PFAS-Containing Surfactants 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

For more than four decades, semiconductor material chemists have optimized lithography materials to enable technology nodes that are quickly approaching molecular dimensions - leading geometries are currently 14 times smaller than the diameter of a COVID-19 virus cell.

Materials containing per and poly-fluoroalkyl substances (PFAS) have become a cornerstone of functionality in semiconductor manufacturing because of their unique chemical properties. In the case of surfactants, PFAS are vital to enabling surface coat uniformity, complete resist removal with low defectivity, improved line roughness and reduced line collapse. While surfactant PFAS concentrations are low (less than 1% by weight [wt]), and overall semiconductor industry usage is low (~10 tons/year) when compared to textiles and firefighting foams (~2,000 to 3,000 tons/year), there are concerns that these materials may be persistent and bioaccumulative. Thus, efforts are underway to remove PFAS-containing surfactants from some lithographic formulations.

As detailed in this white paper, there have been reasonable successes with silicone-based surfactant replacements, as well as efforts to remove PFAS-containing materials from developer rinse solutions. According to surveys conducted by the PFAS Consortium in 2022, PFAS containing surfactants were successfully removed from aqueous developer solutions more than 7 years ago. While we expect there are more replacement opportunities in the industry, it is unclear whether full replacement is possible. This is especially true at leading-edge technologies where PFAS-containing surfactants have driven improved performance at 3 nanometers (nm) or below (~1,000 times smaller than a red blood cell). More R&D will need to be done in this space to clearly understand the feasibility of full replacement.

Assuming the development of non-PFAS containing surfactants for all industry photolithography applications, the timeline from subsupplier development to full device manufacturer implementation is extensive. Iterative testing of non-PFAS-containing surfactants would be required between the subsupplier and supplier to identify materials that match or are better than current solutions. Each solution must be integrated into all the device manufacturers’ process flows and rigorously evaluated against existing performance metrics. Finally, each device manufacturer would need to undertake a multi-phased approach to qualification to ensure that there are no impacts to technology-specific performance and device yield. For leading-edge device manufacturers, this would need to be done across approximately 30 photolithographic materials. Staggered qualifications would be required at all levels due to limitations on R&D resources (engineering staff, metrology, manufacturing equipment and capacity).

A generic roadmap for full replacement - assuming that it is possible for all lithography applications - would be 10 to more than 15 years depending on the complexity of the R&D, the qualification complexity

and device process criticality and sensitivity. Each supplier and subsupplier would require at least $11.25 million* in engineering resources over a 15-year R&D period. Each semiconductor manufacturer would need to expend approximately $10.8 million to qualify the new materials. A conservatively scaled industry-wide cost is estimated at more than $500 million with labor, facilities, metrology, and capital expansion required. Any major yield fallout will cause actual costs to quickly surpass this estimate.

*Note, all cost estimates in this paper are in USD

1.0 Introduction

As defined in this case study, PFAS are fluorinated substances that contain at least one aliphatic carbon atom that is both saturated and fully fluorinated; that is, any chemical with at least one perfluorinated methyl group (-CF_3), at least one perfluorinated methylene group (-CF_2-), or both. PFAS includes a wide variety of chemicals including over 10,000 different compounds.

Many industries use PFAS because of their various and unique properties (Glüge, et al. 2022). PFAS chemicals are very stable, both hydro- and oleophobic, making them useful in surfactants and surface coatings. When used as surfactants, they lower the surface tension of water more effectively than other families of surfactants (such as hydrocarbon or silicone-containing surfactants) (Alexander, et al. 2014); (Ober, Kafer and Deng 2022).

Because of their persistence and bioaccumulative behavior in the environment, PFAS-containing materials have become a notable concern, with their complete restriction under proposal in various regulatory boards. Semiconductor applications would be affected by this restriction, even though the quantity of PFAS-containing lithographic materials used in semiconductor manufacturing remains limited in volume compared to other industries identified as major PFAS users.

The textile and food packaging industries, which use substantial amounts of PFAS in their present processes, have already identified and implemented some alternatives (Lassen, Jensen and Warming 2015); (Organisation for Economic Co-operation and Development 2020). Yet the situation for semiconductor manufacturing and more specifically microlithography is characterized by an absence of demonstrated alternatives for some key material functionalities. This situation, in the case of overly strict regulation, will adversely affect the economy and development of the whole sector, as well as the markets it addresses.

As an example, in 2020 and 2021, when the European Chemicals Agency (ECHA) launched a consultation at Germany’s request to restrict perfluorohexanoic acid (PFHxA) and its salts, the largest use sector was clothing manufacturing, at 70%, while the semiconductor industry was in the smallest sector (0.7%, “Others”) (Committee for Risk Assessment, Committee for Socio-economic Analysis 2021). PFHxA is a C6 telomer used as a polymeric material component of image sensors, an anti-stiction coating for micro-electrical mechanical systems (MEMS) and a surfactant in lithography coatings.

