# SIA PFAS Consortium

## The Impact of a Potential PFAS Restriction on the Semiconductor Sector

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## EXECUTIVE SUMMARY

RINA Tech UK Limited (RINA) were engaged by the Semiconductor per- and polyfluoroalkyl substances (PFAS) Consortium to gather information from members, to establish an evidence base, to inform the semiconductor sector in support of their respective information gathering activities, when considering the potential impact of PFAS restriction. This report comprises an assimilation of this evidence.

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The Semiconductor PFAS Consortium represents 69% of worldwide semiconductor manufacturing capital expenditure as well as 70% of global sales of semiconductor equipment in 2021. Its members represented over $400 billion dollars in revenue and directly provide over 500,000 jobs worldwide. The Semiconductor PFAS Consortium is organized under the auspices of the Semiconductor Industry Association (SIA). For more information, see www.semiconductors.org.

Semiconductor devices (also known as “chips”, or “integrated circuits”) are essential components of electronic devices. Semiconductor devices are extremely complex to manufacture, with leading devices requiring more than 2,000 process steps, hundreds of production materials, and approximately 26 weeks to manufacture and test. This requires the utilisation of process chemicals, manufacturing equipment, and manufacturing facility infrastructure which may contain PFAS. PFAS provide specific and unique capabilities within semiconductor process chemistries, semiconductor manufacturing equipment and facilities, as well as the electronic products they drive. Without PFAS, the ability to produce semiconductors (and the facilities and equipment related to and supporting semiconductor manufacturing) would be put at risk. Considering that the semiconductor industry was estimated as having global sales of $574 billion USD in 2022, the withdrawal of PFAS will have severe economic impacts. These impacts are significantly larger, if the consequential effects of chip supply and the societal impact of loss of device functionality are also considered.

The semiconductor industry has a history of proactively adopting voluntary elimination and reduction strategies, as a result of new information on the environmental concerns of the substances it uses. An example of best industry practice is the substitution of perfluorooctanesulfonic acid (PFOS) in the early 2000's that was found to be persistent, bioaccumulative, and toxic. The World Semiconductor Council (WSC) initiated an international voluntary commitment to phase out PFOS uses worldwide and announced the elimination of PFOS in 2011.[1]

The following are the key challenges the Semiconductor PFAS Consortium members have highlighted, due to their deep understanding of the effort required in terms of resources, challenges, and timeline, are necessary to introduce alternative chemicals into some of the world's most complex technology:

- Semiconductor manufacturing is highly integrated, uses thousands of process steps, and occurs at the nanometre scale.
- Some materials are unique and have such specific technical requirements that it is extremely challenging to find a viable alternative. No known alternatives exist for many of the industry’s uses of fluorocarbon-containing materials and in many instances a successful invention of an alternative substance needs to occur before subsequent steps of qualification can be undertaken.
- The organisation of collaborative research and industry alignment is sometimes needed when making significant changes. For instance, the industry’s voluntary commitments to a PFOS phase-

[1] WSC-May-06-Charter-Amendment-SIGNED.pdf (semiconductorcouncil.org)

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out and perfluorocarbon (PFC) emission reduction were only effective due to the alignment and efforts of the industry as a whole.

- The timeline needed to develop, qualify, and implement alternatives falls into the following four broad categories:
  - **3 to 4 years**: If an existing non-PFAS alternative is available, does not require infrastructure alterations, and can be demonstrated to provide adequate performance for a specific application, then it typically takes 3 to 4 years to conduct the necessary manufacturing trials and implement the successful alternative into high volume manufacturing (HVM).
  - **From 3 to more than 10 years:** In some applications, an existing non-PFAS alternative may be viable but requires tooling and/or process or facility changes before it can be successfully introduced into high volume manufacturing. In these cases, it may take from 3 to more than 10 years to introduce changes to the semiconductor manufacturing and related equipment (SMRE) and/or processes, and then perform qualification testing, and implement the non-PFAS alternative into HVM.
  - **From 5 to more than 25 years and successful invention is required**: For some applications, it is not currently possible to demonstrate that a non-PFAS alternative can fulfil the application-specific performance requirements. In these cases, it may be necessary to invent and synthesise new chemicals, and/or develop alternative approaches to device fabrication that provides the necessary electrical and computational performance. Invention is an open-ended endeavour without a fixed timeline or guarantee of success.
  - **No alternative is achievable:** In some cases, it may ultimately be found that a non-PFAS alternative is not capable of providing the required chemical function. If a non-PFAS alternative chemical cannot be invented, then the integrated circuit device structure may need to be abandoned in favour of an alternative device structure that may or may not provide equivalent performance. In some cases, the fundamental laws of chemistry and physics prevent the use of PFAS-free alternatives.
- This is only an overview and potential alternatives must be evaluated on a case-by-case basis considering technical, regulatory, as well as economic aspects. By its nature, the invention of an alternative has no clearly defined timeline, and, for some applications, there may be no known alternative. **When the alternative is not viable, the process will loop back to invention, research and development steps to find a different chemistry or technology that does not have the same issues.**
- Stringent qualification also has to take place with semiconductor customers to ensure that the semiconductor product guarantees the same function as the semiconductor product did previously.
- Qualification and replacement of critical materials is a highly complex, multi-step, multi-year, challenge which impacts multiple parts of the semiconductor supply chain.
- The possibility of regrettable substitution is an ever-present concern. The selection of alternatives must be well informed and consider current and potential future concerns.
- If alternatives decrease production yield even by very small percentages, significant increases are required in semiconductor manufacturing facility size, resulting in correspondingly increased chemical, water, and energy consumption, as well as waste generation.
- A decrease in the performance of PFAS-free alternatives would increase the consumption of parts and waste generation for some uses.

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Figure 0-1 provides a general overview of the semiconductor manufacturing process steps, operations, and systems evaluated by the Semiconductor PFAS Consortium and is based on the best and current knowledge of consortium members.

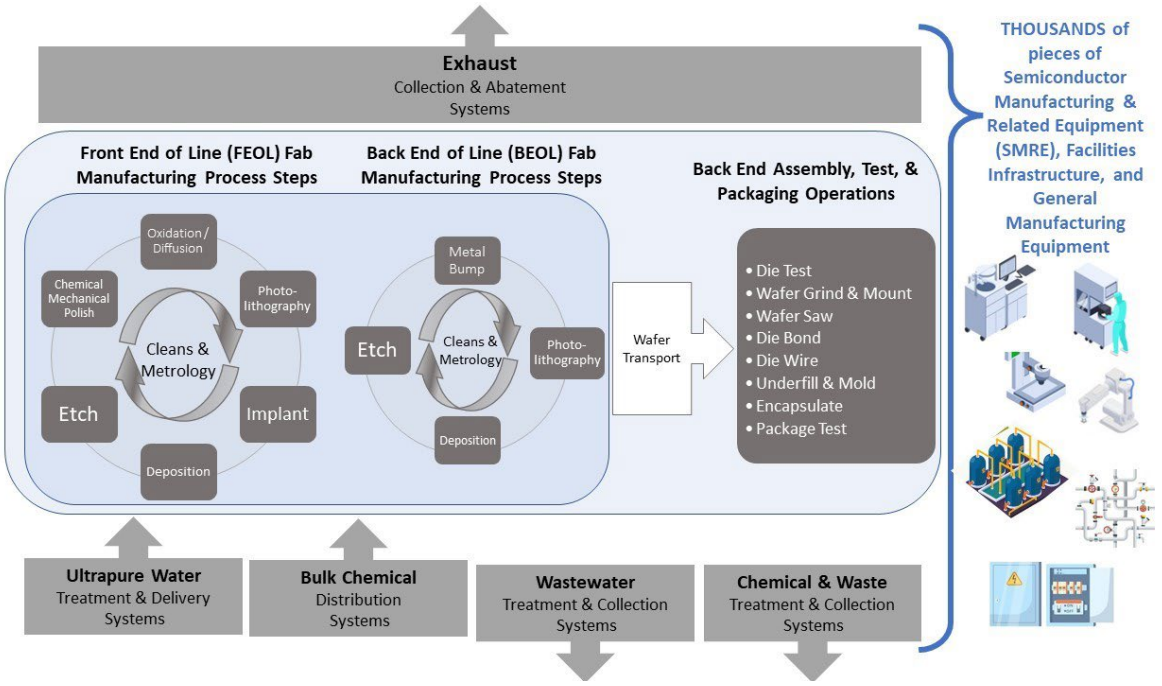


**Figure 0-1 General overview of the semiconductor manufacturing process steps, operations, and systems evaluated by the Semiconductor PFAS Consortium.**

The following highlights key uses and challenges in each of the application groupings which are critical to the semiconductor industry:

- **Photolithography** is a critical semiconductor manufacturing function, providing cutting-edge semiconductor transistor device dimensions from 2 to 180 nanometres in width with tolerances below these dimensions. For context the diameter of a human hair is about 100,000 nm. PFAS-containing materials within photolithography enable nanometre-scale semiconductor dimensions. Photolithography materials containing PFAS are a critical component used within photoacid generators in chemically amplified resists and bottom antireflective coatings, top antireflective coatings, surfactants, barrier layers, photo-imageable polybenzoxazoles and polyimides for dielectric and buffer coat applications, and photoresist applications.

  After more than 25 years of development, whilst some PFAS-free material substitutions may be possible, PFAS-free materials have not been shown to be successful or effective in the vast majority of photolithography applications. Possible PFAS-free alternatives would require total reinvention for many applications. The process of identifying and implementing alternatives involves academic research, material supplier research and development (validation) and scale-up, followed by device manufacturer efforts toward demonstration (verification), integration and implementation, and scale-up to HVM. Although each PFAS use has its own challenges and timelines for development, most lithography uses are expected to take from **15 to more than 20 years** to develop and qualify a PFAS-free alternative, with the exception of PAGs which are expected to take **more than 25 years**. A detailed explanation of photolithography applications and the use of PFAS materials is found in Section 4.

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- **Wet chemistries** are applied within semiconductor manufacturing for cleaning, stripping, wet etching, chemical mechanical planarization, metal plating, and to facilitate other processes. The use of PFAS in some wet chemistries is necessary to achieve the nanometre-sized transistor dimensions. Most wet chemistry applications do not contain PFAS; however, there are some applications that rely on PFAS materials for specific performance requirements. Examples of these applications include but are not limited to; post-plasma photoresist strip, high aspect ratio collapse mitigation, selective film inhibition, wetting of low surface energy substrates, and specific parts cleaning.

  Wet chemistry alternatives are highly application specific and depend on the technology and application for which they are used. What may be a suitable alternative for one application, will not necessarily be a suitable alternative for another. The timeline for implementing alternatives is estimated from **3 to 15 or more years after an alternative is found to be suitable**. A detailed explanation of wet chemistry applications and the use of PFAS materials is found in Section 5.

- **Fluorocarbon uses in plasma (or "dry") etch / wafer clean, and deposition**. Silicon and its compounds are the fundamental components of silicon-based semiconductors; they provide the conductive properties of metal as well as being an insulator. Cutting edge semiconductor technology exists because of the unique properties of fluorocarbon gases which enable extremely high process yields at nanometre width scales. Perfluorocarbons and hydrofluorocarbons[2] are essential for directional etching and cleaning of silicon compounds**.**

  **In the plasma etch/wafer clean application, there are no known viable substitutes for fluorocarbon chemistries due to the basic chemistry and physics of etching silicon and its compounds which are critical for forming semiconductor devices.** While some non-PFAS alternatives have been identified for specific applications – for instance, the use of nitrogen trifluoride in chamber cleans – the alternatives may produce PFAS-containing emission by-products if carbon-containing films are present and may not be suitable for all applications. In some cases, alternatives, such as fluorine gas, may present additional worker and environmental safety concerns. The semiconductor industry has reduced the use of PFAS-containing chamber clean gases over a period of more than 30 years, due to concerns regarding greenhouse gases. While no fluorine-free alternatives have been identified that meet manufacturing needs, the air emissions of PFCs and HFCs have been significantly reduced through industry level best practice initiatives.

  Alternatives would **require a fundamental reinvention of semiconductor devices to replace silicon as well as the process of fabricating semiconductors**. A detailed explanation of fluorocarbon gas applications and the use of PFAS materials is found in Section 6.

- **Fluorinated heat transfer fluids** in use include refrigerants and liquid fluorinated heat transfer fluids (F-HTF) to meet operational temperature requirements in the manufacturing processes and device test applications. Semiconductor devices are tested under a range of conditions to ensure device integrity. Burn-in, thermal shock, and device reliability testing use F-HTFs to ensure that semiconductors can be used within the customers' requirements – including but not limited to aerospace and medical device requirements. F-HTFs provide the unique ability to be simultaneously: electrically non-conductive, compatible with all materials of construction including sensitive electrical components, within suitable toxicity and flammability limits, and resistant to catastrophic contamination.

  PFAS-free alternatives to F-HTF, such as glycol/water, require the complete re-design of SMRE in the limited number of applications where these can be used. For the remaining cases suitable

[2] Such as octafluorocyclopentene, octafluoro-2-butene, hexafluoro-1,3-butadiene, octafluoropropane, hexafluoroethane and carbon tetrafluoride.

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alternative materials have not been invented yet which offer the required technical performance. Key attributes include high boiling points, low pour points, low kinematic viscosity (fluidity) at working temperatures and lower operating temperatures, electrical non-conductivity, compatible with all materials of construction, suitable toxicity/flammability ratings and the prevention of contamination. This unique combination of properties is what enables every manufacturing step to be virtually perfect, with yields well above 99%, which is essential due to the thousands of process steps involved in semiconductor manufacturing.

In the limited number of instances where alternatives are available, from **8 to more than 14 years** is required to implement needed equipment redesign and infrastructure installation. A similar timeline is also required for the substitution of refrigerants within process equipment chillers. Where there are currently no alternatives, an alternative would need to be invented and then an **additional 5 to more than 15 years** would be required to implement (although this could be significantly longer depending on the number of affected cooling systems at a single manufacturing facility). For PFAS-free thermal test methods, **once an alternative has been invented from 8 to more than 14 years** would be required to implement (although this could be significantly longer if a new method is required). A detailed explanation of the uses of fluorinated heat transfer and thermal test fluids is found in Section 7.

- **Semiconductor assembly, test, and packaging** are processes that occur after the semiconductor devices are built on the silicon wafer. A semiconductor package encloses one or more semiconductor devices (also known as die or integrated circuits), protecting the device from the environment. Assembly, test, and packaging processes include the processes of die test, wafer grind, wafer mount, wafer saw, die bond, die wire, underfill, mold, encapsulate, and final semiconductor packaging and device test. Assembly, test, and packaging also has the key function of preparing the semiconductor package so that it can connect to customers' products.

  As packaging becomes more and more complex due to decreased semiconductor size, increased processing speed, and/or increased packaging complexity, the combination of properties necessary are frequently only found in the fluorinated hydrocarbon family. PFAS materials are used to ensure hermetic sealing against moisture, provide environmental and mechanical isolation and stability, to reduce stress on solder joints increasing device durability, and other product reliability purposes. PFAS are used in some packaging fluxes, surfactants, adhesives and encapsulants and as anti-stiction agents inside specialty microelectromechanical system (MEMS) packages. While more simple uses like packaging fluxes are expected to take more than 5 years to qualify an alternative, the vast majority of package related uses of adhesives have sought alternatives for 18 years without success and alternatives are expected to take **20 years or more** to identify and implement.

  Changes to assembly package materials due to their interactions with both the silicon die and the end customer product require additional customer product change notification, product requalification and approval, which require additional time to the timeframes listed above. Customer requalification activities are required to start at least **1-2 years prior to change**, with some applications requiring 6+ years. A detailed explanation of semiconductor assembly, test, and packaging applications and the use of PFAS materials is found in Section 8.

- **Pump Fluids & Lubricants** use PFAS such as polyfluorinated polyether oils (PFPE), or polytetrafluoroethylene (PTFE) micropowders which are critical for use in semiconductor manufacturing.

  Although non-PFAS lubricants such as silicone oil exist, they are unable to meet critical performance requirements such as inertness when used in harsh conditions, low off-gassing and particle generation which is important due to the cleanliness requirements during manufacturing. In addition to this they have a higher likelihood for increased failure rates and human health and safety impacts. As such it is expected that **more than 10 years** would be required to substitute PFAS lubricants in

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general applications and **more than 25 years** for lubricants used in photolithography due to the need for ultraviolet (UV) stability. A detailed explanation of semiconductor uses of PFAS-containing lubricants is found in Section 9.

