

PFAS-Containing Photo-Acid Generators 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-containing materials and will focus research and development 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

Photo-acid generators (PAGs) are a vital component of many semiconductor photolithography formulations, especially chemically amplified resists (CARs). Patterning performance depends on the PAG's ability to interact directly or indirectly with photons and disassociate to form the catalytic photoacid. The effectiveness of the PAG molecule to generate targeted, well-defined, repeatable patterns depends on these attributes:

- The ability to generate a strong nonnucleophilic acid.
- High control of photoacid diffusion.
- Good solubility in existing lithography solvent and good miscibility with matrix polymers.
- High stability.
- Exacting wavelength-dependent transparency/absorption in resist formulations.

PFAS-containing PAGs check the box for every one of these attributes, but the semiconductor industry continues to explore alternatives to PFAS due to increasing concerns about their persistence, bioaccumulation and toxicity.

Initially, the most direct solutions focused on replacing longer-chain PFAS materials with either a more easily degradable short chain four carbon (C4) PAG anion or a shorter-chain single carbon (C1) PAG anion. The industry, as well as regulatory agencies, believed that short-chain PFAS-containing materials were safer than long-chain chemicals. According to Hand, unlike perfluorooctane sulfonate (PFOS), a short-chain PFAS such as perfluorobutane sulfonate (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 European Union in 2003 (Hand 2003). These changes were not an invention of technology, as PAGs continued to use fluorinated carbon molecules for their attributes and reactivity. A full transition to non-fluorinated PAGs would require extensive research and development and years of implementation.

The outlook for fully removing PFAS-containing materials from PAGs industrywide is much more uncertain. Comparative studies of krypton fluoride (KrF) photoresists containing non-PFAS PAGs have shown deficiencies in key properties such as photospeed, diffusivity, transparency at lithography exposure wavelengths, solubility and temperature stability compared to PFAS PAGs. To date, no replacement molecules (either commercially available or in a research phase) have been found that could match the performance of existing PFAS PAGs. None of the aforementioned solutions generate strong enough acids to accommodate 193-nm PAGs, and there is a legitimate concern that it may be chemically impossible to find solutions for some applications.

Even if it is possible to develop non-PFAS PAGs for all applications, the impact and timeline from subsupplier to supplier to device manufacturer is extensive. The development of non-PFAS PAGs will require extensive research and development at every step: between the subsupplier and supplier through high volume semiconductor manufacturing. Iterative R&D will be required to produce non-PFAS PAGs that match all existing quality and performance parameters and targets. If non-PFAS PAGs can be generated, they will need to be incorporated into specific formulations to meet all customers' existing needs and process specifications. It is anticipated that more than 100 different formulations would need to be generated industrywide. Even with an expansion of research and development efforts, this process could take five to more than ten years at an estimated cost of \$25 to \$60 million USD* per material supplier customer.

Likewise, device manufacturers must each qualify a full replacement package of new formulations from the suppliers to prevent any process- or technology-specific impacts to the device performance or yield. These multiphase qualifications can take months to years for a single formulation, depending on the complexity of the application and duration of the yield analysis activities. Six to more than twelve years is anticipated for each device manufacturer to qualify a full replacement suite of materials at the cost of ~\$12 million per semiconductor manufacturer.

Even with R&D expansion, the optimistic timeline for full replacement would be more than twenty years, as there are not currently enough industry resources to qualify all materials simultaneously. It is highly probable that substitutions for many applications will be detrimental to performance and yield, which would stall the progress of semiconductor innovation and computing power progress, and make it impossible to manufacture some existing products.

*Please note that all cost estimates mentioned in this paper are in USD.

1.0 Historical Background and Current Situation

To continue increasing chip performance and lowering device cost, the semiconductor industry has been using a succession of shorter and shorter wavelengths to form ever-smaller patterns in photoresists (Figure 1) (Dammel 2023). First, beginning at the 248-nm wavelength, CARs became the dominant photoresist technology. 193-nm dry and immersion lithography continues to use CARs, as have the first generations of devices made with extreme ultraviolet (EUV) lithography. For advanced chips, most layers are imaged using CARs at the 248-nm (also called deep ultraviolet [DUV] or KrF) and 193-nm (also called argon fluoride [ArF]) wavelengths (Figure 2 (Jones 2020)).

Without CARs, the manufacture of most chips produced today would be impossible. CARs depend on PAGs, most of which contain PFAS.

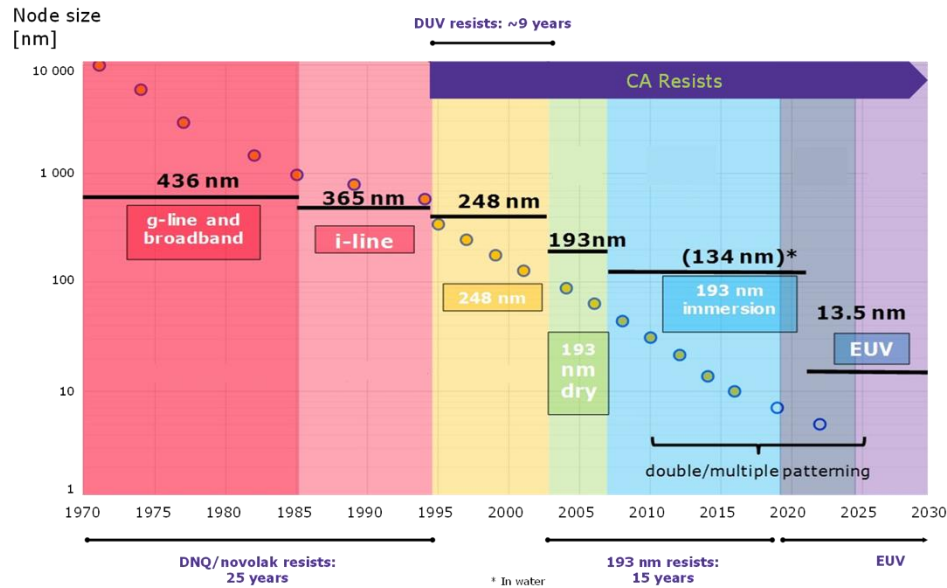


Figure 1: Sequence of exposure technologies used by the semiconductor industry over time (Dammel 2023).

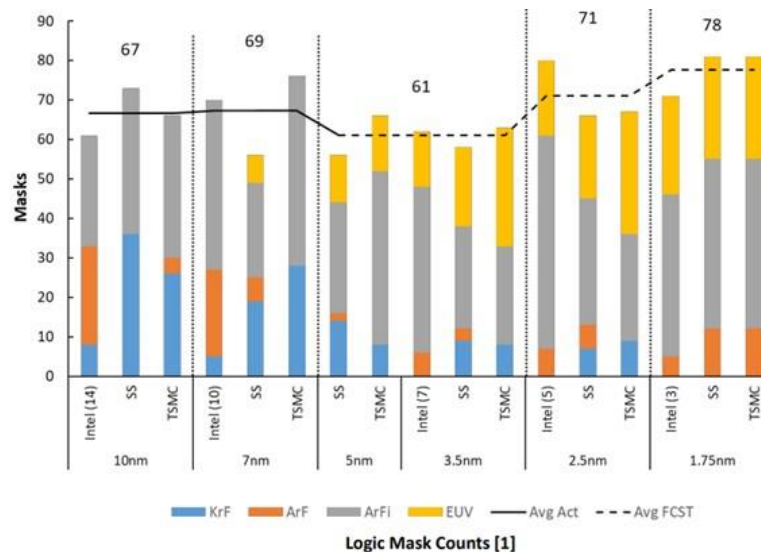


Figure 2: Layer* numbers for advanced logic device nodes by exposure technology (Jones 2020).**

*Layer is the number of photolithographic printing steps for a process. Each patterning step uses a photomask or reticle for optical printing, so the terms mask and layer have the same meaning in this chart.

**Device nodes defined as the smallest reported feature size for a specific device technology. Subsequent technology nodes will have smaller minimum feature sizes. Above generations range from 10 nm to 1.75 nm.

C. Grant Willson and H. Ito at IBM Almaden Research Labs and Jean M. Fréchet, then at the University of Ottawa in Canada, developed the chemical amplification concept used today as a successor technology to Novolak/diazo-naphthoquinone (DNQ) systems, which were not suitable for the DUV wavelength: Novolak resins absorb too strongly in that part of the spectrum (Brock 2007). After much experimentation, polyhydroxystyrene (PHS) emerged as a suitable DUV resin, but it also needed a new

way to switch its solubility on exposure. At the same time, in the early days of CARs, the available light sources (mercury high-pressure lamps) had low light output in the DUV region.