PFAS-containing materials used in industries such as polymer manufacturing, clothing and textiles are estimated at a few thousand tons per year for each sector. An estimate for the overall quantity of PFAS-containing lithographic materials used by the semiconductor industry was evaluated as less than 10 tons/year worldwide, based on a 2022 survey of major photolithographic material supplier sales. The European Semiconductor Industry Association (ESIA), in a final response to the ECHA’s 2020 public consultation, estimated that the current amount of PFHxA is less than 20 kg per year in image sensors and MEMS applications (in the European Union [EU]), with no existing alternative yet identified. Therefore, a derogation of 12 years was finally sent by the ECHA to the EU Commission for a final assessment at Germany’s recommendation to develop and qualify alternatives, with possible extensions granted for those applications where no suitable alternative could be found. This replacement is thought to be complex, but feasible.

2.0 PFAS Uses in Photolithography

PFAS-containing materials have many applications in the photolithography process. The unique chemical properties of PFAS-containing materials have been vital in progressing technology development. In reviewing the kind of lithographic materials used in photolithography (photoresists, bottom anti-reflective coatings [BARCs], top anti-reflective coatings [TARCs], topcoats, underlayers), it is possible to outline five main categories, all corresponding to extraordinarily complex materials, that involved years of research going from proof of concept in many labs and universities to manufacturing. The categories are:

- Photoresists for ultraviolet (UV) lithography (broadband, 436 nm, 365 nm). Most of these photoresists are based on PFAS-free chemistry to ensure photosensitivity (Novolak/diazo-naphthoquinone [DNQ]). As a result, most of these less-demanding formulations are already PFAS-free, with a small number using PFAS-containing materials as surfactants in their formulations.
- Photoresists for deep UV (DUV) lithography: 248 nm, 193 nm, 193 nm with immersion, and extreme UV lithography (EUV). These photoresists are essential for the most advanced nodes of devices in the semiconductor industry. In a 300-mm fabrication plant that produces devices with dimensions from 120 nm down to 7 nm and below, the lithographic portfolio can count more than 100 qualified products, and at least half of them are DUV photoresists. All are chemically amplified resists, an approach developed in 1979 by C.G. Willson, J. Fréchet and H. Ito at IBM that required the unique properties of DUV-sensitive PFAS-containing photoacid generators (PAGs) to release the extremely strong acid needed to catalyze further chemical reactions (Ito 1997). This process delivers the superior patterning performance required for the most advanced microelectronics, as the projected optical image in the photoresist has limited contrast caused by optical diffraction limits at such small dimensions. As a result, these photoresists contain lesser amounts of PFAS compounds (<1% wt) as photosensitive agents. A substantial number of these DUV photoresist formulations also have PFAS-containing surfactants in their formulations, again, at a lower level (<1% wt). When using PFAS-containing surfactants, the semiconductor industry is harnessing critical characteristics such as surface coat uniformity, complete resist removal with low defectivity, improved line edge roughness and reduced line collapse.
- Other lithographic films for DUV lithography. This includes BARCs, TARCs, immersion barriers, silicon-containing anti-reflective coatings (SiARCs) and underlayers. In all these products, adding PFAS-containing surfactants improves coating properties and defectivity.
- Photoresists for image applications. These materials stay in the final device to act as color filters or microlenses for image reconstruction by cameras in cellphones or detection systems for automotive, space or medical applications. There are different versions of color and infrared filters and microlens materials. In a fabrication plant, it is common to have a set of 10 to 15 different photoresists to cover all the different pixel sizes and product generations of image sensors that a complementary metal-oxide semiconductor (CMOS) imager manufacturer may use. The Case Studies for the Removal of PFAS-Containing Surfactants in Lithographic Materials section provides an example of one such surfactant replacement in color resists that started in 2022 in a semiconductor fabrication plant.
- Polyimides and polybenzoxazoles. A significant percentage of these formulations contain PFAS-in their polymer matrix to enhance material properties for device protection and reliability. They can also contain PFAS-based surfactants.

The use of PFAS-containing materials as surfactants in lithographic products occurs in extremely small quantities for vastly different purposes, making their replacement unique for each formulation. As an example, they are employed as:

- Surfactants in pigmented color resists for CMOS image applications (Takahashi, et al. 2020).
- Surfactants in materials to reduce pattern collapse during a development step (Chiu, et al. 2020).
- Surfactants in a rinse solution to also reduce pattern collapse (Kehren, Savu and Pinnow 2013).
- Surfactants in resist formulations to reduce patterning defectivity and improve overall performance (Yueh, et al. 2006); (Yasumasa Kawabe 2000).