- **Articles** PFAS-containing articles are critical to the manufacture of semiconductor devices. SMRE and facility support equipment use millions of articles to enable the technical requirements of clean, and safe manufacturing. Fluoropolymers are a subclass of PFAS that possess a unique set of characteristics that are required for many of the critical articles, including inertness, purity, low flammability, temperature stability, resistance to chemical permeation, low coefficient of friction, optical properties, mechanical properties, contamination control, electrical properties, processability, resistance to bacterial growth, and long service life (>25 years). SMRE and facility support equipment are exposed to environments that include corrosive, high temperature, flammable and toxic materials and therefore, the use of fluoropolymers is often required by safety and insurance guidelines. To maintain the cleanroom and assembly test purity requirements, fluoropolymers are also needed to prevent particle generation, which is detrimental to semiconductor production yield.

  Possible PFAS-free alternatives would require total reinvention for many applications. Depending on the material and its application, **more than 15 years** are needed to implement a suitable alternative**.** Additionally, the semiconductor industry's supply chain is both specific and complex as well as generic and multi-layered, depending on the article or equipment supplied. Substitutions require an industry effort to drive change throughout the supply chain. A detailed explanation of semiconductor PFAS-containing articles is found in Section 10.

More detailed technical information can be found in the respective white papers and case study reports written by the Semiconductor PFAS Consortium (listed in Table 1-2).

It is worthwhile noting that the timelines outlined above have a significant degree of uncertainty. For many of the substances there are no alternative theoretical material chemistries to use as a basis for invention and a whole new area of chemistry and/or technology will be required. There are also concerns that a change process as large as designing out all PFAS has never taken place and the timelines are based on the time to undertake a single change. As highlighted above, there may be interactions between multiple stages in processing which will need to be explored. There will also be limitations on how many suitably knowledgeable people are available given the magnitude and complexity of the task at hand. As such, the timelines could easily be much longer than those estimated.

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## ABBREVIATIONS AND ACRONYMS

| | | | |
|---|---|---|---|
| ARC | Antireflective coating | PCB | Printed circuit board |
| ATPS | Assembly, testing, and packaging | PCTFE | Polychlorotrifluoroethylene |
| BARC | Bottom Antireflective Coating | | |
| BHF | Buffered hydrofluoric acid etch | PDMS | Polydimethylsiloxane fluids |
| BOE | Buffered oxide etch | PFA | Perfluoroalkoxy alkanes |
| C4 | Per and polyfluorinated alkyl substances with a chain length of 4 carbons or less. | PFAS | Per- and polyfluoroalkyl compounds or substances |
| CARs | Chemically Amplified Resists | PFC | Perfluorocarbons |
| CFCs | Chlorofluorocarbons | PFEPE | Poly fluoro ethyl propyl ether grease |
| CMP | Chemical Mechanical Planarization | PFOA | Perfluorooctanoic acid and its salts (a chemical family of substances) |
| CN5 | Pentacyanocyclopentadiene | PFOS | Perfluoro octane sulfonic acid and its salts (a chemical family of substances) |
| CTE | Coefficient of thermal expansion | PFPE | Polyfluorinated polyether oils |
| CZ | Czochralski crystal growth process (for making silicon ingot that silicon wafers are then cut from) | PI | Polyimides and their precursors |
| D4, D5, D6 - ring | cyclosiloxanes containing 4, 5 and 6 silicon atoms in the ring respectively. | POU | Point of use emission abatement system |
| E-beam | Electron-beam processing, also called electron irradiation | PTFE | Polytetrafluoroethylene |
| EG/DI | Ethylene glycol and deionised water | PVDF | Polyvinylidene fluoride |
| ETFE | Ethyl tetrafluoroethylene | R&D | Research and development |
| EU | European Union | RINA | RINA Tech UK Limited |
| EUV | Extreme Ultraviolet, a type of photoactivation for photoacid generators | SDS | Safety Data Sheet |
| Fab / Fabs | Fabrication (facility(ies)) | SEMI | Global industry trade association for electronics manufacturing and design |
| FEP | Fluorinated ethylene propylene | SIA | Semiconductor Industry Association |
| FFKM | American standard (ASTM) short form name for perfluoro elastomers or perfluoro rubber material. Also called Kalrez™. | SiARC | Silicon anti-reflective coating |
| F-HTF | Liquid fluorinated heat transfer fluids | SiC | Silicon Carbide |
| FKM | American standard (ASTM) short form name for Fluoroelastomers or fluoro rubber material. Also called Viton™. | SMRE | Semiconductor manufacturing and related equipment |
| HDPE | High density polyethylene | SVHC | Substance of Very High Concern |
| HFC | Hydrofluorocarbon | TARC | Top Anti reflective coating |
| HFE | Hydrofluoroethers | TIM | Thermal interface materials |
| HFO | Hydrofluoroolefins | UPW | Ultra-pure water |
| HTF | Heat transfer fluid | US / USA | United States of America |

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| | | | |
|---|---|---|---|
| HVM | High Volume Manufacturing | US EPA | United States Environmental Protection Agency |
| IPA | Isopropyl alcohol | USD | United States Dollar |
| MEMS | Microelectromechanical systems / micromachines | UV | Ultra-violet |
| PAG / PAGs | Photoacid generators | WSC | World Semiconductor Council |
| PBO | Polybenzoxazoles and their precursors | WSTS | World Semiconductor Trade Statistics |

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# 1 INTRODUCTION

RINA Tech UK Limited (RINA) was requested by the Semiconductor PFAS Consortium to gather information from members to provide evidence for the semiconductor sector to support information gathering considering the potentials impact of PFAS restriction.

The Semiconductor PFAS Consortium comprises thirty-nine Member Companies representing 69% of worldwide semiconductor manufacturing capital expenditures, as well as 70% of global sales of semiconductor equipment in 2021. Semiconductor device and equipment manufacturing operations performed by Semiconductor PFAS Consortium members represented over $400 billion dollars in revenue and directly provide over 500,000 jobs worldwide. The Semiconductor PFAS Consortium was formed to collect the technical data needed to better inform public policy and legislation, including the:

- Identification of critical uses of PFAS,
- Application of the pollution prevention hierarchy to, where possible: reduce PFAS consumption or eliminate use, identify alternatives, and minimise and control emissions,
- Identification of research needs, and
- Development of socioeconomic impact assessments.

**Table 1-1 PFAS Semiconductor PFAS Consortium members business breakdown.**

| Type of Business | Description | Number of Member Companies | % of market represented in Semiconductor PFAS Consortium |
|---|---|---|---|
| Semiconductor Device Manufacturers | Semiconductor device design and manufacturing firms with operations in Europe, Asia, and North America.<br>Companies include fab, assembly, test, and packaging operations for individual device manufacturers as well as foundries.<br>Semiconductor devices include logic and memory chips, microelectromechanical (MEMs) and image sensor devices. | 10 | 69% of worldwide capital expenditures in 2021 |
| Semiconductor Manufacturing Equipment Suppliers | Specialised semiconductor manufacturing equipment manufacturers and suppliers with operations in Europe, Asia, and North America.<br>Companies include manufacturing equipment for fab, assembly, and device packaging as well as facility support and emissions control equipment. | 8 | 70% of global sales of semiconductor equipment in 2021 |
| Chemical / Material Suppliers | Manufacturers and suppliers of specialised semiconductor process chemicals and formulations as well as semiconductor material suppliers.<br>Chemical / Material suppliers provide: Raw materials, fab chemicals and formulations, device packaging materials, and facility materials.[3] | 21 | Varies |

[3] These materials include, but are not limited to photoresists, chemical mechanical planarization slurries, deposition and etching gases, wet clean formulations, chip package substrates, packaging encapsulant and die attach materials, as well as specialised materials for ultrapure water systems and emissions control and abatement.

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## 1.1 Reporting Methodology

PFAS are used in chemical formulations, components of manufacturing process tools, facilities infrastructure and packaging used to make the semiconductor devices that are integral to our modern world. Given the widespread uses of PFAS in Semiconductor PFAS Consortium members applications, this report has grouped PFAS uses into similar groups to aid in the understanding of this complex picture. The following groupings of use have been used in this report:

- **Photolithography** - A crucial phase in the process of manufacturing semiconductors, of transferring a component or circuit pattern by applying a photoresist and exposure.
- **Wet Chemistry** - Liquid substances used in processes such as wet etching, cleaning, chemical mechanical planarization, surface modification treatment, and other liquid applications in chip manufacturing.
- **Fluorocarbon uses in plasma etch and deposition** - Gases used in plasma etching and chamber cleaning, and metalorganics used in deposition.
- **Heat Transfer Fluids** - Coolants used in the manufacture of semiconductors, during the testing of devices, and in equipment such as chillers.
- **Assembly, Test, Packaging, and substrate material uses** - Materials used to test and attach individual semiconductor devices into chip packages.
- **Pump Fluids & Lubricants** - To provide smooth and precise functionality of fabrication and processing equipment while preventing the generation of particles and outgassing (under vacuum).
- **Articles** - Physical materials used in the construction of semiconductor processing equipment, support equipment, facilities equipment, and infrastructure, and other purchased or produced items containing PFAS. Examples include components within a billion-dollar extreme ultra-violet (EUV) semiconductor lithography machine, plasma tool O-rings, ultra-pure water systems and piping, and environmental control systems such as lined ductwork and wet scrubbers. These PFAS articles are used during semiconductor manufacturing and also in forms which may be present in certain final products.

This report outlines key PFAS uses which are indicative of the technical challenges faced by each use. In addition to this report, the Semiconductor PFAS Consortium has written seven white papers (listed in Table 1-2) and three case study reports to collectively address the principal areas in which fluorinated organic chemicals are used in semiconductor manufacturing, which has been utilised in writing this report.

**Table 1-2 Semiconductor PFAS Consortium papers.**

| Paper Type | Paper Title |
|---|---|
| Whitepaper | Background on Semiconductor Manufacturing and PFAS |
| Case Study | PFOS and PFOA conversion to short chain PFAS used in the Semiconductor Manufacturing |
| Case Study | PFAS-Containing Photo-Acid Generators used in Semiconductor Manufacturing |
| Case Study | PFAS-Containing Surfactants used in Semiconductor Manufacturing |
| Whitepaper | PFAS-Containing Wet Chemistries used in Semiconductor Manufacturing |
| Whitepaper | PFAS-containing Fluorochemicals used in Semiconductor Manufacturing Plasma-enabled Etch and Deposition |

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| Paper Type | Paper Title |
|---|---|
| Whitepaper | PFAS-Containing Heat Transfer Fluids (HTF) PFAS-containing Heat Transfer Fluids used in Semiconductor Manufacturing |
| Whitepaper | PFAS-Containing Materials used in Semiconductor Manufacturing Assembly Test Packaging and Substrate processes |
| Whitepaper | PFAS-Containing Lubricants used in Semiconductor Manufacturing |
| Whitepaper | PFAS-Containing Articles used in Semiconductor Manufacturing |

The information shared by the Semiconductor PFAS Consortium membership in this report provides a snapshot at the point of the information being gathered. RINA devised a questionnaire which was circulated by the Semiconductor PFAS Consortium to its members. The responses from the questionnaire were collated and analysed for common themes, to give a representation of the whole membership. It is understood that many Semiconductor PFAS Consortium members are still developing their strategies and responses to PFAS concerns, and as such have not been able to answer all of the questions asked at this time. It is to be expected, therefore, that views may change or develop with time as more work is done, evidence is discovered, and as requirements emerge.

### 1.1.1 Terminology used within the report

Where the term ‘No known alternative’ is used within this report it is meant that there is no known alternative chemistry or technology within the semiconductor industry and its supply chain that could be investigated as a replacement for this use at this time.

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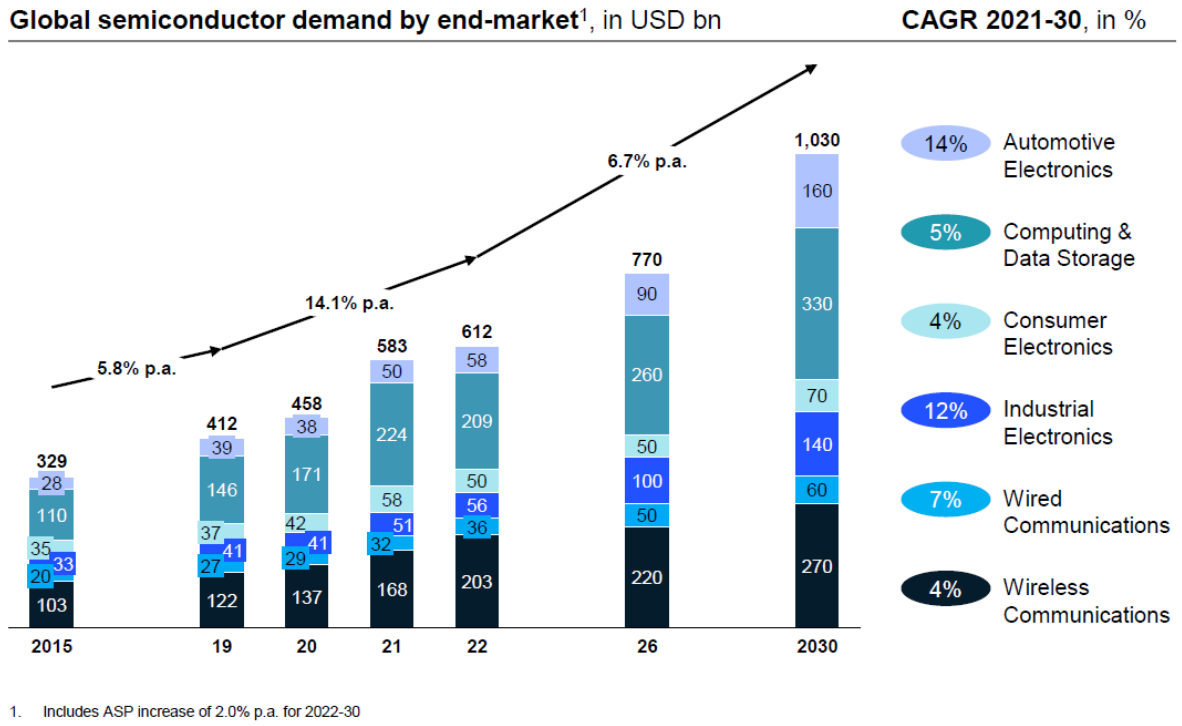
# 2 SEMICONDUCTOR TECHNOLOGY

The overall global semiconductor market was valued at $440 billion in 2020 and increased to $555.9 billion in 2021, an increase of over 26.2% according to data from the World Semiconductor Trade Statistics (WSTS) 2021. In February 2023, the Semiconductor Industry Association (SIA) reported global semiconductor industry sales totalled $574 billion in 2022, the highest-ever annual total and an increase of 3.32% compared to the 2021 total of $555.9 billion.




1. Includes ASP increase of 2.0% p.a. for 2022-30

**Figure 2-1 Global semiconductor demand by end-market, in USD.[4]**

Based on information from SIA[5] and shown in Figure 2-1, the semiconductor industry serves a number of end-use markets, and the information and communication technology sectors typically account for a majority of global sales at two-thirds. However, from 2021 to 2022, the automotive, industrial, and consumer electronics markets' share of sales revenue grew, indicative of demand trends demonstrated by end market growth projections.

The semiconductor value chain is highly complex, as indicated in Figure 2-2, requiring the co-operation of many different companies to support the end use equipment consumers are familiar with.

