is complex, including surfactant replacement, and the replacement of a PAG is even more difficult. Semiconductor device makers invest significant time and effort in plan-of-record (POR) photoresist formulations to integrate them into multiple optimized high-yield chip manufacturing processes. Back-integration of a replacement formulation requires that the replacement formulation performs exactly in every way as the POR photoresist formulation. Every small formulation change that occurs can result in an unwanted change in one or more of many lithographic performance parameters. Any of several performance changes (even minor) can lead to unacceptable yield reductions or require costly adjustments in the semiconductor device maker's processes. Thus, any component change requires in-depth multivariable evaluations on both the chemical supplier and semiconductor device maker sides to prove that the change will not detrimentally impact the form, fit or function of the photoresist product.

Thus, each product requiring PFOS-containing surfactant replacement required in-depth research and development to identify acceptable surfactant replacements and/or PAG replacements that met the critical functional requirements demanded of the surfactant (coating quality, coating uniformity) and/or the PAG (diffusion control, solubility, sensitivity) without detrimentally impacting the other essential lithographic

functions of the photoresist (resolution, image biasing, usable process window, defectivity). After determining a suitable replacement, chemical suppliers generated demonstration data for submission to the affected semiconductor device makers. Chemical suppliers then manufactured qualification samples for the alternative formulation and sent samples to multiple semiconductor device makers for evaluation and validation. Any issues that arose at the semiconductor device maker required either processing tweaks or formulary iterations to finalize their acceptance of the replacement sample. Furthermore, by the time they accepted and qualified the replacement formulation, the supply chain for the replacement component needed to be fixed and assured, with scale-up and high-volume manufacture of the new formulation validated and complete.

Each unique replacement product and each validation and qualification required repeating these tasks at each semiconductor device maker. For each chemical supplier, this typically meant tens of product replacements for tens of customers. This total process took years.

Furthermore, every evaluation of a new replacement formulation at the semiconductor device maker introduced the potential for chemical suppliers to lose business. When semiconductor device makers began new replacement product evaluations, many times they chose to include products from other chemical suppliers in those evaluations. This, many times, led to an elimination of the replacement product from the POR supplier, to be replaced by a competitor's product. Such a loss of business to a competitor would not have occurred if the POR formulation did not require modification. The industry does not have an estimate of the cost to original chemical suppliers given this shift in supply.

3.0 Semiconductor Device Maker Impacts

In line with the regulatory action of the U.S. EPA in the early 2000s, 3M announced a phaseout of their manufacturing of PFOS after PFOS was found in environmental samples globally (3M 2023). Some lithography material suppliers immediately realized the impact of the 3M phaseout and began informing semiconductor device makers of the impending issue. Semiconductor Industry Association member companies immediately raised the phaseout as a topic of discussion among all members, as it meant that companies might not have a future option to use PFOS, or that there was at least a chance of a supply gap.

Semiconductor device makers quickly began discussions with the U.S. EPA and 3M regarding intended actions and the ability to manage a phaseout of PFOS while qualifying alternative chemistries. During many meetings that occurred during the 2001 to 2004 time frame, all parties determined that short-chain PFAS-containing materials would be a viable alternative to PFOS.

Semiconductor device makers worked with materials suppliers to figure out all of the chemical products that contained PFOS and PFOA and determine strategies for those replacements. This was a difficult task because semiconductor device makers did not know exactly which chemical products contained PFOS and PFOA, as safety data sheets do not regularly disclose this information. In many cases, the concentration of the PFOS and PFOA in chemical formulations was extremely low (well below the Globally Harmonized System of Classification and Labelling of Chemicals disclosure threshold of 0.1% or 1% concentration, depending on hazard). In other instances, the use of the substances was classified as confidential business information (CBI) and shared only by generic names such as “surfactant” or “photoacid generator,” without a corresponding Chemical Abstracts Service registry number.

The Semiconductor Industry Association (the trade association representing the collection of device makers) and SEMI (the trade association sponsoring the collection of material suppliers) worked together to share PFOS information discreetly without compromising the supplier's CBI, while sustaining a picture of the industry and the PFOS regulatory impact. Ultimately, each material supplier and semiconductor device maker had to work together to qualify replacements. For PFOA- and PFOA-like

chemical formulations, semiconductor device makers and material suppliers have mostly worked directly on replacements without collective industry involvement.