Restricting the use of PFAS-containing materials will necessitate finding a specific solution for each product that presently contains them. For lithographic films integrating PFAS surfactants in their compositions, it will be necessary to reformulate several tens of chemistries for a single semiconductor fabrication plant. Regarding the quantity of work for each change, it may not be possible to conduct studies in parallel at the same time, and therefore will require a years-long effort from a dedicated team of engineers, as well as dedicated teams at material suppliers, to actively develop and submit to each of their customers PFAS-free alternatives.

Work must first start at the material supplier to design a PFAS-free alternative that has the same performance as the process of record (POR). Research to optimize a few alternative candidates can take months to years by dedicated, highly skilled R&D engineers. The material supplier must conduct material tests as well as some preliminary reliability checks. If the alternative passes this first round of tests, the material supplier would propose the new formulation to the semiconductor manufacturer for evaluation and qualification.

In semiconductor fabrication plants, the replacement studies of one material used in several lithographic steps for various products can represent one to several tens of lithographic levels to control and validate the PFAS-free alternative material. For a whole fabrication plant, use of PFAS-containing surfactants in photoresists corresponds to several hundred replacements. Each of these replacements necessitates a qualification plan, with specific monitoring and reporting of process parameters by R&D engineers that must be approved by the management board of each project affected by the material change. Such plans require months to years of internal studies to cover all technologies using one PFAS-containing material.

Finally, depending on the product or application, process change validation by customers may be mandatory, using their internal qualification procedures. For automotive products, this validation can take multiple years and such change corresponds to a substantial risk of business failure for all parties: the material supplier, the semiconductor manufacturer, and the final customer if for some reason the qualification fails.

3.0 PFAS Applications in Surfactants and Replacement Opportunities

As we have described above, there are many PFAS applications in photolithography. In this paper, we will focus on one of the major uses: fluorinated surfactants. The combination of hydrophilic segments in a surfactant with fluorinated segments allows for unique properties in the resists and polybenzoxazoles for surface-leveling and defect reduction, and development modification and control. In both cases, the perfluoro groups have a greater effect on surface tension than other surfactant functional groups such as cationic groups (quaternary amines), anionic groups (carboxylates and sulfonates), and nonionic surfactants. It is also possible to combine the perfluoro groups with elements of other functionalities, often as a telomeric side chain (perfluoroalkyl unit) attached to the main surfactant.

The resultant surfactants are amphiphilic, having a hydrophilic chain with a hydrophobic head. The perfluoro group is extremely hydrophobic (as can be seen with perfluoropolymer objects). These molecular structures are also both hydro- and oleophobic, a balance that allows tuning of the surfactant for the specific use.

As lithographic challenges increase with a progression to finer and finer geometries (patterning using sub-10-nm design rules), the specific abilities of PFAS-containing materials to achieve the necessary performance goals have been critical in the manufacture of more advanced processors and memory chips. To put these geometries into perspective, a human hair is 50,000 to100,000 nm in width, a red blood cell is about 8,000 nm wide, and a COVID-19 virus particle is estimated at 50 to 140 nm across. With a C-C bond at 0.15 nm, photolithography is approaching molecular dimensions with polymers in resists and surfactants. At these geometries, lithographic development processes no longer experience turbulent flow, rather the hydrodynamics result in laminar flow at the boundaries, which changes the ability to remove the resist cleanly. The photo-diffusion in the resist and diffusion in development steps must enable a challenging sidewall roughness much less than 1 nm (10 Å). The fluorinated surfactants in resists and polybenzoxazoles help to reduce swelling during the develop process. Fluorinated surfactants in the develop rinse solution help to avoid sidewall collapse or webbing. More information regarding the use of fluorinated materials in wet chemistries can be found in the semiconductor PFAS consortium whitepaper "PFAS-Containing Wet Chemistries Used in Semiconductor Manufacturing." Many alternative surfactant types have proven ineffective in lithographic applications, particularly as design dimensions shrink. One alternative is silicone-based surfactants. So far, these appear to be the closest in performance, particularly at larger design rules. This work is still in progress, but the outlook is promising. In other applications, interaction with other processes, especially dry etch, has shown some difficulties, such as the generation of insoluble silicon oxides. With current devices having 70 or more lithography layers, all patterned with different tools and resists, any substitution must be qualified on the layer in question. A fabrication plant cannot afford to use different develop chemistries for each layer.

Furthermore, it may not be possible in all cases to find a drop-in substitute, forcing the use of substitutions that would negatively impact device parameters. One approach has been to move to shorter PFAS chains in the interim to reduce the impact of PFAS-containing materials on the environment, as shorter chains appear to be less toxic. It is also unclear whether common non-PFAS alternatives are themselves without risks. For example, a recent study showed that replacing firefighting foams containing PFAS materials with alkyl or arylalkyl sulfonates can be more hepatotoxic (Yang, et al. 2020).