The chemical amplification concept illustrated in Figure 3 provided an elegant new solubility switching mechanism that also made it possible to achieve the high photospeeds suitable for use with low-power sources (Brock 2007). As Figure 3 also shows, image formation in CARs splits into two steps: a light reaction in which a PAG generates a strong acid catalyst, and a dark reaction in which the photoacid catalyzes a reaction that changes the solubility of the resist in the exposed area, typically during a post-exposure bake (PEB) process. Since the photoacid is a catalyst, it regenerates at the end of the reaction cycle. The original photo event (the absorption of a photon in a PAG molecule, which decomposes to form the catalytic photoacid) is thus amplified by the number of solubility-switching catalytic cycles initiated by the photoacid. The number of cycles can range from hundreds to several thousands.

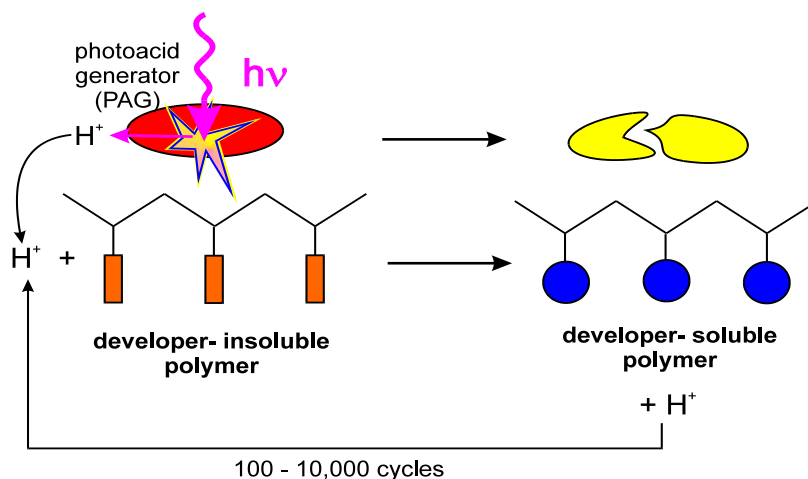


Figure 3: Basic scheme of chemically amplified photoresists: The solubility of a polymer changes during a dark reaction by the action of a photoacid catalyst, which is formed from photolysis of a PAG.

The chemical amplification principle requires strong acids and, for some of its implementations, acids that have anions that are also nonnucleophilic – that is, not prone to side reactions that would destroy the acid catalyst.

Figure 4 shows a catalytic cycle for tertiary alkyl ester deprotection, a type of reaction that underlies at least half of all 248- and all 193-nm CARs. The side reaction is the addition of the anion to the cationic intermediate formed, which destroys the catalyst and interrupts the catalytic cycle.

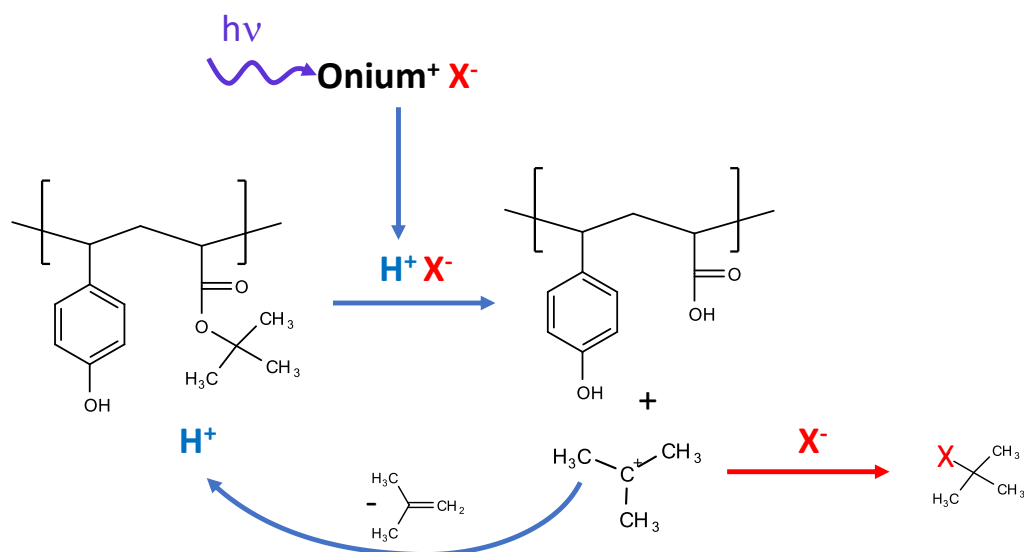


Figure 4: The catalytic cycle for tertiary ester deprotection by a photoacid (blue). A cationic intermediate with the formation of an alkene regenerates the catalytic H^+ . Red indicates the side reaction that destroys the proton catalyst and interrupts the catalytic cycle in the case of a nucleophilic anion X^- .

Early CARs used PAGs that were triphenylsulfonium (TPS) or diphenyliodonium salts of hexafluoroantimonates or hexafluoroarsenates (Figure 5) (Brock 2007). The generated hexafluoroantimonic (HSbF_6) or hexafluoroarsenic acids (HASF_6) are extraordinarily strong and show no tendency to react with cationic intermediates. These acids and their salts are toxic and cannot be discharged into wastewater, however. For this reason, PAG chemistry switched to sulfonic acids such as camphorsulfonic acid, which was used in the first commercial 248-nm photoresists (Ito, et al. 1994).

Other alkyl and aryl sulfonic acids with less bulky groups were not as common, since they were too prone to diffusion that degraded the quality of imaging. Salts of perfluoroalkyl sulfonic acids, in particular trifluoromethane and trifluoromethane sulfonate (triflates) and nonafluorobutane sulfonic acids (PFBS or nonaflates) became common, since they combined good solubility of their onium salts and high acid strength. In particular, the onium salt nonaflates quickly became a favored class of PAGs and turned into the workhorse of the industry.

Early 248-nm resists also used nonionic acid generators different from onium salts; however, onium salt PAGs quickly became the dominant PAG technology for 248 nm. CAR chemistry's migration back to longer wavelengths (predominantly 365-nm i-line lithography) led to the development of nonionic photoacid generators at these wavelengths, many of which contain PFAS (see Appendix A).

PAG Anion	Nucleophilic?	Other issues
PF_6^-	No	dopant
AsF_6^-	No	toxicity (wastewater)
SbF_6^-	No	toxicity (wastewater)
Cl^- , Br^- , I^-	YES	---
R-SO_3^-	No	---

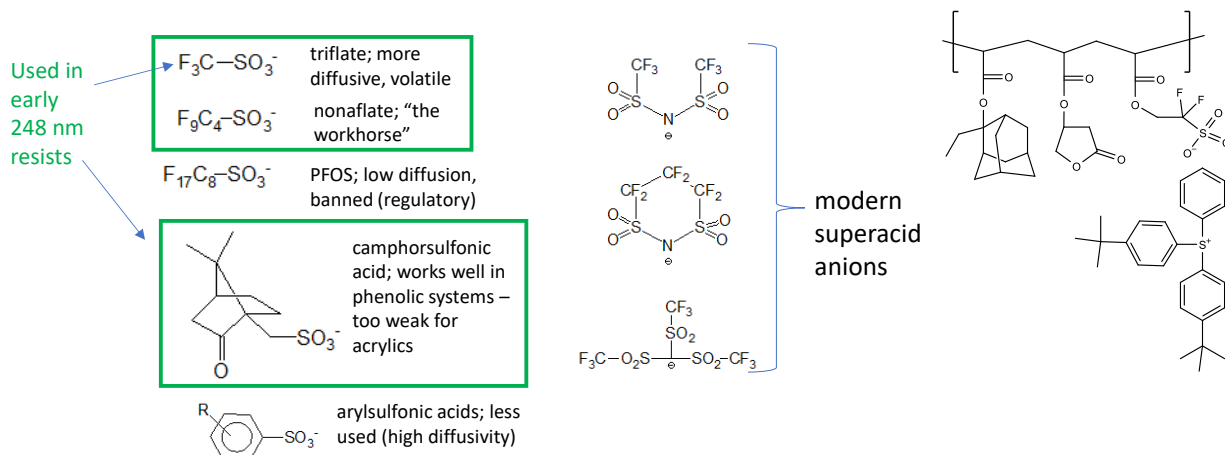


Figure 5: Comparison of anions suitable for use in PAGs: rationale for the selection of sulfonates as suitable anions (top); comparison of PFAS and non-PFAS sulfonates (bottom left); modern C1 and C3 bis-sulfonamide and tris-sulfomethide superacids (center); example of a polymer-bound PAG anion with adjacent onium counteraction (right).