Any one step in the qualification process for semiconductors always has dependencies on prior and subsequent steps as it relates to both chemistry and physics. This creates a multivariate manufacturing issue when you are attempting to replace a previously qualified chemical product with a new, different chemical product. You not only have to be concerned with the reaction chemistry of that specific step, but also with the material on the wafer from the previous steps, how the resulting reaction might impact the next steps' chemical reactions, and subsequently the integrity of the final product of that particular step in the many layers of adjacent films placed on a semiconductor wafer.

Even after determining a compatible alternative chemistry, it is necessary to extensively qualify it with chemical, physical and electrical metrology to ensure that the quality of the replacement meets expectations to produce a working semiconductor that will endure the stresses put on it for the duration of its expected life. To complicate matters further, qualifying a chemical product that can be used in more than one manufacturing technology typically means repeating this qualification in each of those manufacturing technologies, as each process has its own multivariate problem to resolve. Lastly, some semiconductor devices are also under quality change control expectations from their own customers, which then requires each of those customers to qualify the product made using the alternative chemistry before allowing the semiconductor device maker to fully convert their manufacturing line to the new alternative chemistry.

We estimate that the cost and time of qualifications to replace all PFOS, PFOA and PFOA-like materials in semiconductor manufacturing necessitated:

- Approximately 18 chemicals per semiconductor device maker.
 - These 18 chemicals were classified by the Consortium as difficult (requiring approximately 24 months), medium (15 month) and easy (nine month) qualifications.
 - The Consortium estimated there was one difficult, 11 medium, and six easy chemical substitutions needed per semiconductor device maker, estimated at \$1.6 million, \$750,000 and \$350,000 respectively – at a total average replacement cost of \$60.25 million per semiconductor company.
- Five manufacturing lines for each chemical and 40 products each per line, thus reflecting an average of >3,000 separate product qualifications, where qualifications take anywhere from nine to 24 months each.

After initial qualification of the alternative, it must be implemented in each manufacturing process. Thus, a single, qualified replacement may have to occur in several factories simultaneously, further constraining resources. Note that these were the historical costs of substituting from long- to short-chain PFAS-containing materials, which we believe to be comparatively simple. The potential cost of substituting out of short-chain PFAS will be much more expensive – if possible at all – because it will involve a switch from a fluorinated chemical to some yet-to-be-invented nonfluorinated alternative.

The photolithography process requires exposing the silicon wafer by shining incident light through a disc with a pattern etched into it, called a photomask (or mask for short). The wafer is then rinsed in a developing solution (akin to physical photographs), with the result being an image transferred to the surface of the wafer. This is the most critical step of semiconductor manufacturing. If the image is not perfect, no subsequent chemical or physical steps can correct image-transfer issues.

The mask must be etched perfectly such that the incident light leaves behind a perfect pattern. This process takes many mathematical iterations to calculate the perfect pitch of each hole cut into the mask, as well as determining the dimensions of the imaged feature left behind on the wafer. A typical mask can take months of calculation to develop the etching pattern, as well as a month to carve the pattern. A mask must be made for each image change on the surface of the wafer, which can be tens of masks per individual type of semiconductor product wafer.

Complicating the number of masks required is that each semiconductor product has its own variation in patterns/structures, resulting in its own set of masks. We estimate that the cost and time to make these masks to replace PFOS, PFOA and PFOA-related products is \$250,000 per mask, at approximately six to nine months per mask.

Overall management of a large substitution program within a company requires careful management of logistics. Photolithography materials are extremely sensitive substances that in many cases require refrigeration and can still lose quality and capability in a rather short period of time, within as little as a nine- to 12-month shelf life. So it was important to carefully manage the transition from legacy PFOS/PFOA-based chemical products to new non-PFOS/PFOA-based chemical products such that new products were not made too early before completing qualifications, and that legacy products were not made in too much abundance (with a limited build-ahead strategy) such that the legacy products expired before use and had to be disposed of as waste. Similarly, with a phaseout in place, it was important to complete new non-PFOS/PFOA-based chemistry qualifications quickly enough in order to avoid the depletion of legacy PFOS/PFOA-based chemistries.