4.0 Case Studies for the Removal of PFAS-Containing Surfactants in Lithographic Materials

To examine the complexity of replacing PFAS-containing surfactants in lithographic formulations, it is important to examine real-life examples. Here are two examples of device manufacture PFAS-replacement activities. The first example is a case study to illustrate the work associated with the removal and replacement of PFAS-containing surfactants in color resists. The second will cover the removal of PFAS-containing surfactants from develop rinse solutions.

Example 1. Within the last couple of years, a semiconductor fabrication plant, in close partnership with a resist supplier, initiated a study of PFAS-free surfactants in color resists. This study became mandatory after the 2021 ECHA regulation of PFHxA (C6 telomer) used in surfactants. The regulation allowed for a 12-year derogation for the semiconductor industry – as well as a reevaluation period at the end of that timeline – to see whether additional time was needed for development, research, and replacement. These PFHxA-containing surfactants are present in pigment-based color resists for imaging applications to avoid film thickness variations during coating on wafers with high topography (a depth of a few micrometers). They also help stabilize pigmented formulations.

In this case, it is possible to use another class of chemicals for the same purpose - silicone-based surfactants - that may help reduce the striations observed when coating photoresists on topography. Reports indicate that they are less effective, however, and may require a higher amount in the final resist formulation.

The resist supplier team worked for several months on a proposal for material replacement: in this case, each color resist formulation needs a specific adjustment of the surfactant level, necessitating repetition of the optimization study for each photoresist product (this plant uses about 10 versions). Each instance requires the generation of a full set of analyses and tests that include checking basic material properties on flat silicon wafers (in-film defectivity, thickness, optical index); patterning performance (robustness of the process window with exposure condition variations, critical dimension under the same illumination conditions that have defectivity after development of the patterns); and coating characteristics on topography wafers, as these surfactants are mainly there to improve these properties.

After this preliminary work, the resist supplier team submitted samples to the semiconductor manufacturer's compliance/regulatory team for evaluation based on its environmental, safety and health (ESH) policy. This stage was critical depending on local environmental rules and internal policies, as the new formulations may not have passed all the criteria. The new chemistry had to be compatible with existing premises installations (air exhaust, air emission treatment and liquid waste collection and treatment). If the semiconductor manufacturer rejected the formulation, the material supplier team would have to work again to propose a new one.

Once this step was validated, samples were sent to the semiconductor manufacturer engineering team for testing. Because the goal was to replace a product already qualified in production, the resist supplier had to produce wafers (split lots) evaluated with both the POR material and the proposed alternative material. The new chemistry had to be installed on a production track with the same conditions as the reference resist. Here, the difficulty was having available chemical lines for the alternative chemistries, as this reduces manufacturing capacity. Usually, R&D teams have one or two engineering lines available for a lithographic track. All the others were installed with materials running production processes. Semiconductor fabrication plants are not practically positioned to face a massive change for most of their formulations simultaneously. Such changes must be validated one by one and would increase the time to complete the transition of materials.

The resist supplier first repeated material test runs to check whether the PFAS-containing material and its alternative matched and could obtain the same material performance, and then ran tests on production wafers allowing full real device characterizations. The complete qualification of a material change to a PFAS-free alternative must include reliability tests (stress cycles for several hundreds to thousands of hours, depending on conditions), which entailed several weeks of waiting for a pass or fail result.

Regarding the example of replacing PFHxA-containing surfactants in color resists, after several months of development, the resist supplier proposed double-digit samples corresponding to the alternatives of all the resists qualified in the fabrication plant. Because it was not possible to test all of them together, two were selected for full testing and qualified initially: one with the highest level of surfactants and one with the lowest.

The fabrication plant installed resist bottles on the track, but the tests did not match current performance as expected. Indeed, after a few weeks of installation, coated wafers showed a severe drift of film thickness caused by an unexpected viscosity change. The process was then “out of control” (or outside of processing parameters) for manufacturing. Changing a component of surfactants from PFHxA to silicone-based appears to have affected the aging of the entire formulation at room temperature. The resist supplier team was alerted of this drift and retested their retained samples. Indeed, they concluded that there was a change in the shelf life of the product. This first PFAS-free alternative, as proposed, could not meet the necessary shelf-life requirements for semiconductor manufacturing on the track: after about nine months of tests. The supplier had to reformulate their alternative proposal and submit a new one to the semiconductor manufacturing team.

Such an outcome meant restarting all studies from the beginning, going back to the material introduction approval request to the environmental, safety and health department and facilities teams. After a few months of tests, the new supplier sample appeared to work; however, the time from the very beginning of the replacement project to obtaining encouraging data for one single formulation replacement at the semiconductor manufacturer site was almost one year. In addition, there were still the remaining color resist formulations waiting to pass qualification tests.

Even after completing lithographic qualification tests, it was necessary to verify if additional fine-tuning was necessary for integration into the POR process of each device type. This includes verification of integrated defect modes, patterning adjustments, including mask redesign and OPC (optical proximity correction), as well as changes in etch bias.