PFAS PAGs became even more important with the advent of 193-nm lithography, which required a new class of transparent resins: PHS and other phenols were, again, too absorbing. The new resins were based on tertiary esters of aliphatic carboxylic acids and worked very similarly to the tertiary ester resists used in 248 nm, with one significant difference: In these new resins, the dissociation of acids was not assisted by convenient stabilizing groups such as phenols, and all but the strongest acids remained in a undissociated and catalytically inactive form. Acids like camphorsulfonic acid, which worked in phenolic resins for 248 nm, turned out to be completely ineffective in 193 nm (Figure 6). Only the strongest acids – the perfluoroalkyl sulfonic acids – are effective catalysts in 193-nm resists.

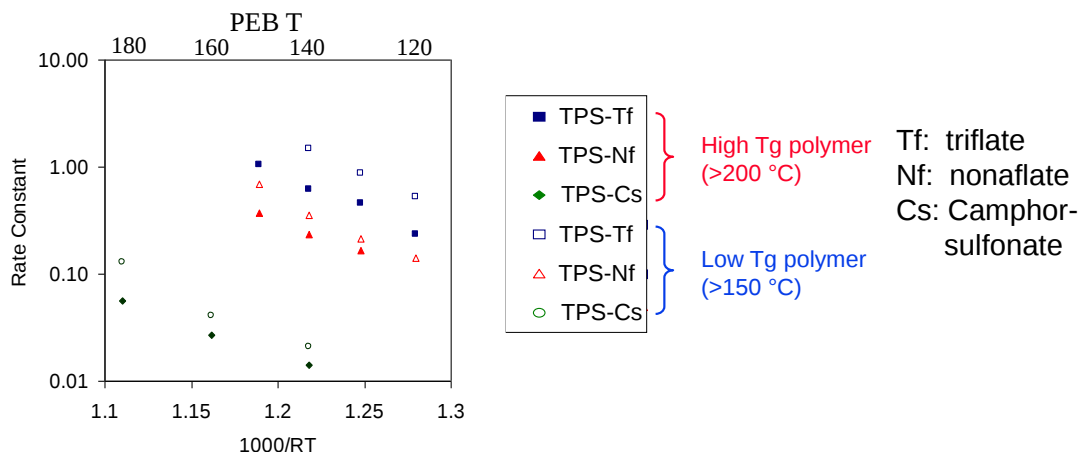


Figure 6: Comparison of rate constants for deprotection of typical tertiary alkyl ester 193-nm photoresists with PFAS-based photoacids (triflate and nonaflate) and camphorsulfonic acid. The activity of photoacids is higher for low glass-transition-temperature (Tg) polymers. The weaker camphorsulfonic acid is ineffective in both types of polymers; only the stronger PFAS acids are suitable for use in 193-nm resists (Pohlers, et al. 2004); (Jeffrey Byers, personal communication, 1998).

Today, the majority of 248-nm resists and all resists for 193-nm dry and immersion lithography use perfluoralkylsulfonates as photoacids. In most cases, they are used as anions to onium salts. Among the PFAS-containing materials used, PFBS accounts for a large fraction of the total. Longer-chain PFAS-containing materials have always been uncommon since they show slow photospeeds, and what use there was has largely been discontinued. Polymer-bound PAGs, where the acid attaches to the polymer backbone to reduce its diffusion, use shorter-chain PFAS-containing materials.

The transparency of PFAS acids allows them to be flexibly used at all optical wavelengths for lithography. They are chemically inert, highly soluble, not prone to side reactions in the chemical amplification resist process, and the larger members of the group (C4 or the modern C1 and C3 superacids shown in Figure 5) have near-optimum levels of diffusivity for many applications.

As shown in Figure 7, this unique set of properties of PFAS superacids makes their use highly attractive, which is why they found such widespread application. No other class of materials is known to combine all of these favorable properties.

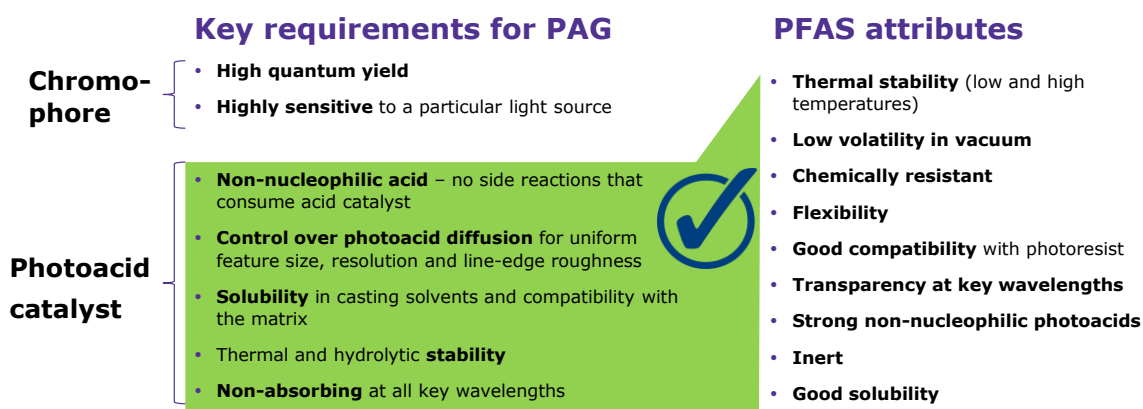


Figure 7: The benefits of PFAS photoacids in PAGs.

2.0 Options for the Replacement of PFAS-Containing PAGs

The replacement of a PAG is a difficult operation that requires reformulating the photoresist to achieve equivalent performance, and even subtle changes in the composition or chemistry of the photoresist polymer, solvent or additives can have drastic impacts to functionality. Even if it is possible to achieve equivalent performance for one mask set or application, you cannot assume that this will be the case for all mask sets or applications.

PAG replacement requires both a redevelopment of the resist at the materials manufacturer as well as significant resources for testing, validation and integration by the photoresist end user. Successive layers in chip manufacturing for advanced nodes are highly connected, and what appears to be a minor change in a photoresist wall angle, for example, can cause major effects in a later layer.

Modern photoresists typically contain more than one (and commonly, as many as three or four) different PAGs formulated to fine-tune cation absorption and quantum yields as well as photoacid strength and diffusivity (see Figure 8). Since it is not possible to easily measure diffusivity and other underlying phenomena quantitatively, the nature of the PAGs and their concentrations are determined by systematically varying formulations and evaluating the effects on lithographic performance. The effort required to change a PAG in such a fine-tuned formulation is nearly equivalent to the effort needed to originally develop the resist.

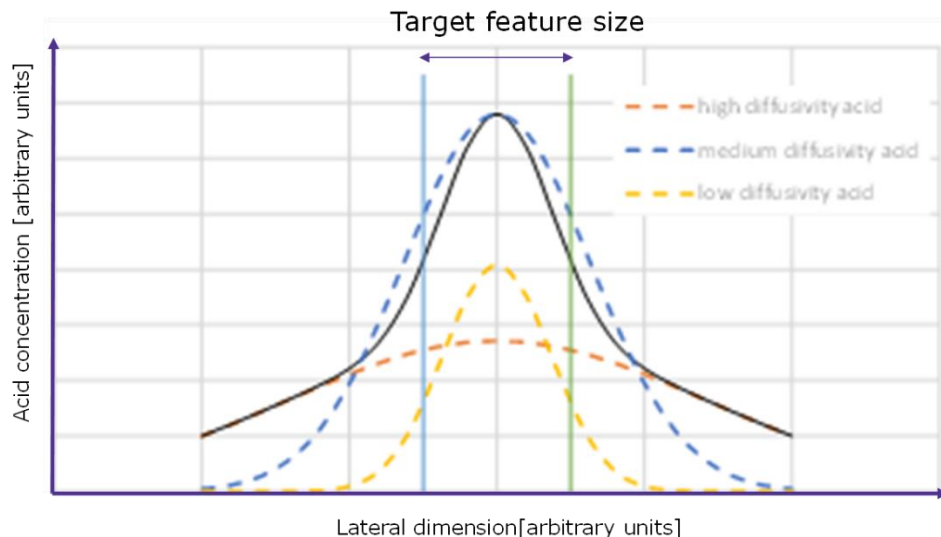


Figure 8: Blending different PAG types to impact acid diffusion profile. In this example, combining a low-diffusivity photoacid with a high-diffusivity photoacid results in a profile with a higher slope at the mask line edge (indicated by the vertical lines) than with a medium-diffusivity photoacid alone. Thus, using only the low-diffusivity PAG would result in a low photospeed, and using only a high-diffusivity PAG would lead to poor resolution.