[4] Omdia (Q3 2022) McKinsey

[5] *Semiconductor Supply Chain Deep Dive Assessment,* U.S. Department of Energy Response to Executive Order 14017, "America's Supply chains" February 24, 2022. https://www.energy.gov/sites/default/files/2022-02/Semiconductor%20Supply%20Chain%20Report%20-%20Final.pdf

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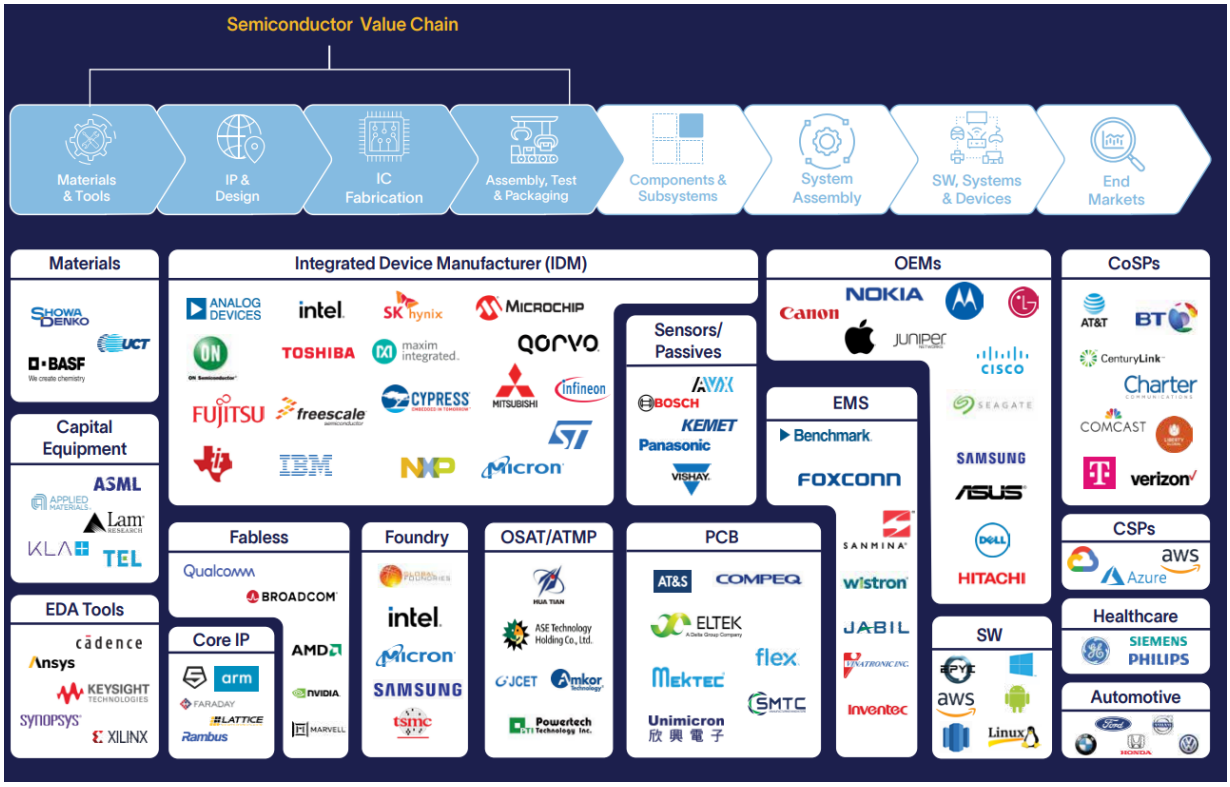


Figure 2-2 Illustrative (non-comprehensive) companies involved in different stages of the value chain.[6]

## 2.1 Importance of Semiconductors to Society

Semiconductor devices are central to the digital economy and an enabling technology for a number of key applications as shown in Figure 2-3.[7]

Semiconductors are at the centre of technological advancements that can make a significant contribution to society. Due to their complexity and key role in technological development, semiconductors have been defined as one of the most complex devices ever created by humans. For example, innovative uses of semiconductor technology have the potential to make significant contributions towards solutions to global climate change. According to the World Economic Forum, semiconductor-enabled technologies, such as digital technologies, can **reduce greenhouse gas emissions by 15%** - almost one-third of the 50% reduction required by 2030.[8]

[6] Source: The Semiconductor Ecosystem: Complex, Global, and Specialized - Altman Solon, EDA - Electronic Design Automation, IP - Intellectual Property, OSAT - Outsourced Semiconductor Assembly & Test, ATMP - Assembly, Test, Markup & Packaging, EMS - Electronic Manufacturing Services, PCB - Printed Circuit Board, OEM - Original Equipment Manufacturer

[7] Sourced from Alex Capri, "Semiconductors at the Heart of the U.S.-China Tech War: How a New Era of Techno Nationalism is Shaking Up Semiconductor Value Chains," Hinrich Foundation, January 2020, p. 13.

[8] https://www.weforum.org/agenda/2019/01/why-digitalization-is-the-key-to-exponential-climate-action/

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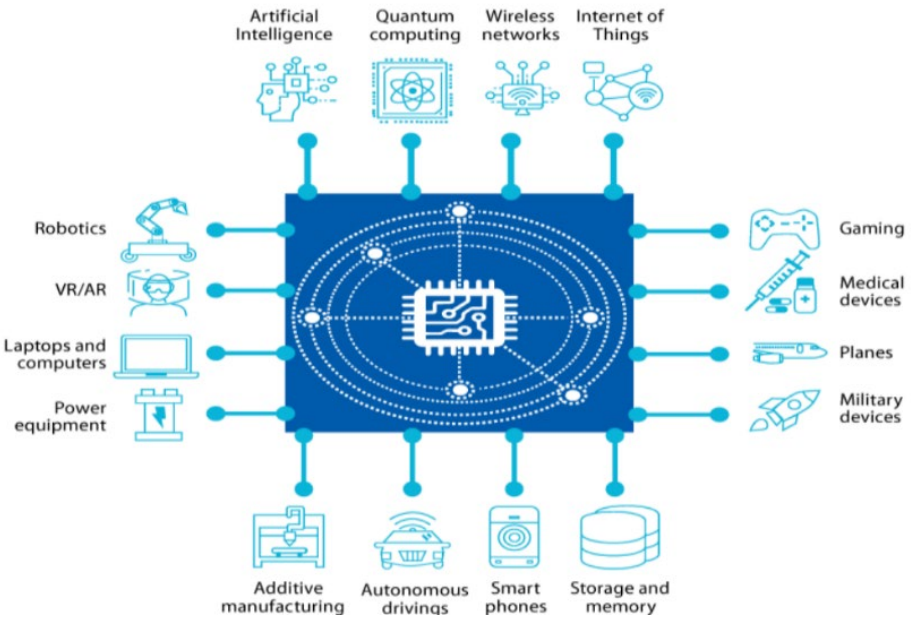


**Figure 2-3 Technologies enabled by semiconductors.**

Within the past several years, industry has witnessed disruptions in the supply of chips, causing shortages across multiple economic sectors and potentially serious societal consequences. Many sectors, including automotive, energy, communication, and health, as well as strategic sectors such as defence, security, and space are under threat by such supply disruptions. Any further disruptions due to PFAS restrictions will likely make the situation more severe.

The current supply chain disruptions have revealed structural vulnerabilities of the value chains. The global semiconductor shortage has exposed dependency on supply from a limited number of companies and geographies, and its vulnerability to third country export restrictions and other disruptions in the present geopolitical context. Building new facilities to manufacture the latest semiconductor devices technologies requires a considerable upfront investment of at least €15 billion and several years to achieve production-readiness with adequate yields. The expenditures to design such chips can range from €0.5 billion to well over €1.0 billion. Research and development (R&D) intensity in the sector is high with more than a 15% investment percentage with respect to sales.[9]

It is estimated that in 2021 the capital expenditure invested was close to $150 billion and was expected to rise to above $150 billion in 2022.[10] This trend will only continue as demand for electronics and connectivity grows. In the automotive space, new vehicles increasingly rely on semiconductor devices for fuel efficiency, safety, and other features. The expected growth in electric cars will only further this reliance. In the long term, as semiconductor devices play an even bigger role in an ever-expanding array of products, global demand for semiconductor devices will continue to rise.

In addition to this the semiconductor industry is growing substantially, with the following calculated by the World Semiconductor Trade Statistics (WSTS)[10]:

[9] *A Chip Act for Europe*, "Brussels, 8.2.2022 COM(2022) 45 final. https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52022DC0045

[10] WSTS Semiconductor Market Forecast Fall 2022

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- Worldwide sales have a yearly growth of 12%.[11]
- The American market is supposed to grow 17.0%.
- The European market is supposed to grow 12.6%.
- The Japanese market is supposed to grow 10.0%.
- The Asia Pacific market is supposed to decline 2.0%.

## 2.2 Semiconductor Manufacture and Supply Chain

Semiconductor devices are extremely complex to manufacture, with leading devices requiring more than 2,000 process steps, hundreds of production materials, and approximately 26 weeks to manufacture and test.[12] A simplified diagram of the supply chain is outlined in Figure 2-4. The materials used for the manufacture of semiconductors have been specially formulated and engineered to meet the exacting standards of the industry which continue to be more and more demanding as the technology evolves. Each step in the process requires extremely high purity, exacting process control and high yields for the overall production to be viable.

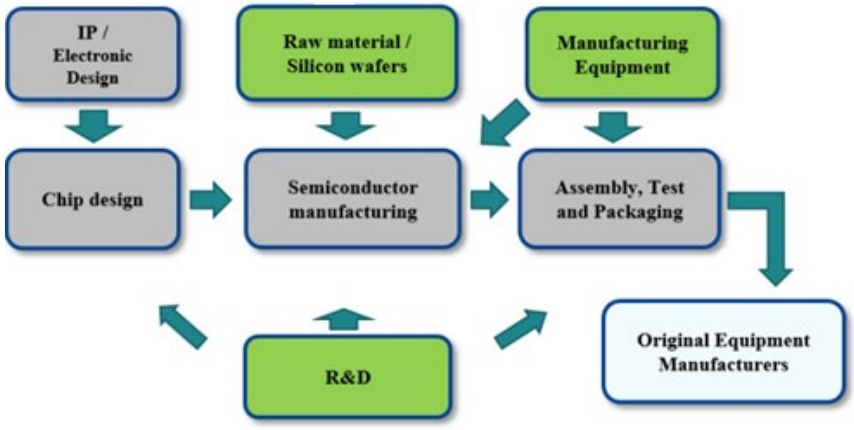


Figure 2-4 Schematic of semiconductor supply chain.[13]

The supply chain for semiconductors starts with a range of unique materials, chemicals and sophisticated equipment and services provided by special vendors to meet the unique needs of this sector. The semiconductor supply chain has a **global footprint and relies upon key technology holders across the globe**. The full supply chain uses components and materials supplied by many tiers of suppliers and sub-suppliers, and those components and materials will typically pass multiple borders before final distribution. If this complex supply chain is broken due to a restriction being placed on the use of PFAS, the effects will be felt globally.

The processes and equipment used are enormously complex. A simplified step by step workflow of the semiconductor manufacturing process indicating where PFAS are used is shown in Figure 0-1, which

[11] Based on 2016-2021 global data.

[12] According to Consortium members.

[13] *A Chip Act for Europe*, "Brussels, 8.2.2022 COM(2022) 45 final. https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52022DC0045

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describes the use of PFAS in the semiconductor product manufacturing process and associated waste streams.

## 2.3 Importance of Innovation

In the past 50 years, semiconductor performance has increased from 10 thousand floating point operations per second, or FLOPs[14], to more than 400 quadrillion FLOPs for the fastest super computers.[15] The need for semiconductor enabled technology to be faster and more powerful comes from the developing and evolving need for digitisation. The demand for faster and more powerful devices is anticipated to continue, requiring the semiconductor industry to invest in next generation innovations.

Further miniaturisation continues, towards smaller node[16] dimensions in the mainstream process technologies along the lines of Moore's law[17], while more energy-efficient solutions are in high demand to ensure that the ever-growing processing footprint remains sustainable. According to the International Roadmap for devices and systems 2022 update[18], by 2037 a 0.5 nm equivalent node size on semiconductors will be necessary. Since the 1970's semiconductor speed and performance has grown exponentially due to these innovations, as outlined by Figure 2-5.

[14] FLOP is a measure of computer performance representing the number of floating point operations performed by a computer in a second.

[15] TOP500 Supercomputer Database.

[16] Typically refers to the technology node, a term used to describe the size of the features in the finished product. Quoted in terms of nanometres (or larger for earlier nodes), the node name refers to half the distance between identical features.

[17] Moore's law is an observation based on historical trend in the semiconductors industry, which shows the density of transistors on an integrated circuit doubles approximately every two years.

[18] International Roadmap for Devices and Systems, 2022 Update, More Moore, IEEE, https://irds.ieee.org/editions/2022

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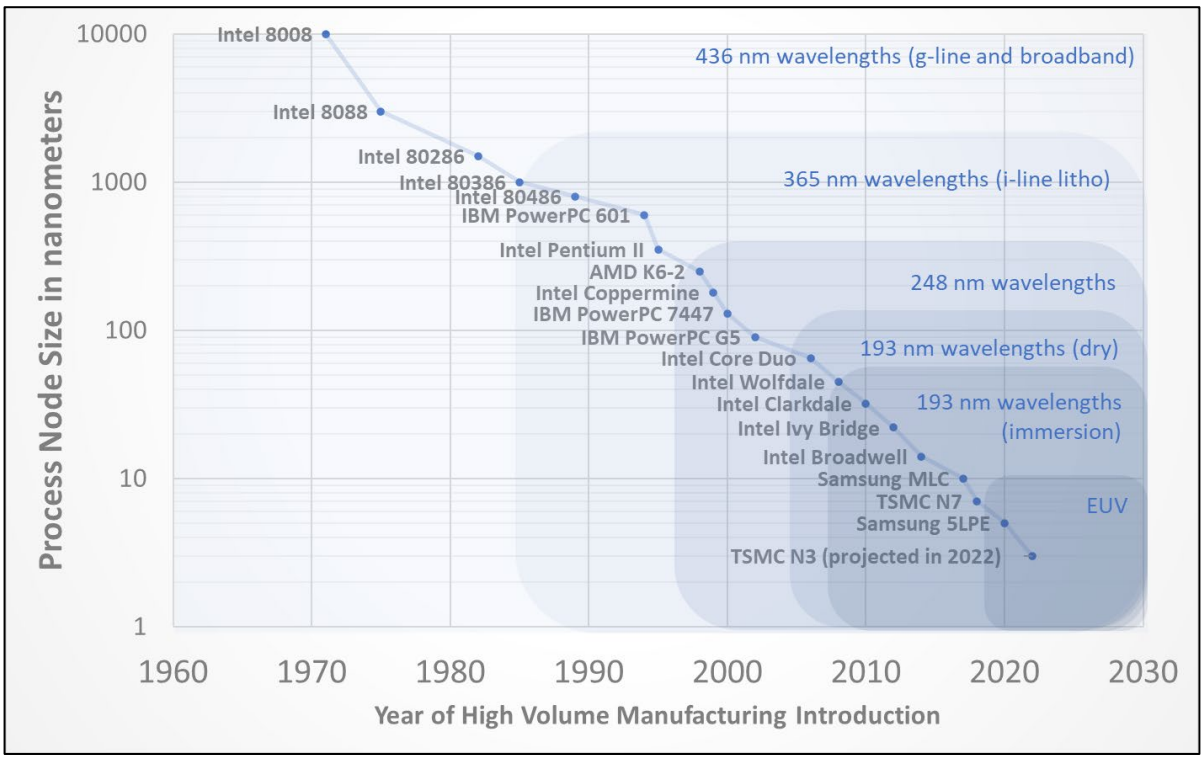


**Figure 2-5 Sample of semiconductor products: exponential decrease in critical dimensions over time (and associated lithographic wavelengths).**[19]

For context the diameter of a human hair is 100,000 nm with Figure 2-6 showing semiconductor node sizes compared to biological references, which explains why the extreme miniaturisation of semiconductors poses so many technical challenges. Many **PFAS are intrinsically linked into the technological advances which have allowed the current node sizes to be achieved**.

Node sizes, and the wavelengths used to create them, are not necessarily replaced by smaller nodes, rather devices can have multiple node sizes or rely on legacy node size technologies. As such, all of the above-mentioned wavelengths are still in use today with the most advanced (i.e., most capable, and most expensive) lithographic technology being used for the most critical layers, and older, less costly technologies for the less demanding ones. Any changes to each of these layers can influence the next, causing a reduction in yield or even catastrophic process failure.