These verification steps can impact the timeline for implementation. Designing a new mask takes weeks and can cost several thousands of dollars per mask. The timeline and cost for 193-nm immersion and EUV mask can far exceed this. Unexpected increases in integrated defect modes from surfactant formulation changes can impact overall device yield, requiring downstream process adjustments may qualification to achieve replacement. One critical process adjustment may be modifying etch parameters. This point is especially important for photoresists when replacing PFAS-containing surfactants with silicon-based surfactants, which limit the etch resistance of the film compared to silicon substrate. The replacement of PFAS-containing surfactants with silicone-based surfactants could increase the time and chemical required for plasma etching. All these process changes could take weeks or months to evaluate a new material with PFAS-free surfactants before pronouncing its full qualification for a certain process.

Example 2. A device manufacturer replacement of PFAS-containing lithographic materials focused on the develop process within lithography, specifically a developer rinse chemistry. During the lithography development process, surfactants within the develop rinse solutions may be formulated with PFAS-containing surfactants, which can effectively reduce the surface tension between adjacent patterned features and prevent toppling or tipping of the pattern. They can also be effective at reducing the amount of resist swelling that can occur when a develop chemistry encounters the photoresist.

Alternative PFAS-free surfactants are being explored, and some are available for use in R&D and production. Their ability to provide equivalent or better performance needs further determination and validation. The work can be extensive, as the performance and interaction between photoresist and develop rinse chemistries can be unique for each type of pattern, and can require significant amounts of material development, testing, validation and implementation across multiple parts and layers.

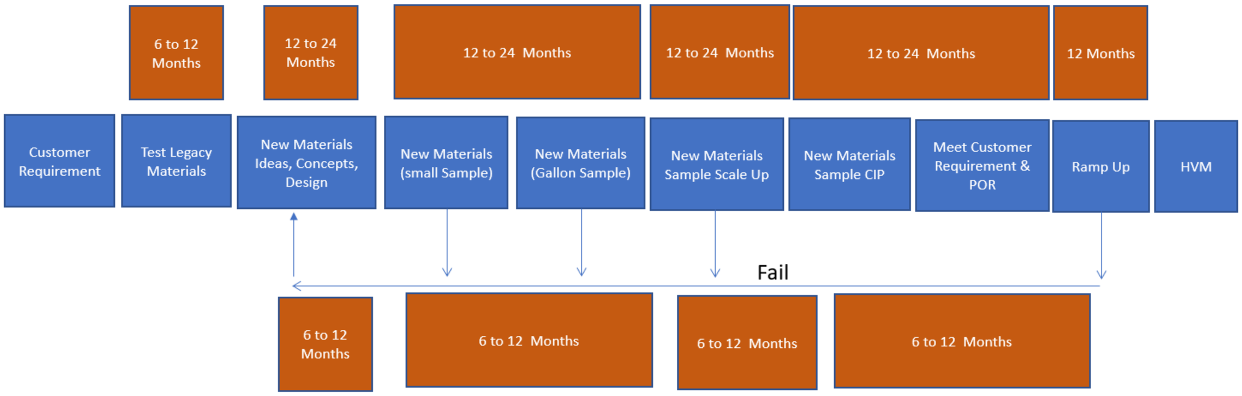
In the case of a surfactant rinse following a lithography develop step, several chemical suppliers have spent months and even years developing PFAS-free surfactants and made these alternatives available for testing by integrated circuit manufacturing companies. Testing and validation of these PFAS-free surfactants can take months to years, depending on the complexity of the patterning involved, along with the number of device types and patterning layers. One PFAS-free surfactant rinse material may show comparable performance at one patterning level with a specific resist, but not at another level that uses a different resist material. Identifying and qualifying multiple surfactant rinse materials for use with the many various resist chemistries is not feasible in the semiconductor industry, since tooling and facilities within a fabrication plant usually only support one or two surfactant rinse materials. Therefore, a non-PFAS-containing surfactant rinse solution needs qualification across all devices and patterning levels. Inferior performance at one patterning level (such as toppling or patterning defects, or even a degradation in pattern roughness) while all other levels show acceptable performance can necessitate restarting the process over with a new surfactant rinse material, then retesting and revalidating. The cost to implement any replacement material within a manufacturing fabrication plant can run into millions of dollars given the cost of engineering time, materials, and silicon - and can last several years.

5.0 Supplier Removal of PFAS-Containing Materials from Surfactants

While the qualification rigors of the device manufacturers have been discussed, the impact of removing PFAS-containing materials has a much broader industry impact in terms of R&D, qualification, and cost. In this section, we will examine the complexity and cost of bringing non-PFAS solutions to commercial realization.