We see three basic options for replacing C2-C4 PFAS-containing PAGs in today's advanced photoresists, which are, in order of increasing difficulty:

- Replacing C4 PFAS with more easily degradable C4 PFAS anions.
- Replacing C4 PFAS with shorter-chain C1 anions.
- Replacing PFAS PAGs with non-PFAS PAGs.

Let's describe each of the options in more detail, while noting that these new PAGs will generally not be drop-in replacements and may not provide required manufacturing characteristics.

2.1 Replacing C4 PFAS with More Easily Degradable C4 PFAS Anions

Figure 9 shows PFBS, the workhorse anion in many CARs, and two other C4 PFBS anions that are close in structure. PAGs containing these anions are close in performance to PFBS-based compounds and are nearly - but not – a drop-in replacement. And while they are more susceptible to degradation than PFBS, these alternative PAGs do not necessarily degrade easily. Their degradation behavior and toxicological profile have not been studied in detail. While these PAGs come closest to drop-in replacements for PFBS, it is not clear whether their use will be more acceptable than that of PFBS itself, and industry research continues and more evaluation will be needed.

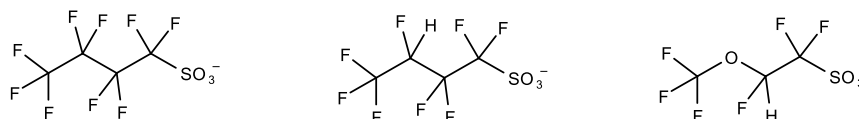


Figure 9: PFBS (left), octafluorobutanesulfonate (center) and 1,1,2-trifluoro-2-(trifluoromethoxy) ethane sulfonate (right).

2.2 Replacing C4 PFAS with Shorter-Chain C1 Anions

The quintessential C1 anion, trifluoromethane and trifluoromethene sulfonate, has been used in 248-nm resists, primarily at larger feature sizes. Because of its small size, however, it diffuses easily, and triflic acid also has an appreciable vapor pressure that can lead to it evaporating from exposed resist areas and redepositing on areas intended to be unexposed (“chemical haze”). Trifluoromethane and trifluoromethene sulfonates are thus not suitable for advanced photoresists and cannot be considered a candidate for replacing a longer-chain PFAS such as nonaflate.

Bis-sulfonamides and tris-sulfonylmethides are a new class of nonsulfonate superacids in advanced resists. While there are C4-PFAS-substituted derivatives and C3 PFAS ring systems (see Figure 5), there are also two C1-substituted anions that combine low diffusion with high acid strength (Figure 10). It is possible to use these anions as PFBS replacements; however, they will not be drop-ins, and photolithographic resists switching to PAGs that contain these alternatives require reformulation. The ease of degradation, environmental fate and toxicological profile of these two anions will require additional evaluation, as it is now generally unknown.

Another consideration complicating the evaluation of PAG alternatives is the various definitions of PFAS. Under the present U.S. Environmental Protection Agency definition, the two structures shown in Figure 10 on the right are not PFAS (although they are PFAS under other definitions used by other regulatory agencies and governmental/nongovernmental bodies) (United States Environmental Protection Agency 2021). Determining optimal replacements includes a review of all environmental, health and safety considerations of such potential alternatives to ensure they are not more impactful than the current solutions as it concerns these metrics.

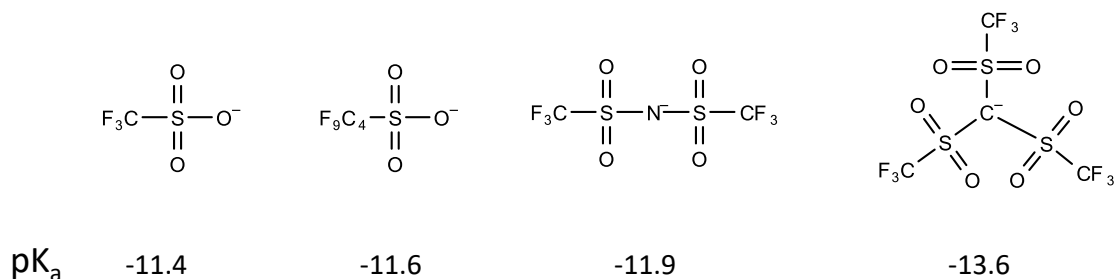


Figure 10: Modern C1 anions suitable for use in advanced resists: bis-trifluoromethylsulfonamide and tris-(trifluoromethylsulfonyl) methide anions, respectively, and the acid dissociation constant (pK_a) values of the conjugated acids (on the 1,2-dichloroethane scale) compared to trifluoromethane sulfonate and PFBS (left) (Paenurk, et al. 2017). The two C1 acids meet or exceed the strength of PFBS, while showing similar diffusivity and a lack of side reactions in CARs.

2.3 Replacing PFAS PAGs with Non-PFAS PAGs

Very few studies have focused on the replacement of PFAS PAGs with non-PFAS PAGs (Glodde, Liu and Varanasi 2010); (Suzuki and Johnson 1998); (Liu, Glodde and Varanasi 2010).

A 2010 publication by researchers from IBM describes what may be the best performance of a non-PFAS photoacid in 193-nm resists: pentacyanocyclopentadiene (CN5; see Figure 11) (Glodde, Liu and Varanasi 2010). CN5 is a superacid with an extremely low pK_a (–20.2 on the 1,2-dichloroethane scale) because its anion is a resonance-stabilized aromatic 6p-electron system, although the acid has low diffusivity

(Glodde, Liu and Varanasi 2010). The onium salts of CN5 and the closely related CN4-C1 are well-soluble in common casting solvents.

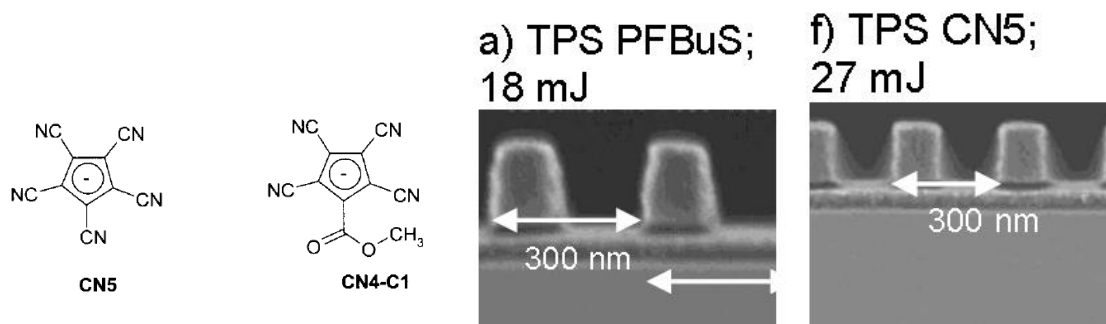


Figure 11: Structures of the CN5 and CN4-C1 anions and cross-sections of 150-nm lines imaged in 193-nm test photoresists using equimolar concentrations of TPS nonaflate (left) and TPS CN5 (right). Note the 50% higher exposure energy needed for TPS CN5, even though the PEB temperature for the TPS CN5 formulation was 140°C vs. 120°C for TPS PFBS (Glodde, Liu and Varanasi 2010).

The CN5 example also highlights the issues that photolithographic resist chemists face when looking for non-PFAS photoacid replacements: not only is the acidity and diffusion relation completely different from the currently used ones (as evidenced by the slower photospeeds even at higher PEB temperatures – see Figure 11), but the use of the CN5 anion is not a good option for 248-nm resists because of its high extinction coefficient (absorptivity) at that wavelength (Figure 12). In contrast, PFAS-based anions are transparent at all optical wavelengths and are suitable for all of them.

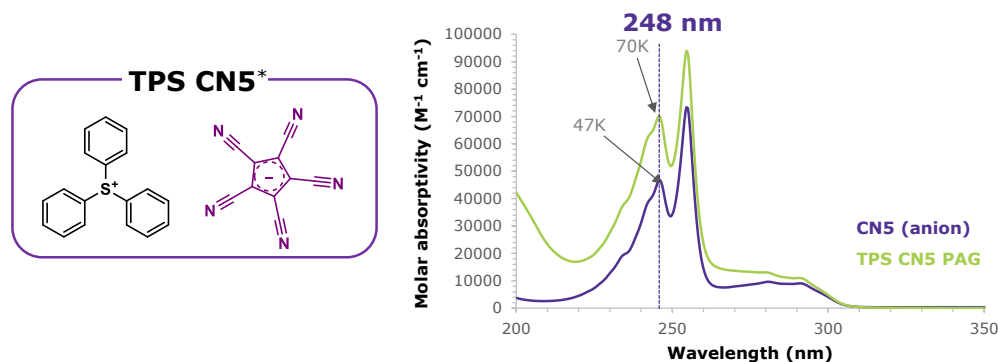


Figure 12: Absorption spectra of the CN5 anion and TPS CN5 (Daniela Carja, personal communication, 2022). While the CN5 anion has low absorption at 193 nm, it has a high molar absorptivity at 248 nm.