[19] File:Comparison semiconductor process nodes.svg - Wikimedia Commons

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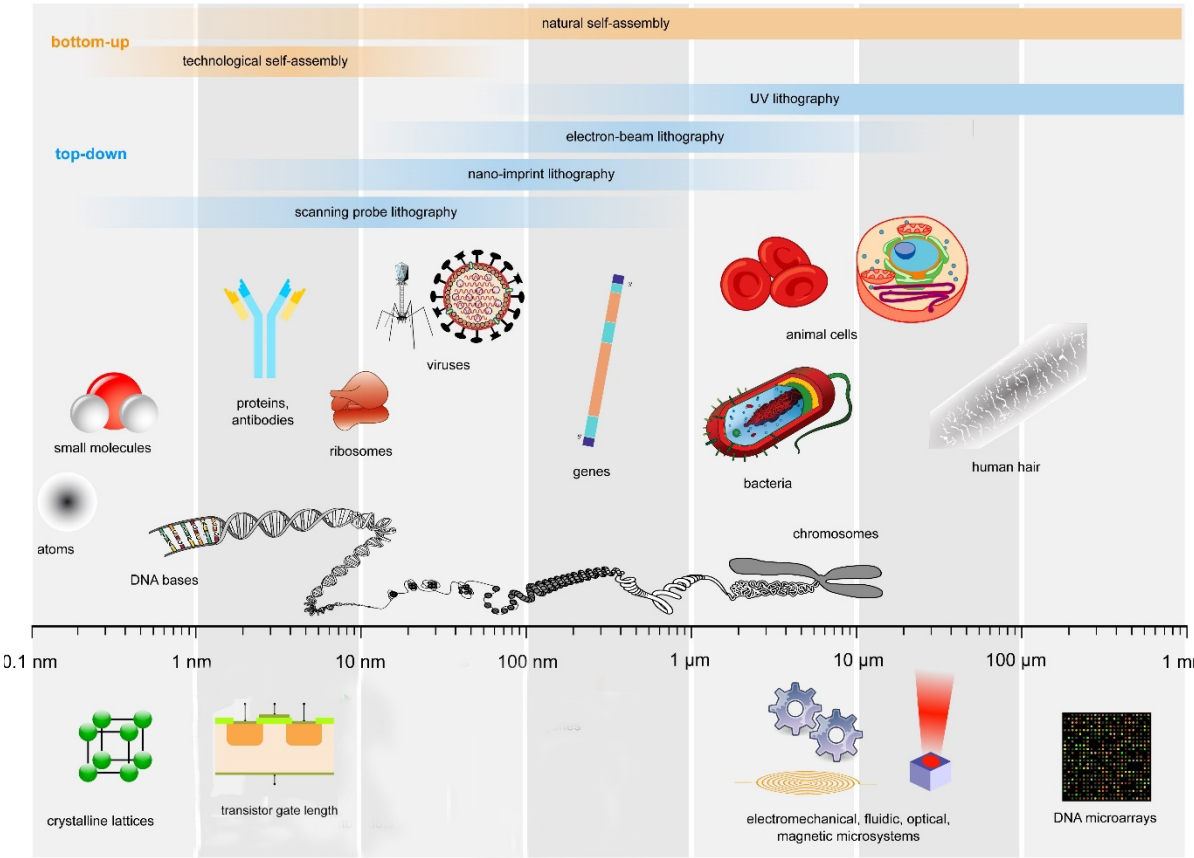


**Figure 2-6 Comparison of various biological assemblies and technological device.[20]**

Products containing semiconductors are essential technologies in everyday life and form the backbone of the technical strategic value chain with strategic objectives in multiple jurisdictions, including Europe via the European Green Deal and digital autonomy.[21] To renew its pledge to innovation, the European Union is committed to its strategic goal to reach at least 20% of world production in value of cutting-edge, innovative, and sustainable semiconductors by 2030, as set out in the Digital Decade Policy Programme.[22]

Innovation fuels continuous advances in microelectronics technologies, which is why semiconductor companies spend so much on research and development expenditure as outlined in Figure 2-7 and is necessary to make the advances in technology. It is only as a result of the high-level innovation that the objectives of the US CHIPs act[23] and the EU Digital Decade Policy are possible.

[20] Modification of Guillaume Paumier, Philip Ronan, NIH, Artur Jan Fijałkowski, Jerome Walker, Michael David Jones, Tyler Heal, Mariana Ruiz, Science Primer (National Center for Biotechnology Information), Liquid_2003, Arne Nordmann & The Tango! Desktop Project, CC BY-SA 2.5 via Wikimedia Commons

[21] https://www.semi.org/en/blogs/semi-news/fluorinated-chemicals-are-essential-to-semiconductor-manufacturing-and-innovation

[22] https://commission.europa.eu/strategy-and-policy/priorities-2019-2024/europe-fit-digital-age/europes-digital-decade-digital-targets-2030_en

[23] *A Chip Act for Europe*, "Brussels, 8.2.2022 COM(2022) 45 final. https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52022DC0045

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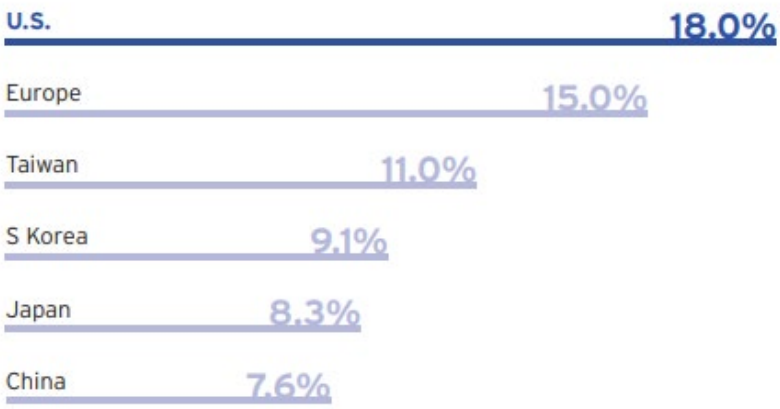


**Figure 2-7 Semiconductor R&D expenditure as a percentage of sales.**

Innovation fuels continuous advances in microelectronics technologies, which is necessary to make the advances in technology which are required to underpin the objectives of the US CHIPs act[24] and the EU Digital Decade Policy.[25]

Moore's law describes the trend whereby the number of transistors on a microchip doubles every two years shown in Figure 2-8. This advancement is important for other aspects of technological progress in computing such as processing speed or the cost of computing.

[24] *A Chip Act for Europe*, "Brussels, 8.2.2022 COM(2022) 45 final. https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52022DC0045

[25] Europe's Digital Decade: digital targets for 2030 (europa.eu)

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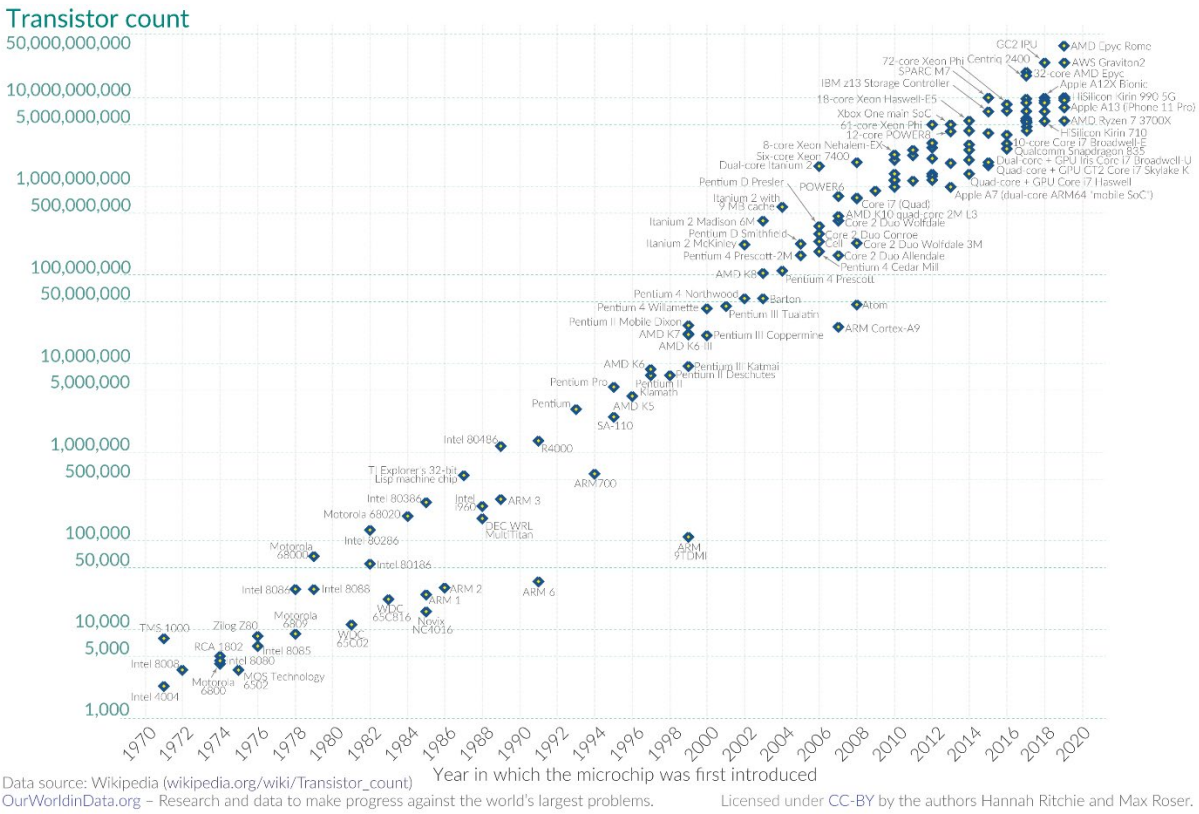


**Figure 2-8 Moore's Law- exponential technological advancement through time.**

The continuing validity of Moore's law for technology could be disrupted by the loss of PFAS which is a key enabling technology to make ever smaller transistors, through the ability to have extremely high purity, high quality, highly directed manufacturing. This is based on the PFAS applications explained in this report. **The impact on the global economy derived from denying access to state-of-the-art semiconductor technology would be significant, because PFAS provide multiple, critical functions which are crucial to production.**

In many instances, PFAS are the only substances known currently to offer the necessary technical performance in semiconductor production. If manufacturers are no longer able to invest in innovations relying on PFAS, a further consequential impact would be significant disruption to the technology roadmap[26] as manufacturers attempt to develop the next materials and equipment, which would be a lengthy and demanding process with no certainty of success. These impacts pose an enormous competitive disadvantage for semiconductor producers based in jurisdictions where there are PFAS restrictions compared to their non-affected competitors.

## 2.4 Importance of Yield

Production yield is the single most important factor for semiconductor manufacturing as not only does it influence the cost, but also the output per unit of input resources, waste generation, environmental and financial sustainability. During the manufacture of semiconductors yield loss is caused for example by defects, faults, process variations and contamination. Examples of contamination and mechanisms

[26] The direction of research and timelines of semiconductor development in the future.

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responsible for yield loss include airborne molecular contamination by the environment or by the tools, process-induced defects, process variations resulting in attributes such as different layer thickness, and many others.

The complexity and sensitivity of semiconductor manufacture and the occurrence of defects have a huge impact on the ability to produce designs, with each individual step needing to meet process control limits set in order to achieve wafer level yields **of greater than 90%**[27] and in lithography well above 99%.

Many PFAS are intrinsically linked to achieving the highly demanding yields, either by contributing to the cleanliness of the system or accuracy of the processing, and so they enable the manufacturing of current semiconductor devices. It is important to keep in mind that the factors which affect yield can rarely be attributed to a single process parameter, which is why multiple variables have to be considered concurrently, as outlined in multiple papers.[28, 29] Considering the widespread uses of PFAS, this too will pose a significant challenge due to the concurrent need to identify possible PFAS-free alternatives.

## 2.5 Essential Use

The Chemicals Strategy for Sustainability Towards a Toxic-Free Environment[30] proposes the development of a widespread essential use concept to apply across chemicals legislation.

The Chemicals Strategy[31] programme has not yet published its definition of 'Essential Use' but will develop criteria for essentiality. At this point it is known that the definition will be based on the criteria that there are no alternatives and that the use of the substance is necessary for health, safety or is critical for the functioning of society.

As is outlined in the respective sections of this report, PFAS substances in most applications do not have a known viable alternative and are key enablers of semiconductors. Semiconductors themselves are essential to the functioning of society and also essential for health as they are embedded in medical devices, power stations, satellite, and every home.

# 3 PFAS SUBSTITUTION OPPORTUNITIES AND CHALLENGES

## 3.1 PFAS substance identification

Many PFAS used in mixtures have not been classified as hazardous per the Globally Harmonised System for classification and labelling. In addition, they have not been listed as Substances of Very High Concern (SVHC) or included on the Candidate List of SVHC for Authorisation. Therefore, **many PFAS are not shown on safety data sheets even though the substance is present**.

In addition to this, chemical supplier companies invest significant time, money, and resources into developing proprietary chemicals to meet the exacting requirements to manufacture semiconductors at nanometre dimensions. In some instances, the use of PFAS is considered to be the intellectual property

[27] Enhancing the Production Yield of Semiconductors | Infosys, 2022.

[28] Data Science in Semiconductor Process Yield | by Brian Mattis | Towards Data Science

[29] Taking the next leap forward in semiconductor yield improvement | McKinsey, April 2018.

[30] https://ec.europa.eu/environment/pdf/chemicals/2020/10/Strategy.pdf

[31] https://eur-lex.europa.eu/resource.html?uri=cellar:f815479a-0f01-11eb-bc0701aa75ed71a1.0003.02/DOC_1&format=PDF

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of the chemical supplier, so the identification of the specific substance is not communicated to customers as companies need to ensure that their investment is protected. Releasing information about certain chemicals to the public would give competitors an unfair advantage and is likely to cause substantial harm to the company's competitive market position. Moreover, when PFAS are used as articles or articles in complex objects, the parts suppliers are currently under **no regulatory obligation to highlight the presence of PFAS**.

As a result of these various factors the discovery of PFAS uses in this sector is extremely challenging.

## 3.2 Timeframes for substitution

Due to the unique attributes of organofluorine chemistry, and the highly specialised function that PFAS provide in numerous semiconductor manufacturing applications, it is not known if PFAS-free alternatives will be viable for all applications. In any case, the timelines to qualify and implement alternatives are lengthy for the semiconductor industry as the following stages need to be undertaken:

1. The first stage in substitution is reviewing all potential alternatives currently marketed, to determine if they offer suitable performance. Sources can vary between commercial off the shelf products, and specialised alternatives developed specifically for the semiconductor sector, with the determining factor of whether they can be taken forward based on the technical needs of the application.

2. For many applications, investment in fundamental research and development is needed to identify a PFAS free alternative, as there is not one currently marketed which is suitable for the semiconductor's industry needs. This can start from fundamental external research undertaken by universities or research laboratories.

3. Once a possible alternative is identified this needs to be researched and developed by the material supply chain and then the semiconductor/semiconductor equipment manufacturer to assess the impact on the product, such that it offers the necessary technical performance through the following:
    a. Integration,
    b. Demonstration including re-qualification to standards or safety evaluations,
    c. Ramp to HVM,

        This can involve significant timeframes as it potentially includes the development, installation, and integration of new equipment and/or new facility installations that manage environmental controls. Additionally, there are checkpoints along the development process to assess the viability of the alternative and the functionality of the material to manufacturing and product requirements.

    d. Impact on the market.

        The concurrent processes of semiconductor design and PFAS material alternative identification and qualification can cause additional delay in overall time to market as well as additional qualification resources to both semiconductor manufacturers and customers.

    Components and substances used in semiconductor equipment often require bespoke parts to be developed and qualified, with solutions potentially only being suitable alternatives for certain applications and therefore **not being a one-for-all replacement**. Therefore, the redesign and testing requirements for each use often is very significant and needs to be **undertaken by each company** due to differences in process. It is anticipated that significant innovation loops will take place between the semiconductor manufacturers and suppliers in feasibility testing of new

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innovations for PFAS replacement chemicals, to discover the appropriate technology platform for PFAS replacement for the numerous uses within the industry.

4. Suitable time to complete supplier change management, including changes to part numbers/drawings/technical and safety information, consumption of stock parts throughout multiple levels in the supply chain. The impact on production yield of a small change can be very significant, therefore the change control process within the semiconductor industry is strictly followed.

5. Assessment of unintended consequences, such as an alternative causing damage or an increase in defects present (Impact to production), which leads to increased safety risk (Impact to people). **When the alternative is not viable, the process has to loop back to earlier steps to find a different chemistry or technology that does not have the same issues.**

6. Additionally, stringent qualification also has to take place with semiconductor customers to ensure that the semiconductor product guarantees the same function as semiconductor product did previously.