4.0 Replacement vs. Wastewater Treatment

As we mentioned previously, 3M announced that it would voluntarily phase out and find substitutes for PFOS given its persistence in the environment, strong tendency to accumulate in human and animal tissues, and potential long-term risk to human health and the environment (United States Environmental Protection Agency 2000). In 2006, eight of the principal U.S. PFOA manufacturers joined in the U.S. EPA's 2010/2015 Stewardship Program to eliminate the production of long-chain perfluoroalkyl carboxylic acids, including PFOA (United States Environmental Protection Agency 2022).

Faced with a choice between continuing the use of PFOS and PFOA under semiconductor industry-specific exemptions as provided under the United Nations Environment Program or pursuing substitution with more benign alternatives, the latter was preferable (United Nations Environment Program 2009). If it was possible to find viable alternatives, their use would mitigate the issues with reliance on chemicals that the world's principal suppliers were eliminating from production, and also eliminated the need to introduce controls and protections against the environmental, health and safety concerns associated with PFOS and PFOA.

Early studies showed that PFOS and PFOA were widely distributed across the globe and both persistent and bioaccumulative across food chains (Giesy and Kannan 2001); (Kannan, Koistinen, et al. 2001). PFOS and PFOA were found to be pervasive in human blood and suggested a multitude of potential exposure routes, including indoor air and house dust associated with the use of consumer products and food packaging, as well as from drinking water (Kannan, Corsolini, et al. 2004); (DeSilva, et al. 2021). Other studies showed that the discharge of wastewater containing PFOS and PFOA into surface waters and the atmospheric transport of fluorotelomer alcohols were important conduits by which fluorinated organic chemicals entered the environment (M. J. Dinglasan, et al. 2004); (Ellis, et al. 2004), with the world's oceans acting as the ultimate sink (Sinclair and Kannan 2006); (Yamashita, et al. 2008).

Based on these concerns, the semiconductor industry collaboratively funded extensive university research studies of the technology for removing PFOS- and PFAS-containing materials from wastewater and waste (Carter and Farrell 2008); (Murray, et al. 2021); (Carter and Farrell 2010); (V. Ochoa-Herrera, et al. 2008); (Ochoa-Herrera and Sierra-Alvarez 2008); (Tang, et al. 2006); (Torres, et al. 2009). Although these works showed that it was possible to remove PFOS, PFOA and certain other long-chain PFAS-based chemistries from wastewater with granular activated carbon, ion exchange media, reverse osmosis and other separation techniques, the efficacy of removal depends on the particular structure and chain length as well as the composition of the particular wastewater. Once removed, concentrated PFAS-containing materials are highly resistant to destruction (Tang, et al. 2006); (Carter and Farrell 2008); (Ochoa-Herrera and Sierra-Alvarez 2008). For instance, research showed that it was possible to readily remove PFOS from semiconductor wastewater with reverse osmosis, but reverse-osmosis performance significantly degraded if a common alcohol like isopropyl alcohol was also present in the wastewater (Tang, et al. 2006). Numerous subsequent works documented the dependency of PFAS removal technologies on the particular wastewater composition and showed the extreme resilience of PFAS-containing materials to destructive methods (Bentel, et al. 2019); (Murray, et al. 2021). Moreover, the commercial availability of validated analytical methods that can evaluate removal and destruction efficacy impedes the development of wastewater treatment and waste treatment technology. At present, only a small percentage of PFAS compounds within typical semiconductor wastewater are detectable and quantifiable using conventional U.S. EPA analytical methods for PFAS-containing materials (Jacob, Barzen-Hanson and Helbling 2021). For instance, research showed that it was possible to readily remove PFOS from semiconductor wastewater with reverse osmosis, but reverse-osmosis performance significantly degraded if a common alcohol like isopropyl alcohol was also present in the wastewater (Tang, et al. 2006). Numerous subsequent works documented the dependency of PFAS removal technologies on the particular wastewater composition and showed the extreme resilience of PFAS-containing materials to destructive methods (Bentel, et al. 2019); (Murray, et al. 2021). Moreover, the commercial availability of validated analytical methods that can evaluate removal and destruction efficacy impedes the development of wastewater treatment and waste treatment technology. At present, only a small percentage of PFAS compounds within typical semiconductor wastewater are detectable and quantifiable using conventional U.S. EPA analytical methods for PFAS-containing materials (Jacob, Barzen-Hanson and Helbling 2021).