Another 2010 paper by the same team of IBM authors describes the use of thiophene derivatives as 193-nm photoacids (see Figure 13) (Liu, Glodde and Varanasi 2010). Again, comparison with a PFBS standard shows that while it is possible to use such PAGs in 193-nm lithography, they are not a drop-in replacement.

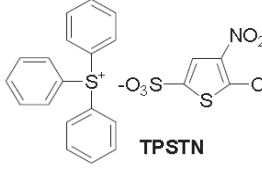
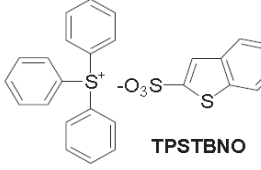
 TPSTN  TPSTBNO			
PAG	Optical density @193 nm [μm^{-1}]	Dose-to-Size for 150 nm L/S [mJ/cm ²]	Structure quality
TPS PFBS	0.99	20	Good
TPSTN	0.93	22	Some top rounding
TPSTBNO	1.11	28	Slight footing

Figure 13: Comparison of resist performance for a test 193-nm resist with 5% weight-in-weight solids TPS PFBS and TPSTN and TPSTBNO at equimolar concentrations to that loading.

There is only one early (1998) systematic comparative study of 248-nm photoacids, but the study is limited to contrast curves and does not report patterning performance (Suzuki and Johnson 1998). From the table of results (Figure 14), it is apparent that only two photoacids come close to the performance of PFBS and triflic acid. One of them is a pentafluorobenzenesulfonic acid, which may or may not be defined as PFAS, but is perfluorinated. The second one, 4-nitrobenzenesulfonic acid, is significantly lower in photospeeds. However, the resin systems used in 248-nm lithography can work with a wider range of acid strengths, so there are more options than for 193-nm lithography.

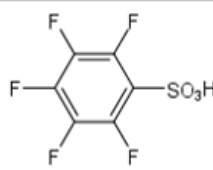
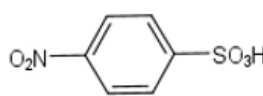
Generated acid	Sensitivity (E_0) [mJ/cm ²]
	14
C ₄ F ₉ SO ₃ H	17
CF ₃ SO ₃ H	21
	27

Figure 14: Excerpt from a table comparing contrast curve sensitivities (open-dose energies E_0) for photoacids used in a 248-nm resin (Suzuki and Johnson 1998).

There is one class of non-onium non-PFAS PAGs for 248 nm already currently in use: bis-sulfonyldiazomethane PAGs. In these PAGs, exposure leads to a loss of nitrogen followed by a rearrangement and hydrolysis that leads to the formation of a strong acid (see Figure 15). These PAGs are unique in that they become more transparent upon exposure (“bleach”), whereas other PAGs typically show no absorbance change or even an increase. However, the special nature of these PAGs does not

make them an easy candidate to replace PFAS-containing onium salts: the acids produced for them are weaker, and the amount of acid formed is lower due to the side reactions shown in Figure 15.

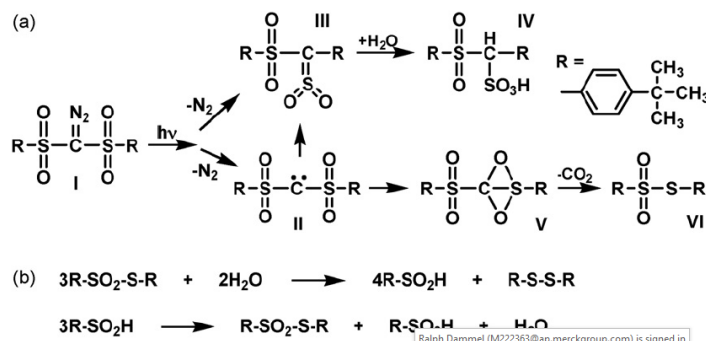


Figure 15: Mechanism of acid formation from bis-sulfonyldiazomethane PAGs in 248 nm (Moon and Kim 2007).

Table 1 compares the performance of PFAS PAGs and the photoacids generated from them to that of the non-PFAS CN5 (Glodde, Liu and Varanasi 2010) and thiophene sulfonate PAGs (Liu, Glodde and Varanasi 2010) reported in the literature. The comparison illustrates the difficulty involved in finding non-PFAS replacements for PFAS photoacids that can meet all performance criteria simultaneously. PFAS PAGs show good to excellent performance for all listed performance criteria. In contrast, no known non-PFAS PAG exhibits the same level of performance for all criteria: while a candidate chemistry might show good acid strength, it will have a lower photospeed because of its lower acid diffusivity, and at the same time the acid anion might be transparent for a single wavelength only. Even if confined to developing wavelength-specific photoacids, meeting the remaining criteria at the same time remains challenging.

PAG/Photoacid performance and environmental criteria	PFAS PAGs/photoacids	CN5 non-PFAS PAG/photoacid	Thiophene sulfonate PAG/photoacid
Photospeed*	excellent	poor	good
Acid strength	excellent	excellent	good
Diffusivity	good to excellent**	lower than PFAS acids	high to too high
Pattern quality/LWR	good	LWR higher than commercial resists	LWR much higher than commercial resists
Transparency at all exposure wavelengths	excellent	Not transparent at 248 nm	Not transparent at 248 nm
Solubility of PAG in casting solvents	good	good	poor to moderate
Lack of side reactions in CA resists	excellent	excellent	excellent
High process temperature requirement	none	yes	none
Uniformity of PAG distribution	good	good	good
Toxicity	moderate to high	high***	moderate
Environmental persistence	highly persistent	assumed to be degradable	assumed to be degradable

* Photospeed is a composite of acid strength, acid diffusivity and PAG quantum yield.

** Very low diffusivity requires polymer-bound photoacids.

*** The cyanide ion is found in rat stomachs when fed CN5.

Table 1: Lithography performance comparison of PFAS-containing and non-PFAS-containing PAGs.

Additional research and invention are required to develop a library of potential non-PFAS photoacids and corresponding PAGs to successfully reformulate current PFAS-containing CARs.

3.0 Timelines for Developing Non-PFAS PAGs and CAR Reformulations

There are four key parameters that interact to define the performance of a PAG (Figure 16). While we have already described acidity, absorbance and diffusivity, solubility in acceptable casting solvents is another dimension that can limit the use of otherwise promising approaches. These four parameters are not independent: changing one property will impact the others. This makes the development of new classes of non-PFAS PAGs more challenging.

What are the key parameters for tailoring a perfect

Photoacid generator

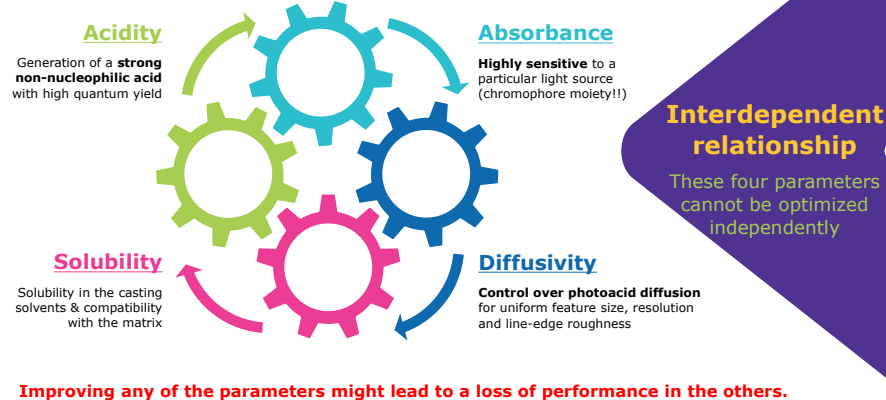


Figure 16: Key parameters for a high-performing photoacid generator.

Figure 17 shows the timeline for the development of new photolithographic materials. To give a historical perspective, the development of CARs took 20 years from the first publications to production implementation. PAG changes will take less time: an estimated three to four years for early invention work, three to eight years for resist formulations, and another approximately ten years for customer process development and integration. The runway from starting research and development to the full production proliferation of a resist containing non-PFAS photoacids is about fifteen to more than twenty years.