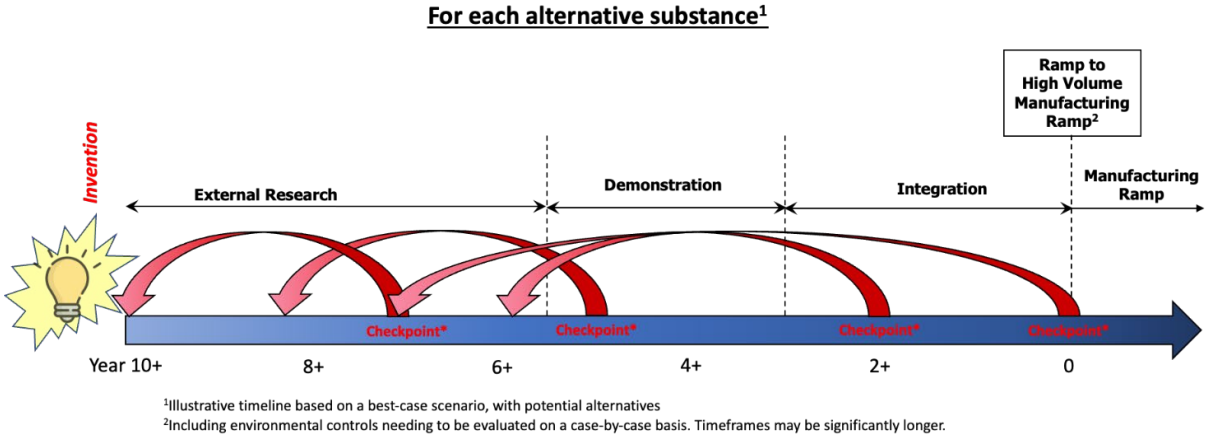


**Figure 3-1 Illustrative timeline for qualification of a single alternative.**

Of course, this is only an overview and potential alternatives must be evaluated on a case-by-case basis, considering technical, regulatory as well as economic aspects. By its nature, the invention of an alternative has no estimated timeline as it can vary significantly, and for some applications there may be no known alternative.

Aspects such as the following further increase the uncertainty of the timelines:

### Technical

- The alternative may not be a drop-in replacement and alternative design changes need to be made, solution may not be backward compatible to designs of equipment which are already in service.
- The technical requirements at each stage must be met, and may require multiple iterations of testing and development, as indicated by the red arrows in Figure 3-1.
- The solution may not address the long-term reliability of the alternative, which may only introduce additional design needs or technical limitations once the alternative has been used for a considerable length of time.

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- The solution may need to be qualified by a certified body which can add additional time.

**Supplier factors**

- Difficulties in identifying a new supplier and their qualification can add considerable additional time to envisaged timeline in Figure 3-1.
- The alternative substance needs to be available in sufficient quantities to meet demand.

The supply chain for semiconductors can be narrow and varied, and highly, highly specialised. An impact to any one of these unique supply chain elements can have dramatic impacts to downstream customers. For instance, only a handful of chemical suppliers have the research and materials capability to support the critical lithographic materials needed for the entire semiconductor industry.

**Delays in testing**

- Unavailability of testing labs due to the expected increase in the demand for testing of other applications/alternatives, or delays in receiving test material from supplier or prototypes for testing.

**Environmental**

- PFAS articles are exposed to hazardous substances during use which might contaminate the proposed alternatives differently, and thus impact recyclability. Therefore, alternative waste manage streams would need to be identified. Additional information about the semiconductor industry's environmental impact, end of life and waste considerations can be found in Section 11 of this report.
- **Technical resources** Significant additional specialised highly educated technical resources will be required in the innovation and commercialisation of PFAS replacement materials. As such there may be additional time required to recruit and train additional people.

The timeframes for qualification of alternatives outlined in this report are wherever possible extrapolated from other qualifications, such as for PFOS and perfluorooctanoic acid (PFOA). Substitutions like these are only single changes and not a full re-engineering of the product, which is unprecedented, as discussed further in Section 3.4.1. Where previous substitutions are not applicable, timelines have been estimated on engineering judgement based on the information to the best of the Semiconductor PFAS Consortium's knowledge at the time of publication of this report. However, many of the timelines have a degree of uncertainty due to the number of steps still left to be undertaken and the possibility of unforeseen challenges yet to be identified.

In addition to these impacts, chemical, material and equipment suppliers would be significantly disrupted if PFAS were no longer able to be used because so many applications in semiconductor production are reliant on these substances. This would represent a critical and continual innovation challenge to industry.

## 3.3 Incentives for PFAS substitution

The semiconductor industry is a global leader in promoting environmental sustainability in the design, manufacture, and use of its products, as well as the health and safety of its operations and impacts on workers in semiconductor fabrication facilities (fabs).

Semiconductor industry companies recognise the importance of substituting PFAS where possible and where it does not create worker or community safety concerns. Despite this, there are still significant technical challenges to be overcome for a large number of PFAS uses in semiconductor applications due to the critical functionality they provide to the industry.

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## 3.4 Challenges to substitution

Capabilities in the fluorochemical and semiconductor industries have evolved synergistically since 1971 with fluorocarbons being a key enabling technology to node size development in all aspects of semiconductor manufacturing. Finding another chemistry and technology which can match and exceed the PFAS application will require for many applications, investment in fundamental research and development to identify a PFAS free alternative.

In broad terms, PFAS offer a unique set of technical characteristics, which include exceptional heat and chemical resistance, high electrical insulation resistance, high purity, low-outgassing and low coefficient of friction. One of the characteristic features of the C—F bond is its strength compared with the C—C bond, due to the intrinsic electron-withdrawing power (electronegativity) of the fluorine atom. This intrinsic attribute is the basis of many of the technical benefits of fluorinated materials in semiconductor processing, but this also leads to its chemical stability and environmental persistence. Fluorination brings unique physiochemical properties and consequent qualitative improvements that are the enabler of semiconductor, performance and manufacture, advancements. These unique properties make substituting PFAS a challenge.

PFAS is used in gaseous, liquid, and solid forms, and is used in many different applications, which need to work together to form a coherent production process. Some of the uses, such as cleaning fluids and lubricants, have dependencies on one another, and finding alternatives for cleaning fluids can only be started once all PFAS containing lubricants are substituted. Removing PFAS from earlier process steps can result in deterioration of performance which makes the later steps in the process impossible due to excessive defect rates, such as moving to a silicone-based alternative resulting in excessive defects. This complexity and interdependency are discussed in Section 2.2.

**Elimination or substitution of a whole class of chemicals, like PFAS, is unprecedented and will add a significant amount of time to identify and implement each alternative** due to the following:

- Each alternative must first show suitable performance in its technical parameters or the combination of its technical parameters but will also need to be tested to ensure that there are no negative impacts to all other substitutions as well. Parameters such as yield, and production performance need to be maintained. This could require changes in the design of the devices, as well as changes in the manufacturing process to accommodate the properties of alternate materials – thus triggering the need for rigorous testing to ensure it does not have a detrimental impact on the function and performance of the device. Due to the number of changing parameters which need to be investigated this poses a significant challenge.
- Availability of skilled engineers and leadership within the market has already been highlighted as limited, moreover, owing to the complexity of the products this shortage has an even higher impact. This limits the ability of manufacturers to implement all of the solutions at any one time and would result in the decrease or halt of research and development activities (R&D). It is important to note that those engineers will be diverted from their normal function of R&D for new innovations and products, production optimisation, and quality improvement activities.

### 3.4.1 Regrettable Substitution

For a PFAS alternative to be successful, it must not only pass through all the qualification timeline stages successfully and provide effective performance for the application, but it must also be a sustainable alternative that can be used without impact to human health or the environment.

When deciding whether to restrict a substance it is always important to consider whether safer alternatives exist. Where alternatives are identified which are more harmful than, or no better than, the

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substances currently in use, these substances should not be considered as a potential alternative and should not be taken forward (e.g., for development) in the Semiconductor PFAS Consortium's opinion.

Potential alternatives can be relatively new substances and/or substances made in smaller quantities where much less research has been carried out regarding their health and environmental hazards, as compared to current substances in use that have been thoroughly studied. Alternatives and their hazards are not always known, and for many of these instances it is not unreasonable to assume that they are likely to present similar concerns to PFAS. This is based on the understanding that their desired characteristics and therefore environmental controls and concerns would be of similar nature to the ones implemented for the use of PFAS. **Informed substitution is therefore crucial.** If the replacement is not carefully considered for its own potentially deleterious effects, regrettable substitution can easily occur.

**A sufficiently long transition time is crucial to ensure proper research into alternatives**. Indications of these timeframes are given in each of the sections below which consider the various stages where PFAS are used.

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# 4 PHOTOLITHOGRAPHY USES

**Summary:**

PFAS has been an enabling technology in the development of ever smaller and more advanced semiconductors over the last 30 years through cutting edge lithographic developments.

- **Photoacid generators** (PAGs) are key components of the Chemically Amplified Resists (CARs) that are used in advanced lithography. They generate strong acids on exposure to UV light, and the chemistry requires sulfonium and iodonium-acid salts with fluorinated anions. The strong electronegativity of the fluorine atom creates a super acids capable of causing the solubility change of the photoresist. All successfully demonstrated PAGs are fluorinated, some down to one $CF_2$ unit, and there are no universally applicable viable fluorine free alternatives for a vast array of lithographic materials. Current photoacid generators have been in development for 25 years, and alternatives are expected to take from **15 to more than 20 years** to reach production. For an alternative to be successful it would have to show acidity comparable to perfluoro sulfonic acids, show similar lack of side reactions, lack volatility, and show minimum diffusivity for high resolution patterns.
- **Top antireflective coatings (TARCs)** require a very low refractive index, low surface energy and excellent barrier properties, which are provided in fluorinated acrylate / methacrylate / styrene-based copolymers. The requirements differ between “193 nm” and “193 nm immersion” lithography, but **no currently, viable alternative materials exist for either application**. Fluorine free systems have resulted in patterning failure in immersion processes.
- **PFAS Surfactants** have unique properties, such as very low surface tension and a combination of hydrophobic and oleophobic behaviour, that have been utilised in various types of photolithographic materials. Applications include photoresists (248nm, 193nm, immersion, thick film, etc.), BARCs, TARCs, colour resists for image sensing, and rinse solutions. The surfactants are used to improve film quality, alter surface interaction, wetting characteristics, and component mixing, all of which helps to minimise various defectivities in the lithographic process and thus increase lithographic impacted yield. It may be possible to find non-PFAS alternatives for less advanced applications using current known potential alternatives, such as siloxane-based surfactants. However, for most advanced applications, siloxane (or other) alternatives cannot duplicate performance characteristics that PFAS surfactants offer and would lead to compromised performance.
- **Immersion top coatings** require very low surface energy (resulting in very high water contact angles), excellent barrier properties and a lack of intermixing with the photoresist, which are provided in fluorinated acrylate / methacrylate / styrene-based copolymers. The requirements differ between “193 nm” and “193 nm immersion” lithography, but currently, **no viable alternative materials exist for either application** and there are not even any concepts for PFAS replacement for this application. Fluorine free systems have resulted in patterning failure in immersion processes.
- Current PFAS materials were designed, developed, and optimised as dedicated substances to satisfy many functions and performance needs in lithographic imaging products. Thus, replacement with a new non-PFAS material will likely require **multiple solutions** depending on the application, which has a significant impact on the estimated timelines.
- The consumption of PFAS for photolithography is quite low with very small releases when compared to global releases.[32]

[32] When compared to 470 Tons of PFAS surfactants in fire foams as described in the European Chemicals Agency reports.

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Photolithography is a patterning process in which a photosensitive film, called a photoresist, is selectively exposed to light to provide a pattern to an underlying substrate, with the chemistry of photoresists and role of PFAS different for different wavelengths. Photolithography is a critical process step in the mass production of a semiconductor, with the most advanced devices requiring over 70 photolithographic steps in their production. On average a minimum of 10 years is required to take a new product to market, from concept through development and deployment. This is assuming alternatives are known and commercially available.

Although the total amount of PFAS used in photolithography is small when compared to global consumption and releases of PFAS[32], the addition of small quantities of fluorinated materials enables patterning capabilities that are otherwise not possible to achieve, this leads to superior device performance. In comparison to the 836,787 tonnes of 2020 EU PFAS brought new to market,[33] the semiconductor industry uses less than 2.3 tonnes per year of PFAS in photolithography in the European Economic Area.

The following uses of PFAS in photolithography have been listed, with a short description of their technical criteria:

1. Component of surfactants,
2. Component of photoacid generators (PAGs) in chemically amplified resists (CARs) and bottom anti-reflective coatings (BARCs),
3. As low refractive index materials in top antireflective coatings (TARCs), which are used to control thin film interference effects in photoresist layers as substrates are not perfectly flat and otherwise this will detrimentally affect the photoresist imaging fidelity,
4. As barrier layers in immersion lithography,
5. Photo-imageable polybenzoxazoles and polyimides for dielectric and buffer coat applications, and
6. Photoresist applications.

The various types of photolithographic materials and their applications have recently been reviewed in the 2022 Ober paper[34], with a key summary of PFAS uses outlined in Table 4-1.

**Table 4-1 Key photolithography PFAS uses and technical criteria.**

| PFAS use area | Function | Types of compounds used | PFAS provide |
|---|---|---|---|
| Photoresists and BARCs – Surfactants | Improved coating uniformity. Post develop rinses: prevention of pattern collapse. | Longer chain PFAS (C6-C8) and telomer alcohols pending form polymer backbones. Now mostly replaced by C4 pendant chains. Rinses: C4 surfactants. | Low surface tension, control of contact angle. |

[33] ANNEX XV RESTRICTION REPORT, Proposal for a restriction, Per- and polyfluoroalkyl substances (PFAS) by European Chemicals Agency 2023, Annex XV reporting format 040615 (europa.eu)

[34] Christopher K. Ober, Florian Käfer, and Jingyuan Deng, "*Review of essential use of fluorochemicals in lithographic patterning and semiconductor processing,*" Journal of Micro/Nanopatterning, Materials, and Metrology, Vol. 21, Issue 1, 010901 (March 2022). https://doi.org/10.1117/1.JMM.21.1.010901

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| PFAS use area | Function | Types of compounds used | PFAS provide |
|---|---|---|---|
| Photoresists and BARCs – PAGs | Precursor for the photoacid catalyst needed for CARs and BARCs. | Perfluoroalkylsulfonates C4 or lower and C4 or lower substituted superacid anions such as C1. For some advanced resists, these are bound to polymers. | PFAS component of PAGs generates strong acids that do not show side reactions that interfere with the chemical amplification process. |
| Photoresists – polymers | Control pattern profile in EUV. | C1 PFAS polymer. | Increases absorbance, improves the dissolution properties, increases resolution. |
| TARCs | Control of thin film interference effects in resists. | Fluorinated water and developer soluble polymers. | High fluorine content is needed to achieve the low refractive index needed to effectively suppress film interference effects. |
| Immersion barriers | Protection of the resist from immersion liquid and of the exposure tool from contamination.<br>Prevent water film pulling and resist component leaching in immersion topcoats. | Spin-on barriers: Water insoluble and developer soluble polymers with fluorinated side chains.<br>Embedded barriers: oligomeric or low molecular weight polymeric highly fluorinated compounds.<br>Fluoroalcohol methacrylate polymers with high water contact angles (in the order of >90°). | Barriers that are soluble in casting solvents, insoluble in water but soluble in developer, and that show no intermixing with photoresists.<br>Hydrophobicity and control of contact angle, inert under 193nm radiation, and transparency. |
| Dielectric Polymers (PBO/PI) | Provide electrical, thermal, and mechanical protection for the semiconductor device. Also protects the device components from the impact of moisture. | Water-insoluble C1 PFAS polymers. | C1 PFAS groups attached to the polymer backbone provide solubility in environmentally friendly casting solvents and enable aqueous development. |

Owing to the changing technological challenges as the wavelength of exposure decreases, different PFAS uses are required depending on the technology used. Table 4-2 aims to outline this differing need at a high level.