The exceptional stability and chemical inertness of PFOS and PFOA are attributed to the high strength of the C-F bond (485 KJ/mol), the shielding of C-C bonds by the fluorine atoms making up the fluorocarbon backbone, and the overall rigidity of perfluorinated chains (Torres, et al. 2009). Generally, fluorocarbon chains are resilient to both electrophilic and nucleophilic attack (Torres, et al. 2009); (V. Ochoa-Herrera, et al. 2008). Although substantive progress toward developing effective destruction technologies continues, it is important for wastewater treatment technology evaluations to incorporate a fluorine balance to effectively mineralize the PFAS-containing material, and not just break it into smaller and less well-characterized fluorinated degradation products (Bentel, et al. 2019); (Singh, et al. 2019).

Concurrently with industry efforts to develop and evaluate technology for the removal of PFOS and PFOA from wastewater and wastes, a growing body of information indicated the viability of substituting shorter-chain homologs and/or analogs in several semiconductor applications (Hake 2002). Shorter-chain perfluoroalkyl sulfonates, like those based on perfluorobutane sulfonic acid, appeared to be effective substitutes for many PFOS applications, and to have significantly lower bioaccumulative properties and toxicity (Hake 2002); (Conder, et al. 2008). Consequently, semiconductor devicemakers and chemical suppliers worked together to reformulate photolithograph and other semiconductor chemical formulations with shorter-chain PFAS alternatives. Substituting out the longer-chain PFAS-containing materials

mitigated the associated environmental and health and supply-chain risks associated with trying to use discontinued long-chain PFAS-containing materials.

5.0 Replacement of PFOS, PFOA and PFOA-like TARCs

In the semiconductor industry, one of the main uses of PFAS is in TARCs. In photolithography, TARCs help suppress swing curve effects – the periodic dependence of photoresist dose-to-print on photoresist film thickness that is observed over topography, and which is a major cause of line-width variation. TARCs are spun on from an aqueous solution on top of the photoresist and are popular because they add only minimal process complexity. They are particularly useful on implant layers where other processes using anti-reflective solutions (such as bottom anti-reflective coatings) may damage the substrate surface, or on contact hole layers, where they solve the missing contact defect problem. In such applications, long fluorocarbon chains previously provided the low refractive index that is key to the operation of these materials.

Material suppliers began looking for substitution options for PFOS-based chemistries in TARCs. Any such material needed a high level of fluorination to maintain a low refractive index, or the TARC would not operate correctly. It also needed to be water- and developer-soluble, show no intermixing with the photoresist, and ideally replicate the surfactant actions of PFOA and PFOS.

One of the early contenders, acrylates with pending PFAS telomer alcohols, was ruled out when it was found that these materials decomposed in the environment with the release of PFOA (M. J. Dinglasan, et al. 2004). Efforts soon centered on polymeric materials, since those were expected to have low bioavailability. One successful TARC polymer consisted of a perfluorinated main chain connected through a linker unit to a short-chain PFAS-containing material bearing a water-solubilizing substituent (Figure 3). After its introduction in 2004, this type of polymer saw widespread adoption and became the dominant material in the market. Although the new product had superior performance and otherwise came very close to being a drop-in for the old ones, it took over five years for the sales of PFOS- and PFOA-based TARCs to end completely.