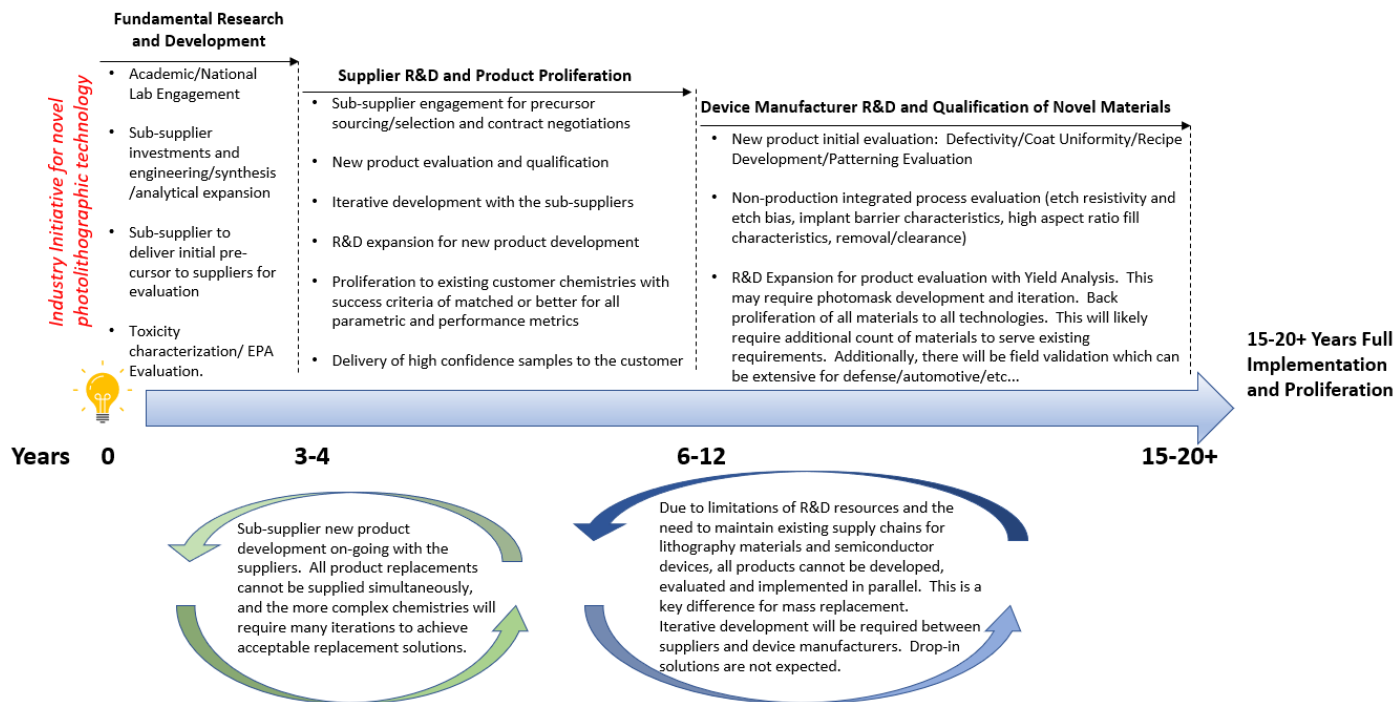


Figure 17: Conceptual timeline for the bulk replacement of existing lithography technologies with novel materials.

4.0 Supplier Research and Development for New PAG Materials and Associated Photoresists

The process for developing new PAG materials for photoresists is nontrivial and time-consuming. PAGs dictate patterning performance for lithography photoresists (Pawlowski, et al. 1991). While PAGs have been around since the 1980s, the demand for increased specificity has continued to grow. Technologies have progressed steadily per Moore's law (as illustrated in Figure 18) over the last four decades, with patterning target requirements of 1000 nm in the 1980s (1/80th the diameter of a human hair) to the leading-edge technology today of 7 nm (three times the width of a human DNA strand and approaching molecular dimensions) (Maestre 2021); (Bloemen 2015); (API 2020). Figure 19 refers to these types of industry dimensions and comparable biologic examples. In addition to the patterning targets, there are more stringent requirements on photospeeds, depth of focus, line-edge roughness and the ability to pattern more challenging high-aspect ratio features (Gogolides, et al. 2006).

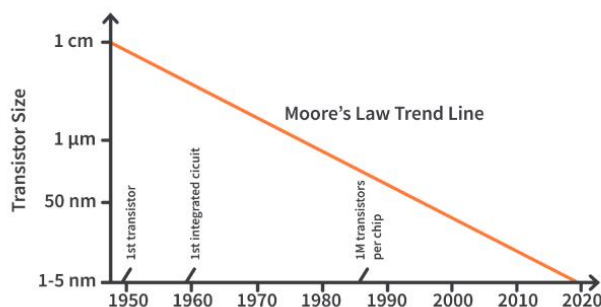


Figure 18: Moore's law trend for transistor size (1950-present) (Maestre 2021).

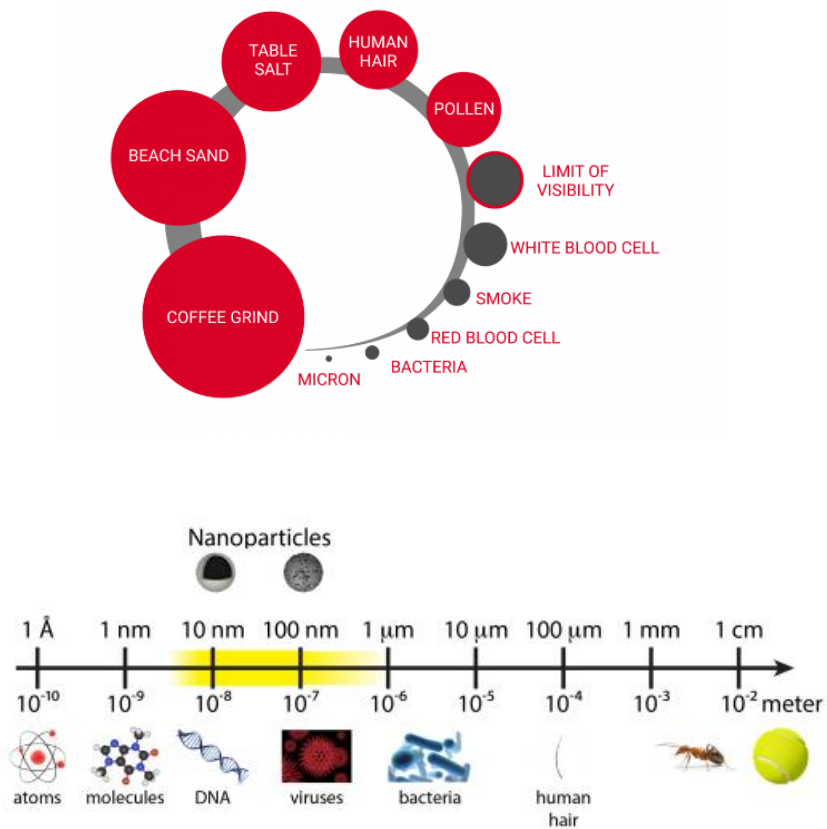


Figure 19: Micron size comparison (API 2020); (Bloemen 2015).

As demand for computing processing power and efficiency grows worldwide, so too must lithography scanner technology, which has progressed steadily from 248 nm to 193 nm to 193-nm immersion tools and beyond. These exposure platforms were necessary to achieve smaller and smaller transistor sizes to drive increases in processing power (Thakur 2022). Each of these platforms will require specific photoresists and associated PAGs.

While not specifically related to PAGs, it will be necessary to explicitly engineer formulations for customer requirements related to etch resistivity, implant barriers, viscosity and thickness, along with compatibility with various suites of anti-reflective underlayers, overcoats and industry solvents. All components of photoresists (monomers, resins, PAGs, quenchers, surfactants, additives) must work in harmony to achieve customer requirements. The sheer number of new formulations within the industry will quickly grow to the hundreds and continue to increase.

5.0 Supplier Case Study for PFAS Removal in PAGs

The following supplier R&D case study assumes the ability to replace all PFAS-containing PAGs with non-PFAS PAGs that perform identically. There are currently no technologies available to achieve this replacement, and there are legitimate questions as to whether this is even possible for some photoresists. With that understanding, the estimated timeline for supplier R&D of non-PFAS-containing components will be modeled.