**Table 4-2 PFAS use in photolithography according to exposure technology.**

| Wavelength (nm) | PFAS use | Technical requirement |
|---|---|---|
| 365 nm and larger | • Mostly surfactants<br>• Some PAGs in niche photoresists<br>• Photoimageable polybenzoxazoles<br>• Polyimide | Surface levelling, resolution enhancement. |
| 248 nm | • Surfactants<br>• Photoimageable polybenzoxazoles and polyimide<br>• PAG | 365nm resists were insufficiently transparent so alternative CAR resists were developed requiring PAG. |

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| Wavelength (nm) | PFAS use | Technical requirement |
|---|---|---|
| 193 nm | • Surfactants<br>• Photoimageable polybenzoxazoles and polyimide<br>• A limited number of PAGs<br>• Immersion barriers | 248 nm resists were insufficiently transparent, requiring a new chemistry for 193 nm resists that only works with PAGs that make very strong acids. |
| 13.5 nm (EUV resists) | • Surfactants<br>• PAGs (frequently polymer bound) | Low acid diffusivity in photoresists and underlayers.<br><br>Increases absorbance, improves the dissolution properties, increases resolution. |

Material changes for lithographic materials are not easy nor quickly achieved, with PAGs in chemically amplified resists having been under development for at least 25 years. Current PFAS materials were designed, developed, and optimised as dedicated substances to satisfy many functions and performance needs in lithographic imaging products. Thus, replacement with a new non-PFAS material will likely require multiple solutions depending on the application.

Each new material must satisfy multiple performance characteristics that may be impacted by the change, as outlined in Table 4-3. As a result, each new non-PFAS replacement product containing the new non-PFAS material(s) must be optimised to satisfy multiple performance characteristics, while not detrimentally impacting others to fully meet all customer requirements.

**Table 4-3 Photolithography potential PFAS replacement viability and timeline uses and technical criteria.**

| PFAS use area | | Timeline to develop | Concern of alternative | Criticality for manufacture |
|---|---|---|---|---|
| Surfactants | CARs and BARCs: silicon-based surfactants developed for some applications; not suitable for all applications. | Commercial replacement materials exist.<br>For applications that do not have existing commercial replacements, invention is required. | At high levels, silicon surfactants may cause etch defects. | Replacement maybe possible in many applications, but there will be exceptions due to replacement capability/functionality. |
| | Rinses: non-PFAS aqueous surfactants – active area of research. | Active area of research; time to prototype 1-2 years. | Still need to demonstrate equivalent performance. | Critical for advanced lithography. |
| | | **Total development time for surfactants up to 15 years after invention.** | | |
| PAGs in CARs and BARCs | PFAS free alternatives do not show suitable performance. | PFAS free PAG 5+ years of invention, estimated | A PFAS free PAG of equivalent performance has never been | Critical: currently most CARs for any node use PFAS. PAGS and all production of chips below |

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| PFAS use area | | Timeline to develop | Concern of alternative | Criticality for manufacture |
|---|---|---|---|---|
| | | timeline to implement from **15 to more than 20 years after invention.** | developed so this may not be technically possible for all applications or wave-lengths. Any substitution will likely have to be limited to certain applications only. | 40 nm node is impossible without PFAS CARs. See Table 4-4 for more information. |
| | Currently only possible to replace for 248nm resists or those exposed at larger wavelength. | | | |
| | Replacement with shorter chain, lower molecular weight PFAS fails due to volatility and diffusivity. | Substitution with lower chain PFAS: **10+ years** to re-qualify and assess impact on subsequent process steps. | Substitution with lower chain PFAS: requires significant work to be undertaken and resources would have to be diverted from developments in innovation. | |
| TARCs | Originally salts of PFOA or PFOS were used but replaced ~ 2004 with other PFAS that show lower bioavailability and bioaccumulation. | New research needed. | Refractive index of 1.3 -1.4 needed to be effective. For ease of use and defect control, it is advantageous to spin TARCs on using water as the solvent. | Current implant processes use TARC as an effective way of reflectivity and defectivity control. Alternatives are more complex and require additional processing. |
| | Concepts for replacements exist but are unproven and need to offer suitable performance in terms of thickness, uniformity, coat quality, surface energy, edge bead, roughness, gap-fill, and aging at various temperatures. | Timeline for invention 5+ years and development another 8+ years. | Some concepts for PFAS-Free TARCs unavoidably lead to significant loss of wafer throughput, e.g., dyed TARCs[35] have a 20-30% wafer throughput loss. | |
| | Silicon anti-reflective coating materials are under evaluation. | **Total development time from 11 to more than 13 years after** | | |

[35] Ralph R. Dammel and Robert A. Norwood, “Light-absorbing antireflective coatings with improved performance due to refractive index optimization,” US patent 6,274,295 B1 (2001) and, Wu-Song Huang, William H. Heath, Ranee Kwong, Wenjie Li, Kaushal Patel, Pushkara Rao Varanasi, "New 193-nm top antireflective coatings for superior swing reduction," Proc. SPIE 6153, Advances in Resist Technology and Processing XXIII, 61530S (29 March 2006); doi: 10.1117/12.656641

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| PFAS use area | | Timeline to develop | Concern of alternative | Criticality for manufacture |
|---|---|---|---|---|
| | | **invention for TARCs.** | | |
| Immersion barriers | There currently is no known concept for a non-PFAS material that can combine all the necessary properties. Properties include soluble in casting solvents and developer, but insoluble in water, no intermixing with photoresists, very high-water contact angles (>90°) to prevent watermark defects. | Current assessment is that replacement requires invention, but **no concept currently exists for replacement**. | Production of chips below the 40 nm node is not possible without immersion barriers. | Critical – no known alternatives to PFAS, no concepts for replacements. |
| Dielectric Polymers (PBO/PI) | PFAS free alternatives either don't show suitable performance or require the use of highly toxic casting solvents. | New research needed to develop soluble PFAS free polymers. | PFAS free alternatives currently require the use of highly toxic casting solvents. | Critical for advanced semiconductor packaging. |
| | | **Total development time of 15+ years after invention for PBO/PI.** | Lack of PFAS in the backbone can result in resolution and aqueous development issues. | |

## 4.1 Photoacid Generators (PAG)

Photoacid generators (PAG), are photoactivated acid compounds which, when irradiated with high energy light (deep ultraviolet or EUV), undergo photodissociation generating extremely strong, non-reactive and stable acids. Currently there are somewhere between 100 and 150 PAGs used in CARs worldwide. They are used in relatively small quantities overall.[36] The individual use of a PAG is dependent upon the overall parameters that must be met in the CAR – the chemical, physical and imaging/print quality characteristics. Because of this, there is no single PAG that is suitable for use in all CAR applications.

PAG precursors need to be sufficiently soluble in good casting solvents. The acids need to be sufficiently strong to cause the solubility change, non-absorbing at key wavelengths to avoid pattern disruption, have a low volatility to not evaporate from the resist films and not undergo side reactions which would destroy the acid catalyst.[37] In addition to this, with smaller node sizes the right amount of diffusivity is also required. However, when investigating alternatives, the following properties also need to be investigated; final resolution, exposure latitude, focus window, wall angle, top retention, or isolated to dense feature bias. These parameters result in different optical proximity correction requirements and

[36] As outlined in Table 4-5 Organic Polymers of which PAGs are a portion thereof has a consumption figure of 9,276 kg/year globally for 2021.

[37] Something that standard strong acids such as hydrogen chloride or bromide would readily do.

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hence in the need to procure a new mask set for the resist. Finally, the wafers patterned with new resist have to be tested for performance in subsequent process steps. This process is sufficiently demanding that most chip manufacturers have special integration teams assigned to it and this often takes 3 years or more.

Non-PFAS PAGs generally lack the acidity to perform in current platforms and this prevents the required reactions from progressing. Potential alternatives such as pentacyanocyclopentadiene (CN5) were investigated,[38] however, it was found to have strong absorption at 248nm preventing it being used at that wavelength. Its use in 193nm was found to have half of the processing speed of PFAS alternatives, and toxicological testing in rats found the presence of cyanide. Nitro-substituted thiophene was also investigated by the same team but also found to have an inferior standard of performance. There are initial indications that bis-sulfonyldiazomethanes might be suitable in 248nm but not at 193nm due to the weaker acids generated, however this needs to be fully investigated.

Amongst known substitutes, IBM have developed non-PFAS PAGs (CN5 and thiophene sulphonate), which has highlighted the difficulty of developing formulations that meet all performance criteria simultaneously, as shown in Table 4-4. As such, non-PFAS PAGs are for a narrow range of use applications only, as no known non-PFAS PAG/photoacid exhibits the same level of performance for all criteria. While a candidate chemistry might show good acid strength, it will have lower photospeed[39] because of lower acid diffusivity, and at the same time the acid anion might be transparent for a single wavelength only. PFAS PAGs, on the other hand, present simultaneously good to excellent performance for all listed performance criteria with the notable exception of environmental persistence.

**Table 4-4 Comparison of the performance of PAGs versus alternatives.**

| Performance criterion | PFAS PAGs/photoacids | CN5 non-PFAS PAG/photoacid | Thiophene sulfonate PAG/photoacid |
|---|---|---|---|
| **Photospeed[39]** | Excellent | Poor | Good |
| **Acid strength** | Excellent | Excellent | Good |
| **Diffusivity** | Good to excellent[40] | Lower than PFAS acids | High to too High |
| **Pattern quality/ Line width roughness** | Good | Line width roughness higher than commercial resists | Line width roughness much higher than commercial resists |
| **Transparency at all exposure wavelengths** | Excellent | Not transparent at 248nm | Not transparent at 248nm |
| **Solubility of PAGs in casting solvent** | Good | Good | Poor to moderate |
| **Lack of side reactions** | Excellent | Excellent | Excellent |
| **High process temperature requirement** | None | Yes | None |

[38] Martin Glodde, Sen Liu, and Pushkara Rao Varanasi, "*Fluorine-free photoacid generators for 193 nm lithography based on non-sulfonate organic superacids*," J. Photopol. Sci. Technol. 23 (2), 173-184 (2010) and Sen Liu, Martin Glodde, and Pushkara Rao Varanasi, "*Design, Synthesis and Characterization of Fluorine-free PAGs for 193nm Lithography*," Advances in Resist Materials and Processing Technology XXVII, Proc. of SPIE Vol. 7639, 76390D (25 March 2010); doi: 10.1117/12.846600

[39] Photospeed is a composite of acid strength, acid diffusivity, and PAG quantum yield.

[40] Low diffusivity requires polymer-bound photoacids.

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| Performance criterion | PFAS PAGs/photoacids | CN5 non-PFAS PAG/photoacid | Thiophene sulfonate PAG/photoacid |
|---|---|---|---|
| **Uniformity of PAG distribution** | Good | Good | Good |
| **Toxicity** | Moderate to high | High[41] | Moderate |
| **Environmental persistence** | Highly persistent | Assumed to be biodegradable | Assumed to be biodegradable |

So far, the only non-PFAS alternatives for 193 nm applications or lower are not technically viable due to their potential for a prohibitively high decrease in yield (estimated by a Semiconductor PFAS Consortium member to be 1-2%), and lower performance. If alternatives decrease yield even by very small percentages at a fab production site, this results in significant **increases in extremely high-cost waste generation**. The current feature sizes would not be able to be achieved as a significant invention still has to be undertaken, moreover it is not certain if suitable materials can be developed for all applications. As such all **manufacturing of these devices have to rely on PFAS** until wavelength-specific, alternative superacids have been developed. This significantly increases the amount of invention and development that needs to be done as all of the above-mentioned steps would need to be completed for each alternative analysed.

Additionally, even if performance criteria can be met, the replacement of PFAS PAGs by non-PFAS alternatives with fundamentally different acidity and diffusion profiles are likely to result in even larger differences in photoresist behaviour, which means that the above-mentioned task of resist re-qualification and integration is even more demanding. This would be in addition to the requirements for product development, customisation, product scale-up, commercialisation, customer product evaluation (with potential product optimisation/evaluation loops between suppliers and customers), and final qualification at the customer site.

## 4.2 Top antireflective coatings (TARCs)

Top antireflective coatings (TARCs) previously used PFOS and PFOA. Activities to replace these began in 2004 to use other fluorinated polymers that show lower bioavailability and bioaccumulation. This replacement has been completed and it is believed that no PFOA/PFAS-based TARCs are on the market. This substitution activity highlights challenges in identifying and qualifying alternatives as it took manufactures between 4-15 years depending on their use of PFOS and PFOA. As a result of this change, a number of unintended consequences also occurred; the developer use increased by 25%, the cycle time increased ~25% and in some cases of previous PFOS use the yield significantly dropped, all of which have **negative environmental and production cost impacts**.

## 4.3 Immersion Barriers

Immersion barriers include spin-on barriers and embedded barriers. Spin-on barriers are coated on the resist from an alcohol solvent, whereas embedded barriers as part of the photoresist solution are initially homogeneously distributed in the resist but migrate to the resist surface through phase separation. Both types are removed during the development step of production and are a key part of the immersion lithography process. Chip manufacture at and below the 40 nm node is not currently possible without them.

[41] Cyanide ion is found in rat stomachs when fed CN5.

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Although PFAS-free silicon-based barriers are available, they are not developer-soluble, are not stable under 193 nm exposure and could lead to $SiO_2$ deposits on the lens element. If deposits occur, the entire production tool would need to be shipped back to the manufacturer for repairs, causing it to be out of commission for 6 months or more. No other potential alternative has yet been identified offering suitable technical performance, as such the replacement of PFAS in immersion barriers is currently considered **technically not possible at this time**.

## 4.4 Surfactants

Another fundamental application of PFAS compounds in photolithography is the use of PFAS surfactants. Surfactants in general are “surface-active agents” that consist of a hydrophobic segment and a hydrophilic unit. Surfactants can be used in a variety of coating applications for improving film quality and component mixing, and changing surface interaction, and wetting characteristics. One specific performance advantage of fluorinated surfactants is that the surface activity is much higher than equivalent hydrocarbon or silicone surfactants as indicated by the requirement for less surfactant material in a formulation to achieve its critical micelle concentration. Fluorinated non-ionic surfactants have been used in a wide range of lithographic processes due to their very low surface energy, thermal- and mechanical stability, and low refractive index and they can be used to improve photoresist deposition and eliminate defects during photoresist coating.

The majority of non-PFAS alternatives contain silicon, which can lead to potential compatibility and defectivity issues as outlined in Section 4.3. Polyalkylene glycol based and alcohol ethoxylate based surfactants were also screened in bottom anti-reflective coatings but were not able to show suitable performance. Replacements are most likely to be **less problematic for older, less advanced technologies** (i.e., i-line photoresists[42]), but for **advanced lithographic photoresist technologies**, direct replacement of PFAS surfactant with non-PFAS options is more challenging and **requires invention**. There is the concern that PFAS-free surfactants will lead to shorter shelf-life stability due to the comparative strength of the carbon-fluorine bond not being able to be matched, which would impact the supply chain logistics 40otentiallly result in an increase in extremely high-cost wasted products.

## 4.5 Dielectric Polymers: polyimides (PI) and polybenzoxazoles (PBO)

The development of next-generation semiconductor products has become reliant upon advanced semiconductor packaging technologies. These advanced packaging technologies have enabled the modular integration of several small chiplets[43] designed to meet specific functions within a larger completed package, like on-chip memory, accelerators, controllers, and chip-to-chip interconnections. Advanced semiconductor manufacturing technologies have new performance requirements, such as the need to control heat generation within the new stacked configurations, as well as the need to maintain electric integrity through control of electrical leakage and mechanical integrity during thermal cycling in operation. These materials are non-fugitive and stay with the device for its service life. The cured material is insoluble in either aqueous or organic media and is sandwiched between inorganic layers. These materials must therefore have sufficient thermal, mechanical, and electrical properties to survive the harsh environments in which the devices made with them are used, as predicted by highly accelerated stress testing.

The new performance requirements of advanced semiconductor packages have been met through the development and implementation of novel photo-imageable dielectric materials. These dielectric

[42] A general purpose, multi-wavelength resist designed to cover a wide range of film thicknesses, 1–10 µm, with a single coat process.

[43] Chiplets are small, modular chips which are part of a processing module that makes up a larger integrated circuit.