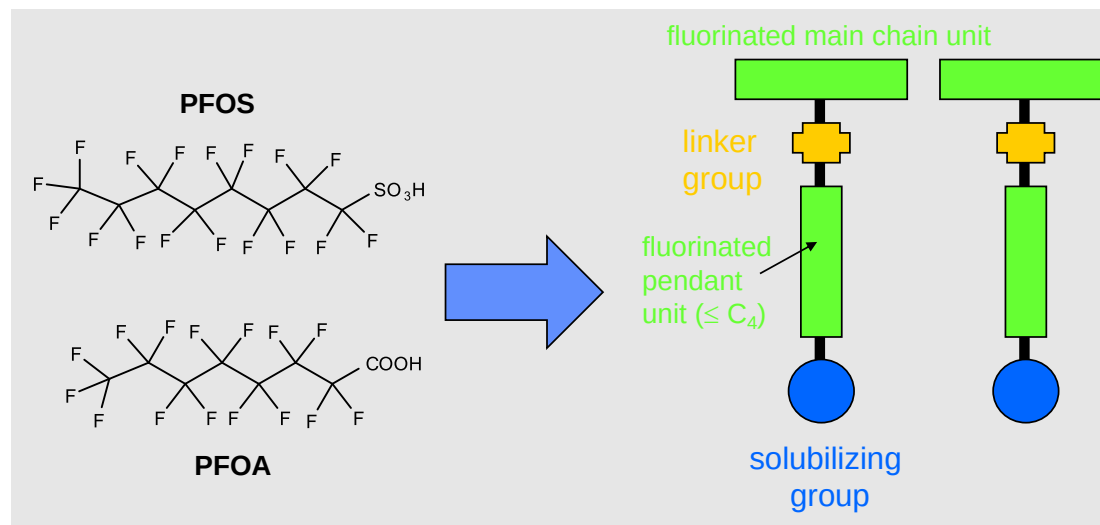


Figure 3: Substitution of PFOS and PFOA in TARCs with a polymeric PFAS-containing material that has shorter-chain units.

TARCs are aqueous formulations and can be the main source of PFAS wastewater releases from photolithography steps because aqueous wastes are typically sent to the industrial wastewater drain.

Some device makers collect the majority of TARC as a separate waste; however, as with photoresists, small wastewater releases occur because the TARC layer coated on the resist layer is highly fluorinated and further dissolves in the develop step. According to the 2021 Semiconductor Industry Association PFAS sales survey, TARCs constituted over 50% of the total PFAS-containing materials used in photolithography, and an even larger share of PFAS emissions in wastewater. The replacement of PFOA and PFOS with a polymeric material (as shown in Figure 3) that is not bioavailable and has low toxicity had been considered a major step toward a more environmentally friendly product that could provide a long-term solution, but recent heightened concerns about polymeric and shorter-chain PFAS-containing materials have led to considerations on how to mitigate or eliminate the emission of this type of material from TARC products into fabrication wastewater. Further research and actions are under development by the Semiconductor PFAS Consortium to quantify and address PFAS wastewater releases from semiconductor manufacturing.

6.0 Conclusions

The semiconductor industry and its chemical suppliers have a demonstrated track record of taking action to address the use of chemicals that, based on evidence, pose threats to human health and the environment because of their persistence, bioaccumulation and toxicity. The industry's phaseout of long-chain PFAS-containing materials and PFOS provides a roadmap of how it is possible to accomplish this conversion to less harmful chemistries while balancing the competing demands of contributing to the economic progress of society through technological innovation.

It took over 20 years to successfully accomplish the conversion away from long-chain PFAS and PFOS in the semiconductor industry. Several factors unique to the semiconductor ecosystem influenced the timeline for the phaseout of these materials. Despite their extremely low concentrations, these chemistries provided critical functionalities in semiconductor material performance, and were essential to maintain and advance technological progress. It took chemical suppliers many years to research potential alternatives, formulate multiple candidate materials, and verify the performance of the selected final chemicals.

Given the complexities and large number of process steps in semiconductor manufacturing, a change to any one step has the potential to impact the performance of many other manufacturing steps. Making simultaneous changes to chemistries used in multiple process steps takes many years to complete and qualify. The quality requirements of end markets such as automotive – where semiconductor device reliability is critical to safety – further extend the timeline.

The semiconductor industry substituted long-chain PFAS with shorter-chain PFAS which provide necessary functionality and were thought at the time to be safe alternatives; however, there is now scientific evidence that shorter-chain PFAS can impact human health and the environment and shorter-chain PFAS are now under regulatory scrutiny. Substituting an entire class of fluorinated organics with presently unknown alternatives would be a serious challenge. To date, despite significant research by photolithography chemical suppliers, almost all cases of fluorine-free alternatives have been unable to provide the essential properties present in current PFAS systems (Ober, Kafer and Deng 2022). To avoid a major disruption of the semiconductor industry, with its accompanying effect on society, adequate research and development time and funding is required to continue to explore potential replacements of shorter-chain PFAS-containing materials, followed by lengthy qualification and process integration efforts as described in this case study if suitable alternatives can be found. One particularly important aspect of the search for benign alternatives is the need for thorough evaluation of the environmental, health and safety properties of proposed alternatives to ensure that they are not later found to be “regrettable substitutions.”

7.0 References

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