Component replacement in a photoresist is complex, including surfactant replacement Device makers invest considerable time and effort in “process 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 formulation performs exactly as the POR photoresist formulation in every way. Every small formulation change that occurs can result in an unwanted change in one or more of many lithographic performance parameters. And any of several performance changes (even minor) can lead to unacceptable yield reductions or require costly adjustments in the device maker’s or customer’s processes. Thus, a component change requires in-depth, multivariable evaluations at both the supplier site (verification) and the device maker site (validation) to prove that the change would not detrimentally impact the potential performance of the photoresist product.

As a result, each surfactant replacement requires in-depth R&D to identify acceptable surfactant replacements that meet the critical functional requirements demanded of the surfactant (coating quality, coating uniformity) without detrimentally impacting other essential lithographic functions of the photoresist (resolution, image biasing, usable process window, defectivity). After determining a potentially suitable replacement, the supplier would provide demonstration data to device makers, along with small volume alternative formulation qualification samples. They would then provide the device makers with larger production scale samples for further evaluation and validation. Any issues that arise at the device maker require either processing adjustments or formulary iterations to finalize device maker acceptance of the replacement sample. Furthermore, by the time the device maker accepts and qualifies the replacement formulation, the supply chain for the replacement component may need to be secured, with scale-up and high-volume manufacture of the new formulation which would require further device maker validation. The individual qualification tasks would need to be repeated for each of the formulations that make up a customer's material suite. For each supplier, this typically means tens of product replacements for tens of customers, a total process that can take years. Figure 1 illustrates the flow and scope of such development and qualifications. This is a generic graph, however, and timelines can shift with device manufacturer qualification resources and the number of iterations required to meet the final product goals.



- Approximated Replacement Timeline for a Single Product Line from Sub-supplier to Supplier to Manufacturer 7.5 to 14 years.
- Note that this is dependent on the complexity of the replacement as well as the number of materials and Device manufactures will be doing this with several suppliers.

Figure 1: Example development and qualification flow for a PFAS surfactant replacement.

Furthermore, the potential for suppliers to lose business is present with every evaluation of a new replacement formulation at the device maker. When a device maker begins new replacement product evaluations, many times they choose to include products from other suppliers in those evaluations. This may lead to the customer selecting another supplier for this product. Such loss of business to a competitor would not have occurred if the POR formulation did not require modification.

Let us estimate the cost of substitution, just in terms of the R&D engineering budget, for a single supplier per replacement chemistry, assuming viable replacements for all formulations. There is no guarantee that given enough time and resources that some of the technical challenges of the replacement are feasible.

- Example staffing needs:
  - Two full-time R&D engineers (Ph.D. level).
  - One full-time manager.
- Total salary costs: $750,000/year.
- Time for development and high-volume manufacturing approval: 15 years.
- Cost for a single replacement: 15 × $750,000 = $11.25 million.

It is reasonable to assume that about half of the cost is from the supplier side, but half of the cost would come from the manufacturer of these surfactants, the device makers to evaluate them and ongoing support for troubleshooting and customer support.

Therefore, the approximate total cost of R&D staff needed to drive the replacement of PFAS containing surfactants for a supplier and associated subsupplier would be $11.25 million × 2 = $22.5 million over 15 years.

Note that this is only an estimate for the labor investment required by the material supplier. There may also be investment needs for manufacturing facilities, metrology equipment, external laboratory support and many more. While these would be extremely costly, it is complicated to estimate until replacement activities are underway.

6.0 Device Manufacturing Qualification of Surfactants in Photoresist and Develop Rinse Solutions

Beyond specific examples of removing PFAS-containing materials, it is also necessary to look at generic qualification timelines, complexity, and costs to understand the impact of a full replacement activity in the semiconductor industry. The qualification of lithography materials for semiconductor device manufacturing is a laborious and costly endeavor. Lithography continues to carry the highest degree of complexity for chemical qualification in the semiconductor industry because of its sensitivity and need for specificity. Of these chemicals, photoresist qualification requires the most intensive and rigorous qualification standards.

A photoresist formulation is highly process specific. Each material is designed for specific types of lithography applications (Bulgakova, et al. 2014), including 248 nm, 193 nm, and 193-nm immersion and EUV (Uzodinma 2020). Within each of these exposure methodologies are materials specifically formulated for line spaces and holes, with differing requirements and capabilities to achieve an optimal depth of focus, minimum feature size, line-edge roughness and aspect ratio (Campbell 2008). In addition to the optical requirements, the materials must be compatible with existing industry standards for solvent, chemical vapor deposition (CVD) films, etch chemistries and develop rinse solutions. Furthermore, there are integrated process requirements in terms of etch resistivity, temperature stability, cross-wafer coat uniformity, coat thickness and implant and diffusion buffer requirements (Li, et al. 2018).