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materials are virtually exclusively selected from two families of polymers: polyimides and polybenzoxazoles. These polymeric materials protect the semiconductor device by effectively preventing electrical leakage, thermal stress, and corrosion of the underlying semiconductor circuitry. The PI and PBO materials are required to be photo-imageable to meet the required high-resolution requirements for chiplet interconnects through the use of PFAS ingredients typically found in photolithographic chemistries such as surfactants, photoacid generators and polymers. PI and PBO materials used in advanced packaging applications typically employ C1 PFAS groups attached directly to the polymer backbone to impart solubility, transparency, and moisture resistance in the dielectric film as well as clean development of patterns in aqueous processing.

The essential properties enabled by the use of the C1 PFAS in the polymer are:

- Optical transparency
- Thermal stability
- Low moisture absorption
- Lower cure temperature
- Cleaner development
- Aqueous development of PBO materials
- Higher resolution of solvent developable polyimides
- Good mechanical properties (e.g., elongation at break)
- Improved electrical properties
- Solubility in environment, health & safety friendly solvents elimination the need for more toxic solvents

Currently no PFAS-free materials are known to be viable as photo-imageable dielectric materials for use in advanced semiconductor manufacturing processes.

Photo-imageable dielectric materials can be deposited through either a spin-on process, or as a dry film. Wastes generated from spin on application is similar to that from a photoresist, where waste photo-imageable dielectric chemistry and solvent based developer is collected within a bulk waste solvent collection system and managed as hazardous waste through thermal destruction at an incinerator or within a cement kiln. Aqueous based developer waste is collected in a separate, aqueous waste stream, neutralised, and filtered/separated prior to release to the aqueous waste stream.

With the demands of the industry for improvements in lithography and packaging, the replacement of C1 PFAS moieties on the polymer backbone with currently known alternatives would significantly compromise the performance required for these applications.

Moving away from PFAS in photoresist applications, is likely to require a **change in the entire photolithographic process**. Photoresists are not interchangeable; they are designed to work with a specific photolithography method and are needed for the life of that manufacturing facility which is dedicated to the particular device technology (generation) being manufactured. Qualifying an alternative as a drop-in photoresist replacement part way through the life of a facility would not be possible in many cases and would need assessing for each facility individually.

## 4.6 Environmental Considerations in Photolithography

Worldwide, a total of 33,745 kg of PFAS are used by semiconductor manufacturers in photolithography annually based on SIA's members survey of 2021 sales capturing well over 90% of the materials market, as shown in Table 4-5. TARCs are the largest single product type, accounting for over 50% of total PFAS use in photolithography. The total PFAS use for photolithography in Europe is estimated to be **2,248 kg** annually, or about 6.7% of the worldwide semiconductor use.

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The total worldwide PFAS discharges from photolithography range between **1,282 to 17,433 kg/year** (of which the EU is estimated at 6.7%, or 86 to 1,168 kg/year), depending on the amount of spin bowl waste collection. SIA estimates from previous surveys that about 50-60% of TARC users collect and properly dispose of the waste so the emissions are expected to be on the lower end of this scale. With full TARC spin bowl waste collection, the **estimated amount discharged to wastewater in the European Union is 56 kg per year**.

**Table 4-5 Results of SIA 2021 sales survey and an example release mass balance.**[44]

| Total PFAS Used in Litho (2021 SIA Survey) | | | | | Split Organic Polymer by type | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| PFAS (kg/yr) | Aq non-polymer | Aq polymer (TARC disp to WW) | Aq polymer (TARC disp collected) | Org non-polymer | Org Poly Immersion Top Coat | Org Poly Solv Dev PB/PI | Org Poly Aqeous PB/PI | Org Poly Resist | Total w/o TARC collection | Total w/ TARC collection |
| **Total PFAS used in photolithography (kg/y)** | **229** | **17,182** | **17,182** | **9,726** | 1652 | 2147.6 | 2147.6 | 660.8 | 33,745 | 33,745 |
| **Disposition in the materials balance model:** | **(kg/y)** | **(kg/y)** | **(kg/y)** | **(kg/y)** | **(kg/y)** | **(kg/y)** | **(kg/yr)** | **(kg/yr)** | **(kg/yr)** | **(kg/yr)** |
| pfas collected at dispense for disposal | 215 | 0 | 16,151 | 9,142 | **1,553** | 2,019 | **2,019** | **621** | 15,569 | 31,720 |
| pfas in dispense step to ww | 0 | 16,151 | 0 | 0 | **0** | **0** | **0** | **0** | 16,151 | 0 |
| pfas in developer ww | 11 | 859 | 859 | 243 | 83 | 0 | 54 | 17 | 1,267 | 1,267 |
| pfas to plasma strip | 0 | 0 | 0 | 156 | 0 | 0 | 34 | 11 | 201 | 201 |
| pfas to wt strip ww | 0 | 0 | 0 | 12 | 0 | 0 | 3 | 1 | 16 | 16 |
| pfas to solv strip waste | 0 | 0 | 0 | 75 | 0 | 107 | 17 | 5 | 205 | 205 |
| pfas to solid waste | 1 | 43 | 43 | 24 | 4 | 5 | 5 | 2 | 84 | 84 |
| pfas collected as solvent waste in tool cleans | 2 | 129 | 129 | 73 | 12 | 16 | 16 | 5 | 253 | 253 |
| Total pfas waste & efl: | 229 | 17,182 | 17,182 | 9,726 | 1,652 | 2,148 | 2,148 | 661 | 33,745 | 33,745 |
| Total dispensed | 229 | 17,182 | 17,182 | 9,726 | 1,652 | 2,148 | 2,148 | 661 | 33,745 | 33,745 |
| **Total release to to the environment (WW) :** | **11** | **17,010** | **859** | **255** | **83** | **0** | **56** | **17** | **17,433** | **1,282** |
| % of use discharged to the env: | 5.0% | 99.0% | 5.0% | 2.6% | 5.0% | 0.0% | 2.6% | 2.6% | 51.7% | 3.8% |
| | | | | | | | | | | |
| **Total PFAS used in Europe for photolithography[kg/y]** | 0 | 598 | 598 | 531 | 130 | 169 | 169 | 52 | 2,248 | 2,248 |
| **Total release to to the EU environment (WW) :** | 0 | 592 | 30 | 14 | 7 | 0 | 4 | 1 | 618 | 56 |
| % of use discharged to the EU environment: | 0.0% | 99.0% | 5.0% | 2.6% | 5.0% | 0.0% | 2.6% | 2.6% | 51.7% | 3.8% |

The following assumptions were used in the calculation:

- During spin on processes, 95% of the dispensed material was left in the spin bowl as waste, whereas 5% remained as a coating on the wafer.
- For aqueous development, 100% of the TARC and immersion topcoat material was removed in development and discharged to wastewater.
- For photoresists, an average of 50% of the coating is dissolved in aqueous developers and discharged to wastewater, and the other 50% would remain on the wafer and be removed in subsequent strip operations.

[44] For this table, the presented acronyms and their meaning are as follows: Litho (photolithography), Aq (aqueous), Org (organic), Poly (polymer), Solv (solvent), Dev (developer), PB/PI (polybenzoxazole / polyimide), wt (wet), efl (effluent), env (environment), WW (wastewater), w/o (without), and y or yr (year).

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# 5 WET CHEMISTRY USES

**Summary:** Wet chemical processing is the terminology used to describe several different semiconductor fabrication processes that involve dispensing a liquid chemical mixture to clean, etch, dry, planarize, or electroplate. The composition of wet chemical process formulations varies greatly depending on the application-specific performance requirements. Different companies and even different fabs within the same company do not all manufacture the same products, and therefore there are important inter- and intra-company differences in the wet chemical processing formulations and technologies in which they are employed. It follows that the need for a PFAS component in a wet chemical formulation depends on the application-specific performance requirements that, in turn, depend on the specific wafer processing technology being manufactured.

The timeline needed to develop, qualify, and implement alternatives falls into the following four broad categories:

- **3 to 4 years**: If an existing non-PFAS alternative is available and can be demonstrated to provide adequate performance for a specific application.
- **3 to 15+ years**: In some applications where an existing non-PFAS alternative may be viable but requires tooling and/or process changes before it can be successfully introduced into high volume manufacturing (HVM).
- **Successful invention required (from 5 to more than 12 years)**: For some applications it may not be possible to demonstrate that an available non-PFAS alternative can fulfil the application specific performance requirements. In these cases, it may be necessary to invent and synthesise new chemicals, and/or develop alternative approaches to fabricating a device structure that provides the necessary electrical and computational performance. Invention is an open-ended endeavour with no guarantee of success.
- **No alternative achievable**: In some cases, it may ultimately be found that a non-PFAS alternative is not capable of providing the required chemical function. If a non-PFAS alternative chemical cannot be invented, then the integrated circuit device structure may need to be abandoned in favour of an alternative device structure that may or may not provide equivalent performance.

Fluorinated organic chemicals have several unique physicochemical properties that, in some applications, are essential to the successful performance of the process. However, there is no general *a priori* means to determine whether a non-PFAS alternative will be capable of working for a particular application. Instead, the evaluation of potential alternatives must begin with experimental trials using available non-PFAS candidates as guided by chemical theory and experience. The timeline as outlined in the Executive Summary and Wet Chemicals uses Summary.

The majority of wet chemical formulations do not utilise a PFAS additive. Where PFAS are used in wet chemical processing they are typically shorter chain PFAS (4-perfluorocarbon or less). Many of the shorter chain PFAS have been implemented relatively recently as alternatives to the longer chain homologues like PFOS and PFOA that they replaced. For instance, one device maker spent 8 years replacing the PFOS (8-perfluorocarbons) in a buffered hydrofluoric acid (BHF) formulation with a 4-perfluorocarbon alternative by working with several chemical suppliers. In contrast to the technical challenge in substituting from a long chain to a shorter chain PFAS homologue, it can be anticipated that substitution from a short chain PFAS to an entirely PFAS-free alternative represents a significantly more difficult technical challenge.

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The move to shorter chain PFAS, despite there being evidence that they have lower bioaccumulation factors[45], is now seen as a regrettable substitution and highlights the need for comprehensive cross discipline evaluations of the alternatives that are offered as replacements for currently used PFAS.

## 5.1 Wet Chemical Processing

Wet chemical processing encompasses several different semiconductor fabrication processes including wet chemical etching, planarization, electroplating, and also wafer cleaning, rinsing, and drying. Although these involve very different wafer processing operations, with different objectives, the common factor is that they involve contacting a wafer with a liquid chemical mixture.

Wet chemical etching and cleaning operations are typically conducted in specialised “wets” SMRE or tools that bring a liquid chemical mixture into contact with wafers either by dispensing it onto a spinning wafer or by immersing one or more wafers into a tank for “batch processing wets tools”.

In most wet etch, chemical mechanical planarization (CMP), electroplating operations, and in many wafer cleaning operations, the areas of the wafer that are operated on by a wet chemical processing step are isolated to very specific regions of the wafer defined by a photolithography “masking” operation. In assessing the complexity and challenge of conducting a wet chemical process, therefore, it is essential to consider the dimensions and geometric complexity of the integrated circuit features that are being fabricated. Although semiconductors are typically fabricated from crystalline silicon “wafers” that are generally either 200 mm or 300 mm in diameter, and in the order of 0.8 mm thick; the individual integrated circuit device structures often have critical dimensions that typically measure in nanometres and thus are often at the molecular scale. It is the dimensions and materials complexity of the device features, not the wafer as a whole, that presents the challenge in wet chemical processing.

Figure 5-1, for instance, illustrates schematically a typical wet chemical etching operation where a patterned photoresist is used to delineate the region of the wafer substrate that the etchant operates on. The etchant must transport into, react with, and transport reaction products out of the region that is masked by the photoresist layer, and must “stop” at, and not remove material from the underlying substrate. The difficulty of the wet etch application generally increases with the need to etch features that are very narrow and deep (high aspect ratio). The difficulty of an etch operation also depends on the number and type of materials that are exposed to the etchant, and the relative removal rate for each material.

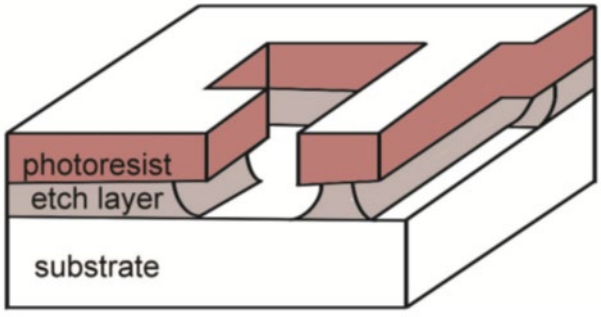


Figure 5-1 Conventional simple wet etch application.

[45] Burkhard, L.P., 2021. Evaluation of published bioconcentration factor (BCF) and bioaccumulation factor (BAF) data for per- and polyfluoroalkyl substances across aquatic species. Environmental toxicology and chemistry, 40(6), pp.1530-1543.

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Figure 5-2 illustrates the geometry of a current generation memory cell, where the etchant needs to penetrate between “nano sheets” that may be only tens of nanometres wide, and down into a channel that can be thousands of nanometres deep. The aspect ratio of the region into which etchant must transport, and etchant products must be removed, is more than 100 which introduces highly demanding technical requirements.

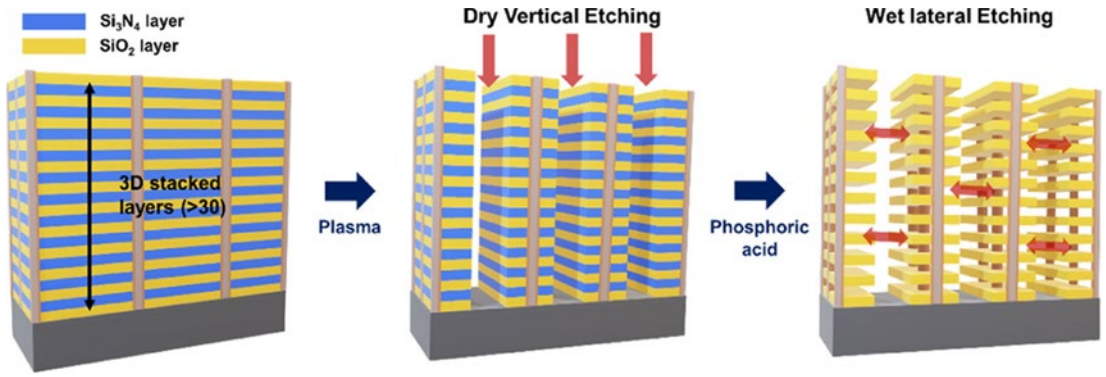


**Figure 5-2 3D NAND flash memory manufacturing process and wet lateral etching. Each layer is on the order of 25-40 nm thick, and 4,000 nm deep.[46]**

The rinsing and drying of a modern wafer is also challenging due to the narrow dimensions causing immense capillary forces to be generated by the liquid on the walls of the structure, as illustrated in Figure 5-3 and can result in “pattern collapse” as illustrated in Figure 5-4. The phenomenon of pattern collapse requires the use of specialty fluids, these are used to either reduce the surface tension of the fluid that enters a channel or change the surface properties of the channel walls. Fluorinated surfactants and fluorinated surface modification chemicals, which are capable of lower surface forces than other known materials are often required to solve pattern collapse issues. With the increasing geometric complexity and narrow dimensions associated with advance integrated circuit fabrication, there will be continuing, if not increasing need to employ specialty fluorinated liquids in these applications.

[46] Lee, H.I., Kim, H.S., Tikue, E.T., Kang, S.K., Zhang, H., Park, J.W., Yang, S. and Lee, P.S., (2021). Green Manufacturing of Silyl-Phosphate for Use in 3D NAND Flash Memory Fabrication. ACS Sustainable Chemistry & Engineering, 9(14), pp.4948-4956.