New formulations will undoubtedly require an expansion of existing subsupplier relationships and supply lines, as well as engagements with new subsuppliers. There are timelines associated with this preliminary

portion of the R&D of new PAGs. The subsuppliers need development time to produce and evaluate samples. Development time will include many iterations to meet existing supplier specifications for performance, purity and other key material parameters. After obtaining a suitable candidate, it will be necessary to complete negotiations for price and volume expansion activities (including sub-supplier vessel and tooling scale-up). The supplier R&D timeline would take two to four years for existing technologies (shortening fluorinated carbon chains) but could be more extensive (approximately 10 years) for non-PFAS technologies given the complexity of chemical and molecular requirements and the amount of R&D expansion required. Subsuppliers will need to commit extensive facility and engineering resources to these activities, requiring new investments in headcount and facilities. Once those resources are available, the expenditure would need to achieve return-on-investment expectations. More simply stated, if the industry need is exceptionally low in terms of volume, there is little reason to perform the R&D in the first place. It is also reasonable to believe that larger volumes of PFAS-containing materials will still be in high demand in regions of the world where there are few to no restrictions. This has the potential to make non-PFAS precursor material rare and extremely costly.

Once the supplier has access to the precursors and non-PFAS PAGs, they can begin development, including the testing and fine-tuning of formulations. Depending on the application, each photoresist will require multiple iterations to achieve existing coat uniformity, fill characteristics, patterning performance and etch/polish/diffusion parameters with low defectivity. Even slight changes to any portion of the formulation could have unexpected and critical impacts on performance. As such, reformulations with non-PFAS PAGs will take extensive, individual efforts for all customer products. Industry experts within the Semiconductor PFAS Consortium estimate the development timeline for a single formulation at one to more than five years.

It cannot be overstated that the removal of PFAS in PAGs would be a fundamental change to the industry, requiring a reimagining of the fundamentals of lithography. It took the semiconductor industry roughly 20 years to convert PFOS-based chemistries to short-chain PFAS-containing materials in lithographic formulations, a timeline driven mostly by the fact that PFAS was not novel technology but represented moving from longer- to shorter-chain fluorinated chemistries. Novel technology replacement of nonfluorinated replacement timelines will require even longer timelines (see Figure 17). Even minor changes to PFAS-containing PAGs can take years to fine-tune, while its removal involves the novel pathfinding of innovative chemistries and processes technologies.

The cost to transition from PFAS to non-PFAS-containing PAGs is difficult to model. Historically, only a handful of different formulations are under development and evaluation at one time. This type of bulk conversion would require an expansion of R&D resources with a significant increase in engineers (on average, an expected seven to 12 new hires per supplier). There would also need to be an expansion of synthesis, metrology and analytical tooling. And as this would represent new and novel technology, the evaluation methodology would be much more stringent and time-consuming. As described earlier, the anticipated time and costs for securing subsupplier volumes will be extensive and may require upfront capital spending to offset subsupplier expansion and fabrication costs. Because the overall volume of PAGs is low from an industrial standpoint, it is difficult to predict how many subsuppliers would be willing to expend upfront capital for development, even at a substantial increase of subsequent raw materials costs. Estimates for a single new material would be \$5 to \$10 million. While this does not scale linearly with all new resists (because it is possible to leverage equipment and headcount to multiple materials), there is still the expectation that each new material could cost \$2 to \$5 million to develop. Investments for a single semiconductor device manufacturer could be \$25 to \$60 million.

The overall timeline for a full transition to non-PFAS PAGs will be extensive. There will need to be a balance between R&D expansion and long-term volume forecasts. It will not be possible to develop these materials in parallel without jeopardizing the supply chain for all device manufacturers. This concern is also true of the subsuppliers who will need to produce the precursors and the device manufacturers who will need to produce the final product.

The implementation of non-PFAS PAGs into new R&D technologies at device manufacturers has the potential to be more rapid than back-proliferation to existing technologies, which have fully established process flows. A reasonable timeline for the sample readiness of all materials with non-PFAS-containing PAGs into R&D technologies would be four to seven years for sample preparation after identifying a viable replacement candidate. This viable candidate development timeline is currently unknown. Back-proliferation is much more complex and would have timelines on the order of five to 10 years for sample readiness.

We must again stress the highly unlikely assumption in this evaluation that there will be available PFAS-free PAGs that accommodate all commercial products. There are currently no commercially available substitutes for most of the formulations. There is also evidence that replacements may be chemically impossible for many applications. While there were successful industry efforts to remove PFOA and PFOS from components such as surfactants and PAGs, these removals involved building on existing technologies (shorter fluorocarbon chains and existing, capable substitutions). For PAGs specifically, it may be chemically impossible to create strong and stable acids with nonfluorinated substitutes, especially as we enter the realm of molecular feature sizes. Full PFAS restrictions have the potential to completely change the landscape of photolithography, undoubtedly stalling the progress of semiconductor innovation and leading to supply-chain disruptions and elevated costs to customers.

6.0 Device Manufacturing Qualification of New Photoresists

The qualification of lithography materials for semiconductor device manufacturers is a laborious and costly endeavor. Lithography continues to carry the highest degree of complexity for chemical qualification in the semiconductor industry given its sensitivity and need for specificity. Of these chemicals, PAGs and the associated photoresist qualification require the most intensive and rigorous qualification standards.

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

As technologies and process nodes progress from 14 nm to 10 nm to 7 nm, the resultant lithography layer count increases as well, with more than 70 photolithography layers for leading-edge technology (see Figure 2 in the Historical Background and Current Situation section of this paper) (National Nanotechnology Initiative 2022). Likewise, the need for specialized photoresists continues to increase throughout the industry to support ever-increasing design complexities (Wu 2020). Historically, as qualification opportunities have arisen for defect reduction, cost reduction or performance improvements, it has been rare to find a drop-in solution. Each substitution needs tuning for the specificity of the layer(s)

on which it is used, a trend likely to continue with non-PFAS substitution candidates, as demonstrated in Table 1 of this case study. As described earlier, approximately 100 or more of these photoresists within the industry would need replacing. It is highly likely that replacing these materials would result in additional photoresists for each technology.

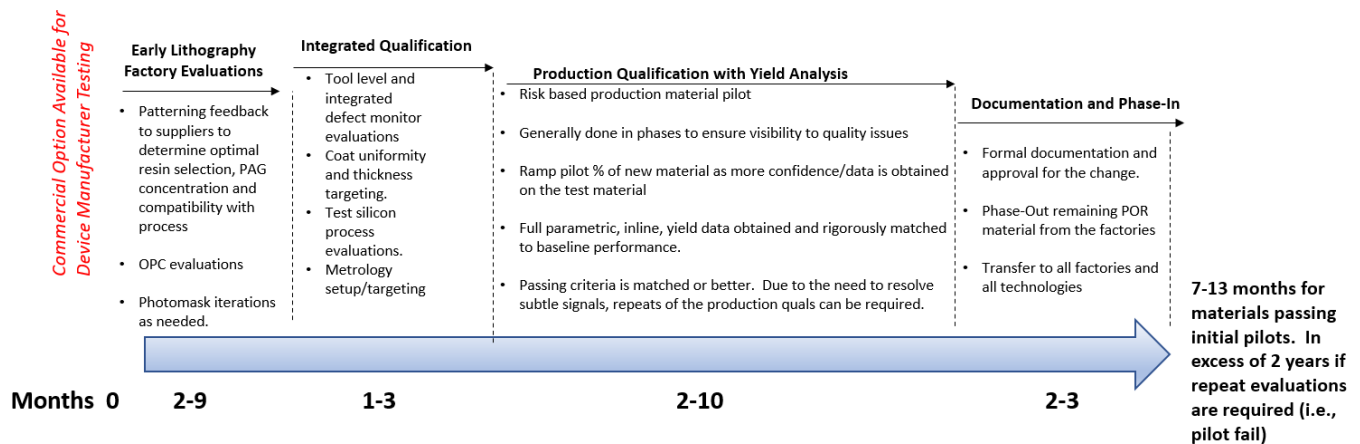
Consider a reasonable hypothetical for a generic semiconductor device manufacturer who replaces 20 PFAS PAG-containing photoresists. Assuming a drop-in success rate of 70% (which is almost certainly an overestimate), you would need 26 photoresists to accommodate existing lithography needs. These 26 photoresists would need to receive full factory qualification and ramp into high-volume manufacturing. Each material would need to pass rigorous patterning qualifications and meet the exacting performance standards of existing materials. Early evaluations require fine-tuning of the resin, PAG, PAG concentrations and additives. Early patterning evaluations such as optical proximity collection (OPC) take an average of two to five months to settle on a formulation that meets existing layer specifications. This timeline can expand by one to four months depending on the need for photomask iterations to accommodate the new material.