While develop rinse solutions are less process- and layer-specific compared to photoresists, they must still pass all patterning qualifications required for each lithography layer. Develop rinse solutions are critical to the lithography process at all layers. Additionally, surfactants can significantly affect patterning resolutions and patterning process margins (Shimada, et al. 1994). There are significantly fewer develop chemistries used to accommodate positive- and negative-tone photoresist materials The nature of the develop process itself does not lead to as many downstream interactions, as the intention is the full removal of chemistries from the wafer before leaving lithography (Xiao 2012). Outside of patterning metrics, the only integrated impact of concern is defectivity.

As technologies and process nodes progress within the industry, the resultant lithography layer count increases as well. The need for specialized resists likewise continues to increase throughout the industry (Wu, et al. 2020). The number of photoresists scales as the specialization requirements increase. However, unlike formulation changes for photoresist (such as PAGs and resins), changes to surfactants tend to have less impact on the process, as alternatives have generally been well matched in performance. This is also true for develop rinse solutions. The complication arises from the need to fully characterize the impact over a broad set of layers for either the photoresist or develop rinse, which has an even larger layer impact because it will be used across many photoresists.

Let us consider a reasonable hypothetical of a factory working to replace 15 photoresists and two develop rinse chemistries that have PFAS-containing surfactants. New surfactants can have an impact on a molecular level that can change patterning performance. We do not know how to easily predict steric differences that could cause processing shifts or variations. It is highly likely, though, that the device manufacturer would not choose to add additional develop rinse solutions into the chemical delivery systems given the excessive cost of replumbing the factory and associated tools. Thus, the onus falls on the supplier to continue producing different iterations of surfactants until they find one capable of meeting existing manufacturing processes requirements.

Each of these materials would need to pass rigorous patterning qualifications and must meet the exacting standards of existing materials. Early evaluations may require some fine-tuning with suppliers to achieve identical performance. These early patterning evaluations take, on average, one to three months to determine a formulation that meets existing layer specifications.

Following lithography-specific qualification, the material undergoes an integrated process qualification. Again, this material must pass the existing requirements and be completely matched compared to the PFAS-containing develop rinse solutions. This includes defectivity, coat uniformity, thickness targeting and initial test product evaluations. While some of these parameters are not specifically related to surfactants, they still require evaluation and would impact the overall qualification timelines. Iterations of the formulations – including filtration, viscosity, and surfactant concentrations – would be possible during this phase. Again, this phase would require one to three months, depending on the availability of new test material and processing and metrology equipment at the factory.

The final qualification requires piloting this new material on a fraction of the baseline production material to obtain yield data. Depending on the criticality of the layers, the line segment of the layers and the need for risk-based phase-in, the pilot itself can take two to four months. At this point, a data comparison would be required for performance, reliability, and multiple fallout bins for yield. Such comparisons are critical to ensure line health if the material were approved for full production integration. The process regularly requires additional production commitments to rectify flier signals and low-level mismatches, with similar time frames already mentioned. This additional qualification can lengthen the timeline reported above by one to three months.

Finally, the material needs formal documentation in the process, with high-volume batches fully replacing existing stock. Even with a rapid transition, this process would take two to three months. For materials that pass yield qualification on the first attempt, the overall timeline for qualification would be six to 13 months per individual material. This timeline could extend up to 16 months if yield signal verification requires repeating production pilots. To complicate things further, it would not be possible to qualify all these materials at the same time. There are limitations on processing tool and metrology availability as well as engineering availability. Most importantly though, depending on the layer(s) that use these resists, qualifying multiple resists can convolute yield evaluation and cause an increase in repeat qualification, which means that some of these materials would require qualification serially rather than in parallel.

Qualifications are costly. There is a cost for additional labor from the technician hours spent readying the material on the tool for qualification, from the engineers to plan, execute and evaluate the qualification, and from the teams that oversee and approve the full qualification and implementation into the process. There is also a cost associated with a loss of output on production tools. Particularly, a loss of processing time on scanners is extremely costly. These tools are expensive (tens of millions of dollars to more than 100 million dollars), so the factories tend to run with a minimum quantity of equipment to meet output goals (Levinson 2019).

Given the length of the qualification, materials costs can also be high, including the cost of qualification resists, metrology costs and ancillary/support chemistries. Overall, an estimate for each qualification would be approximately $350,000 for resist and $500,000 for develop rinse solutions. This price tag can rise sharply if there is resulting yield fallout from the qualification, but such instances are rare for a surfactant substitution.

While we have only discussed resists and develop rinse solutions in this case study, the removal of surfactants in lithography chemistry would also be necessary with underlayers (carbon hard masks and SiARCs) as well as topcoats for immersion technologies. This action could raise the number of materials that a single factory must replace to 30 or above. The overall cost to replace these chemistries would be ~$10.5 million, with five to eight years for qualification and implementation once samples are available.

This cost estimate does not include any resulting fallout from failed qualifications, which are complicated to model and predict. Different technologies and products may require separate qualifications. There should be an opportunity to conduct these qualifications in parallel to avoid impacting the overall timeline estimate, but it would scale the qualification costs.

7.0 Conclusions

PFAS-containing materials encompass a wide variety of chemistries (more than 10,000 compounds) used in various industrial and commercial applications. For two to three decades, semiconductor material chemists have optimized lithography materials to enable technology nodes that are quickly approaching molecular dimensions (leading geometries are currently 14 times smaller than the diameter of a COVID-19 virus cell).

For many specialized applications, PFAS-containing materials have become the cornerstone of functionality. PFAS-containing materials have unique properties that make them critical for various use cases, with attributes that include high stability (nonreactive, low heat degradation). They are also hydro- and oleophobic and form strong and stable anions. These optimal properties make them highly essential in the photolithography space as PAGs; surface protectors (immersion lithography barriers); and photoresists, ARCs, and develop rinse surfactants.

Given health concerns over the bioaccumulative nature of PFAS-containing materials, use cases and waste generation are under increased scrutiny. While the criticality of PFAS-containing materials in the semiconductor industry (and lithography specifically) cannot be overemphasized, the relative usage quantities and subsequent release compared to all industries and uses make up only a fraction of a percent (~10 tons/year) of the overall usage. This is low compared to industries such as textiles and firefighting foams, which use ~2,000 to 3,000 tons/year individually.

The lithography use of PFAS molecules is specific to this chemistry's unique nature. Specifically, these molecules are highly effective at protecting photoresists during immersion lithography while not swelling the photoresist. They form extremely effective surfactants compared to quaternary amines, carboxylates and sulfonates.

PFAS-containing surfactants are critical for surface coat uniformity and fill characteristics. When used in develop rinse solutions, PFAS-containing surfactants aid with resist removal, improve line roughness, reduce surface defectivity, and avoid line collapse. With these critical functionalities, surfactants are used widely throughout lithography materials. These specialized functionalities are becoming even more critical as patterning geometries shrink below 10 nm.

There has been some traction with the replacement and removal of PFAS surfactants for some chemistries. The industry material suppliers have had reasonable successes with silicone-based surfactant replacements, as well as efforts in the removal of PFAS-containing materials from develop rinse solutions. There is no drop-in solution that would fit all applications, however, making the replacements of these materials costly and time-consuming. Full replacement of PFAS-containing materials may not be possible for some of the most exacting applications.

Material suppliers have spent a significant amount of time and resources over the last 25-plus years to develop suitable solutions for device manufacturers to meet all application constraints. Newer lithography technologies could have 70 or more lithography layers. Many of these layers require three to five materials for patterning, and many of these would contain PFAS surfactants. Even very slight changes to any of these materials can have adverse impacts on the device manufacturer's yield performance. As such, extensive research must occur for any replacement material, with rigorous pre-characterization and qualification. It would be necessary to repeat this process for every formulation where PFAS surfactants existed for every customer. The estimated cost alone for the additional engineering support would be ~$111.25 million for each supplier and subsupplier in the industry – an estimate that does not include equipment expansion, subsupplier cost increases, metrology and characterization costs and the possible loss of business if device manufacturers underwent renewed material selection activities. These costs could quickly outweigh the already expensive engineering investment.

Much like the suppliers, the characterization of new, non-PFAS surfactant formulations would need rigorous qualification for all applications, including at the chip manufacturer, and functional and reliability testing at the final device manufacturer. Each photoresist, ARC, and carbon hard mask requires high specificity to the application and must be analyzed for coat uniformity, fill characteristics, defectivity, patterning performance and integrated process performance (such as post-etch critical dimensions, profile and diffusion, and implant barrier performance). Likewise, it would be necessary to evaluate develop rinse solutions over a broad set of existing chemistries throughout the process flow. A factory primarily uses bulk chemical delivery systems for a set quantity of develop chemistries, and any replacement would have to be capable of handling all existing applications.

Even the smallest changes to formulations can have detrimental and unexpected impacts to the device manufacturer's process flow. These impacts are often process-specific and not easily anticipated by the supplier, thus requiring full yield analysis for each formulation change. The qualifications cannot all occur simultaneously because of tooling and engineering resource limitations, as well as yield data resolution concerns. Iterative evaluations would need to occur from subsupplier to supplier to device manufacturer. In the case study for color resists, 10 individual formulations needed evaluation before a candidate was acceptable. This case study, if held up as an example, would push the anticipated timeline of full replacement of PFAS-containing surfactants to 10 to 15 years (assuming it is even possible for all applications). Each device manufacturer would have to replace approximately 30 chemistries at an estimated cost of $10.8 million. Scaling this to all subsuppliers, suppliers and device manufacturers, we would anticipate total costs of over $500 million for the semiconductor industry for labor, metrology and equipment investments and materials cost.

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