Following lithography-specific qualification, the material undergoes an integrated process qualification. Again, this material must pass existing lithography and integrated performance parametrics and specification limits for the PFAS-containing resists, including defectivity, coat uniformity and thickness evaluations, as well as initial test product evaluations. While some of these parameters are not specific only to PAGs, their validation is required for any process change and will impact qualification timelines. Iterations of the formulations, filtration and viscosity are common during this phase and will require one to three months, depending on the availability of new test material and the processing and metrology equipment at the factory.

Final qualification requires piloting the 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 to perform risk-based phase-in, the pilot itself could take two to six months. At this point, it will be necessary to perform a data comparison 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. This process regularly requires additional production commitments to rectify flier signals and low-level mismatches with similar times already mentioned, impacting the timeline reported earlier by three to four months.

Finally, the material needs to be formally documented as the process of record (POR), with high-volume batches replacing existing stock fully. Even with rapid transition, this process will take two to three months. For materials that pass yield qualification on the first attempt, the overall timeline for qualification would be seven to 17 months. These time frames have the potential to extend to more than two years if mask iterations and yield evaluations need repeating.

It will not be possible to qualify all of these materials at the same time: an additional complicating factor. There are limitations on processing tools and metrology availability, as well as engineering availability. Most importantly, though, depending on the layer(s) on which these resists are used, qualifying multiple resists can convolute yield evaluation and cause an increase in repeat qualification. In other words, some of these materials will have to be qualified serially rather than in parallel. Figure 20 shows a generic timeline for replacing a PFAS-containing PAG and subsequent photoresist.



Note: timeframes are estimates and can vary depending on materials and technology applications.

Figure 20: Device manufacturer timeline for the replacement of a single PFAS-containing material.

The timeline to integrate and replace the materials on leading-edge R&D technologies is three to more than six years for qualification and implementation once samples are available. In these situations, pathfinding resources such as coat and develop units, scanners, metrology, and development engineers are available and evaluating new materials regularly. The replacement of chemistries in fully developed and ramped technologies is much more complex, however. Tool availability and engineering workforces are at a premium. There is no current infrastructure to support a full conversion of new photoresists for device manufacturers. Even if there were sufficient resources to qualify and implement these new materials, they could not be done in parallel for the reasons described in the preceding paragraph. The timeline would double for full replacement to six to more than 12 years, which is congruent with the device manufacturer qualification and replacement of PFOS-containing PAGs at device manufacturers' facilities after the commercialization of shorter-chained replacement options.

Manufacturer material qualifications are costly from a labor and materials perspective. Engineering and technician time is at a premium and must be leveraged heavily during the planning, execution and analysis phases of the qualification. These activities also reduce the amount of production wafers that can be processed on the tools which adds to overall manufacturing cost. Lithography tools are expensive (tens of millions to over 100 million), so the factories tend to run with minimum tool capacity versus their output goals (Levinson 2019). This lean tool capacity can impact the overall timeline for production qualification. Given the length of the qualification, the dispensed material costs can be high, as well as less direct costs such as OPC development, new photomasks (as needed), metrology costs and ancillary/support chemical usage. Overall, an estimated qualification cost for a single photoresist would range from \$350,000 to \$1.6 million, depending on the complexity of qualification and any resulting production yield fallout or die loss.

Returning to our hypothetical scenario assuming a 70% drop-in solution (moving from 20 to 26 resists to satisfy all layer needs) and an 80% yield qualification success rate, the overall cost to replace these chemicals would be approximately \$12 million. This is a generic device manufacturer cost estimate that will increase if a leading-edge technology uses a larger quantity of photoresists, or if there is unforeseen, severe-yield fallout during qualification.

Qualification may be required separately for different technologies and products. There should be an opportunity to perform the qualification pilots for multiple technologies in parallel, so it should not impact the overall timeline estimate, but it will scale the qualification costs.

7.0 Conclusions

CARs are a critical component in modern photolithography, helping reduce transistor size and improve chip performance. CAR performance depends heavily on adding PAGs, most of which depend on PFAS-containing materials for exacting patterning capabilities. PFAS-containing materials have unique attributes that are unavailable in other existing commercial products. They form strong nonnucleophilic acids with controlled/predictable diffusivity and are very stable in terms of temperature and side reactions. They are also highly compatible with photoresists in terms of being nonabsorbing at key wavelengths and highly soluble within existing base solvents. However, it is necessary to explore alternatives to PFAS due to increasing concerns about their persistence, bioaccumulation and toxicity.

The most direct replacement of existing C4 PFAS is by substitution with more easily degradable, shorter chain PFAS (especially C1) (much like what was done in the case of PFOS/PFOA). This would require extensive development and evaluation, with drop-in replacements unlikely. The full removal of PFAS from PAGs would be extremely complicated. No other replacement molecules (either commercially available or in the research phase) have been found that can match the performance of existing PFAS PAGs.

The removal of PFAS in PAGs would be a foundational change to the industry, requiring a reimagining of the fundamentals of lithography. There are currently no commercially available substitutes for most of the formulations. There is also evidence that replacements may be chemically impossible for many applications. Making the highly unlikely assumption that it is possible to develop non-PFAS PAGs for all required applications, we can only estimate the impact and timeline from subsupplier to supplier to device manufacture and finally, end product (20+ years depending on the material and the complexity of the application).

The development of non-PFAS PAGs will require extensive R&D, an engagement of new subsuppliers, and an expansion of facilities and research team support. Not all subsuppliers will be willing or able to invest the capital to generate new materials given the low volumes required from the industry, creating the potential to make non-PFAS precursors rare and subsequently much more expensive than existing materials.

Again, assuming it is possible to produce these materials, they will need rigorous evaluation from suppliers. After achieving performance matching of all existing characterization metrics, non-PFAS PAGs must be incorporated into photoresists that match the performance and functionality of existing PFAS-containing photoresists. It is unlikely that non-PFAS PAGs will be able to replace PAGs in all existing formulations, requiring the development of new photoresists to fit all use cases. We anticipate the generation of well over 100 formulations industrywide.

Because of existing limitations on engineering resources, metrology and synthesis equipment, as well as lead times for expansion, we predict that full sample readiness would take five to 10 years at an estimated cost of \$25 to \$60 million for each customer's material suite. Note that each device manufacturer's production plan will require differing and often custom lithography materials.

Much like supplier evaluations, device manufacturers must qualify each new photoresist for all existing applications. Even exceedingly small changes to formulations (surfactants, additives, filtration as examples) can have unintended consequences in a device process flow. These interactions are

complicated for suppliers to predict, and as such would require extensive yield analysis. And because we are discussing a change to one of the most important aspects of photoresist formulations, the qualification rigors are even more tedious. There would be no way to qualify all materials simultaneously given yield impact resolution and the availability of engineering and equipment resources. We expect six to 12 years for full evaluation and integration of existing materials from PFAS containing to non-PFAS containing, at a cost of \$12 million per device manufacturer.

The overall - optimistic - timeline of full implementation for all products is 15 to more than 20 years. The strain on resources and additional costs at all levels of the semiconductor industry for full PFAS replacement would be extensive. It is reasonable to believe that there would be significant supply-chain shortages of critical products during this switchover. All semiconductor products would likely increase in price and not recover due to the expected elevated costs of non-PFAS precursors.

We must stress again the assumption in this evaluation that there would be PFAS-free PAGs available to accommodate all commercial products. There are currently no commercially available substitutes for the vast majority of the formulations, for the reasons illustrated in Table 1 of this case study (Glodde, Liu and Varanasi 2010); (Liu, Glodde and Varanasi 2010). There is also evidence that replacements may be chemically impossible for many applications. While there have been successful industry efforts to remove PFOA and some PFAS from components such as surfactants and PAGs, this involved building on existing technologies (shorter fluorocarbon chains and existing capable substitutions). For PAGs, it may be chemically impossible to create these strong and stable acids with nonfluorinated substitutes, especially as we enter the realm of molecular feature sizes.

Additionally, we expect a massive competitive disadvantage for the U.S. and Europe if other regions do not adopt similar PFAS restrictions. Customers in regions with restrictions may have to switch to semiconductor device manufacturers from regions that continue using PFAS-containing materials. This has the potential to disrupt supply chains for applications such as defense, automotive, 5G, emergency services, transportation, health care and energy. Even if regulations allowed the importing of critical chips, demand would overwhelm manufacturers and lead to massive supply shortages across all industries.

It is not an overstatement to say that full PFAS restrictions have the potential to completely change the landscape of photolithography given the need to reimagine imaging technology. This could stall the progress of semiconductor innovation and computing power progress and make it impossible to manufacture some existing products.

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Appendix A: PFAS-Containing Nonionic Photoacid Generators