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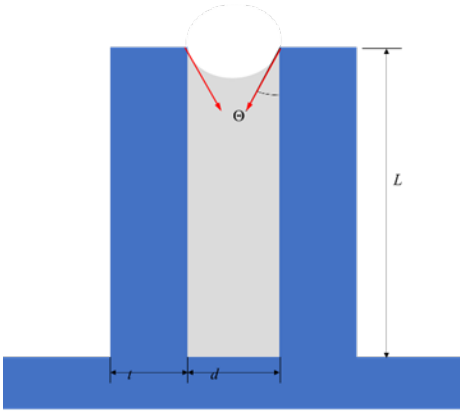


Figure 5-3 Diagram illustrating the capillary forces exerted by a wetting fluid on the walls of the material holding the fluid.[47]

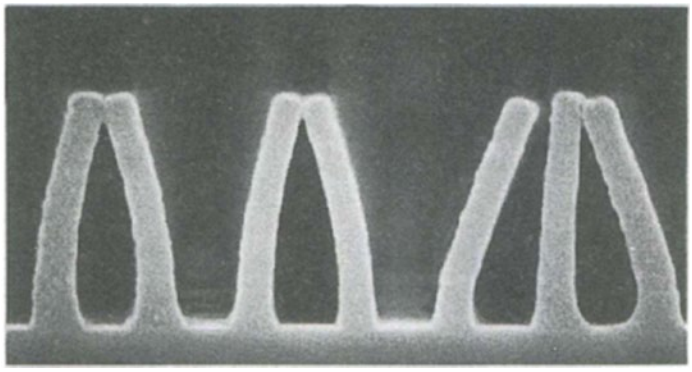

Figure 5-4 Image of line collapse that has been caused by capillary forces.[48]

## 5.2 Surfactants

Wet chemical formulations vary greatly depending on the particular application. Surfactants are commonly needed in wet chemical formulations, and in some applications, a fluorinated surfactant is used because of the superior performance they provide as described below. However, in addition to use as surfactants, other types of PFAS are also employed as surface modifying agents and solvents. Additional detail regarding these uses is provided in the Wet Chemical Processing White Paper, as outlined in Table 1-2.

In general, surfactants are often added to semiconductor chemical formulations to achieve the necessary process performance which include:

- The ability to reduce surface tension at low concentrations and to allow for the penetration of aqueous solutions into narrow, high aspect ratio features with hydrophobic sidewalls,

[47] https://www.tel.com/product/cellesta.html

[48] Image provided by Bassett (2019) TEL.

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- Stability in strong mineral acids and bases,
- Rapid adsorption at solid/liquid interface to provide improved wetting which improves etch rate uniformity of films,
- Adsorb to a surface to prevent the deposition of metals that are introduced into the solution during an etching process,
- Adsorb to a surface to suppress etching of one material while another material is preferentially removed. For instance, in the removal of $SiO_2$ from the surface of a Si substrate, a surfactant is employed to selectively adsorb to the Si surface and suppress its etching while the $SiO_2$ is removed,
- Ease of rinsability from surfaces, and
- Low foaming to mitigate the formation of air bubbles that can form and cause failure of the etching of contact holes.

The selection of a particular surfactant for one of these applications varies depending on the application specific requirements. Important factors that can drive a requirement for a fluorinated surfactant include the following:

- If the surfactant must resist decomposition under chemically reactive conditions, including acidic, basic, oxidising, or reducing conditions, then organofluorine (a PFAS substance) surfactants may be required. Fluorocarbons have the strongest bonds known in organic chemistry.
- If the mixture must achieve very low surface tensions or contact angle, then a fluorinated surfactant may be required. Fluorinated surfactants can achieve lower aqueous surface tensions (15 – 20 dyne/cm) than hydrocarbon (~ 30 dyne/cm) and other known materials including fluorosilicates. This is due to a combination of low polarizability, high molecular surface area, and conformation of the perfluorocarbon tail groups.
- If the surfactant must retain its surface activity at very low pH, then a fluorosurfactant may be required. Fluoroalkyl acid surfactants, for instance, typically have near zero pKa[49] values and therefore their headgroup remains ionized and hydrophilic even if the pH approaches zero.
- If the surfactant must be surface active in a non-aqueous media, then a fluorinated surfactant may be required. Surfactants with perfluorinated tail groups are oleophobic as well as hydrophobic.

In many applications, several if not all of these factors together are essential to the performance of a fluorosurfactant.

### 5.2.1 Wet Clean applications

Wet cleaning occurs after virtually every wafer processing step, to remove residue and restore the substrate surface to a pristine state before proceeding to the next wafer fabrication step. Aqueous clean processes such as those known as standard clean 1 (SC1 =$H_2O_2$ and $NH_4OH$) and standard clean 2 (HCl and $H_2O_2$) are typically simple inorganic formulations that generally do not contain surfactants or other additives.

Organic solvent etch and clean formulations are used in some applications due to their unique solvency properties, and/or surface activity. Among the physicochemical attributes that are important in certain

[49] pKa, or acid dissociation constant, is a measure of the strength of an acid.

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applications are specified melting and boiling points, viscosity, surface activity and polarizability, solvency, hydrophobicity, and dielectric properties.

Multiple stage wet cleans use both aqueous and organic based cleaners and may be critical to ensuring the nanometre level device critical features and high aspect ratios. Each cleaning regime is specific to the product being cleaned, technology, type of chip and its end function.

### 5.2.2 Wet Chemical Etching

Wet chemical etch processes are used to selectively remove one material in the presence of others, often in the presence of extreme geometric complexity. Each etching operation must be highly uniform across a wafer, from wafer to wafer, from run to run, and regardless of variations in feature sizes and pattern densities. A variety of different aqueous etchant formulations are used in wet chemical processing. Commonly used aqueous etchants include BHF, the generically named “metal etchant” that typically consists of a mixture of phosphoric and other acids and aqueous tetramethylammonium hydroxide.

BHF, for instance, is used to wet etch or clean a variety of different wafer substrate materials including silicon, polysilicon, silicon oxide, silicon nitride, aluminium, copper, and photoresists. The challenge in conducting these operations varies greatly depending on the juxtaposition of materials and the geometric complexity of the feature being etched. In one common application of BHF, silicon oxide is selectively removed from a silicon surface. Another common application involves the etching/cleaning of contact holes, which vary significantly in their critical dimension and aspect ratio depending on the particular application.

PFAS-free BHF formulations are known to work for some BHF applications, but not all as fluorinated surfactants are still required where the following requirements are needed: very low pKa as needed to maintain a charged headgroup for surfactant properties at a low pH, very low surface tensions, or resiliency in highly aggressive chemical solutions. As such, depending on the number of technical challenges yet to be overcome and the need for systems level qualifications, the exact timeframe for qualification is very uncertain.

### 5.2.3 Chemical mechanical planarization (CMP) and Post CMP Cleans

CMP utilises water-based slurries typically comprised of mixtures of abrasive particles with chemical components such as acids, bases, oxidisers, chelating agents, metal passivating agents, surfactants, and other selectivity control agents to remove a wide range of film types ($SiO_2$, SiN, W, Cu, etc.). Surfactants are routinely used in the formulation of CMP slurries and post-CMP cleaning solutions, and in some applications the surfactant may be a PFAS. Typically, the surfactants serve to disperse the particles, improve slurry stability, control the wettability of films and polishing pads, and reduce corrosion of some films. Although only used in very specialised instances, fluorosurfactants can be found in the formulation of certain types of CMP slurries for targeted performance improvements, including the enablement of selective film inhibition and the wetting of low surface energy substrates.

### 5.2.4 Metal Plating

A variety of electrolytic and electroless plating operations are used in semiconductor wafer manufacturing (fab) and post fab packaging operations. Plating solutions commonly contain surface-active components, that in some formulations may contain PFAS to:

- Lower surface tension to:

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  - Improve wetting and access of the plating bath solution to geometric features with high aspect ratios,
  - Mitigate the inclusion of hydrogen gas that is generated at electrodes, into the metal deposit,
  - Reduce bubble size and mitigate acid mist formation.
- Provide a surface-active material as a co-reactant to form a deposition conjugate with the plating metal.

In addition to conventional plating operations, electroless plating of Cu is conducted in trench/via fill operations, and sometimes requires a surfactant to prevent interference from the hydrogen that is generated as a by-product. In these applications, a surfactant may need to be fluorinated in order to achieve the particular surface tension and wettability requirements, and/or for resiliency to the oxidation and reduction reactions.

Table 5-1 provides an overview of the PFAS uses in wet chem applications, all of which require from **3 to more than 15 years** to develop a PFAS-free alternative depending on whether qualification and implementation of existing alternatives, or invention of new materials and processes is required.

Historically, there were many more wet chemical uses of PFAS, but the majority of uses have already been substituted, in some cases to a shorter chain PFAS, with a limited number remaining. One such example, is the historical use of PFOS and PFOA as surfactants, which were substituted with shorter chain perfluoroalkyl sulfonic and/or perfluoroalkyl carboxylic acids. This change was the result of substantial effort over a period of up to 16 years for this application. Substitutions have impact across the supply chain. For example, one chemical manufacturer changed the design of over 20 products by incorporating alternatives. Those products were then, in turn, qualified and used by a hundred different customers. Some PFC gases are also used for cleaning, and these are discussed in Section 6.

The semiconductor industry expects PFAS-free alternatives to be much more difficult to find than the transition from PFOA or PFOS to shorter chain PFAS substances. This is because in many cases there are no known chemical alternatives that are capable of providing equivalent chemical functionality and performance to fluorinated organic chemicals. In some applications, a non-PFAS chemical may be viable, whereas in other applications currently known alternatives may not be able to provide the necessary performance requirements and therefore may be essential.

In some situations, it is likely that entirely new molecules may need to be synthesised and evaluated. To prevent regrettable substitution, the timeline must include evaluations of the chemical behaviour and toxicity of the proposed alternatives, including characterisation of the controls necessary to prevent impact to human health and the environment. Owing to these considerations, a specific timeline cannot be predicted. However, once the invention of a viable alternative has been accomplished, the demonstration, qualification, and transfer to HVM may take **more than 15 years**.

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Table 5-1 Examples of etches and cleaning operations utilising PFAS.

| PFAS use area | Role of PFAS additives | Concern of alternative | Criticality for semiconductor devices manufacture |
|---|---|---|---|
| **Aqueous etch/clean formulations**<br>**Organic based etch formulations** | a) Facilitate entry of the wet etchant into, and reaction products out of, a capillary space by reducing the surface tension of the fluid and the contact angle with the solid.<br>b) Adsorb to a surface to prevent the deposition of metals that are introduced into the solution during an etching process.<br>c) Mitigate the formation of air bubbles.<br>d) Adsorb to a surface to suppress etching of one material while another material is preferentially removed. | a) The surface-active agent must resist decomposition under chemically reactive conditions.<br>b) Fluorinated surfactants can achieve lower aqueous surface tensions (15 – 20 mN/m) than hydrocarbons (~ 30 mN/m) and other known materials including fluorosilicates.<br>c) Fluoroalkyl acid surfactants have uniquely low pKa values that enable them to remain ionized and hydrophilic even if the pH approaches zero.<br>d) Surfactants with perfluorinated tail groups are oleophobic as well as hydrophobic, and therefore are surface active in organic solvents as well as aqueous etchants. | PFAS additives are **critical for some, but not all wet etch applications**. The requirement for a PFAS additive depends on the physical dimensions and aspect ratio of the device feature being etched, and the particular set of materials exposed to the etchant during etching. |
| **Chemical Mechanical Planarization** | Surfactants and surface-active materials are critical components of CMP slurries and post-CMP cleaning solutions. These components must:<br>a) Disperse the particles.<br>b) Provide slurry stability.<br>c) Control the wettability of films and polishing pads; and<br>d) Reduce corrosion of some films. Fluorosurfactants are critical to achieving CMP performance requirements in certain situations. In particular, they are used where necessary to enable selective film inhibition and the wetting of low surface energy substrates. | a) The surface-active agents must rapidly adsorb to the substrate during polishing and rapidly desorb with water rinse.<br>b) they must be non-foaming to prevent foaming.<br>c) In situations where a very low surface tension is required, only PFAS surfactants can lower surface tension of aqueous solutions to values below ~ 20 (mN/m) rapidly.<br>d) In chemically aggressive CMP formulations a PFAS surface active agent may be necessary to prevent degradation by reactive oxygen species produced in oxidising systems. | PFAS additives are **critical for some, but not all CMP applications**. The requirement for a PFAS depends on the materials properties of the exposed surfaces that need protection, surface tension reduction requirements, and aggressiveness of the CMP formulation. |

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| PFAS use area | Role of PFAS additives | Concern of alternative | Criticality for semiconductor devices manufacture |
|---|---|---|---|
| **Organic solvent based clean formulations** | Organic solvents are required for some wafer clean/strip formulations and also some cleaning operations that are conducted on parts outside of the fab cleanrooms. In some applications these mixtures are comprised of fluorinated organic solvents and/or fluorinated organic alternatives in order to provide the necessary solvency and fluid handling characteristics. | The ability of a solvent to dissolve and solubilise a material from the surface of a wafer or part depends on their respective chemical characteristics, as often represented by the Hansen Solubility parameters (dispersion, polar, and H-bonding intermolecular forces). In some cases, therefore, a fluorinated component is necessary to remove fluorinated materials from a surface. | PFAS containing solvent mixtures are **critical for some, but not all solvent clean applications**. The requirement for a PFAS depends on the materials properties of the substance that needs removal. |
| **Pattern collapse mitigation** | PFAS are used in a number of different formulations that are used to mitigate pattern collapse issues, including surfactants, surface modification treatment materials, displacement fluids, and organic solvents. Historically associated with photoresist, pattern collapse is now a critical and evolving challenge in the etching and drying of narrow dimensioned, high aspect ratio device features like nanosheets and 3DNAND structures. Pattern collapse occurs when the capillary forces created by liquid menisci formed between high aspect ratio features exceed the structural strength of the material forming the walls of the capillary space. | The ability of a non-PFAS alternative to serve effectively as a means of pattern collapse mitigation depends on the particular application. Several different approaches that are in use, or being pursued, as means of mitigating pattern collapse issues that are evolving with increasing use molecular dimension device structures. | **Some PFAS containing formulations used to mitigate pattern collapse may be essential**. Development of new solutions for the evolving pattern collapse issue may be able to avoid the use of fluorinated organics depending on the application specific performance requirements. |
| **Plating and electroplating** | Plating and electroless plating utilise surfactants and surface-active materials to:<br>a) Reduce surface tension to improve wetting and access of the plating bath solution to geometric features with high aspect ratios.<br>b) Mitigate the inclusion of hydrogen gas that is generated at electrodes, into the metal deposit.<br>c) Mitigate bubble and/or mist formation.<br>d) Function as a co-reactant to form a deposition conjugate with the plating metal. | a) The surface-active agent must resist decomposition under chemically reactive conditions particularly at plating electrodes;<br>b) Fluorinated surfactants can achieve lower aqueous surface tensions (15 – 20 mN/m) than hydrocarbons (~ 30 mN/m) and other known materials including fluorosilicates;<br>c) Fluoroalkyl acid surfactants have uniquely low pKa values that enable them to remain ionized and hydrophilic even if the pH of the plating solution approaches zero.<br>d) Ability to function as a co-reactant depends on the materials present in the plating operation. | PFAS containing plating mixtures **are critical for some, but not all plating applications**. The requirement for a PFAS is application specific and therefore depends on the materials properties of substance being plated, as well as the dimensions and aspect ratio of the features being plated. |

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## 5.3 Environmental Considerations in Wet Chemistries

Semiconductor facilities generate organic and aqueous waste streams which are treated in accordance with local and federal waste and wastewater regulations. Organic waste is typically collected and disposed of as a blended fuel by high temperature incineration or reprocessing.

Historically, the majority of aqueous chemicals employed in fab manufacturing processes are discharged to an industrial wastewater drain system that conveys wastewater for treatment of specific regulated pollutants in accordance with local and federal regulations, and subsequently discharged to a publicly owned treatment works or surface water. Most PFAS are not regulated pollutants and therefore unless company specific provisions are in place, the wastewater from processes that use aqueous wet chemical formulations that contain PFAS would likely be discharged to the publicly owned treatment works without substantive removal of the PFAS. The industry is actively researching PFAS wastewater releases and treatment technologies.

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# 6 FLUOROCARBON USES IN PLASMA ETCH/WAFER CLEAN AND DEPOSITION

**Summary:** Perfluorocarbons (PFCs) and hydrofluorocarbons (HFCs) are essential for semiconductor manufacturing and are used in thin film deposition, plasma etch/wafer clean, and chamber cleaning processes, but are already subject to separate greenhouse gas regulations. The semiconductor industry has a demonstrable history of engineering solutions to reduce both the consumption and emission of HFC/PFC gases in response to environmental concerns. The industry can employ this substantial knowledge base to further improve the performance of abatement systems if exemptions are granted.

**PFAS alternatives either do not exist** at present, or if they do, they create **PFAS by-products if a carbon containing film is present.** The intrinsic properties of silicon wafers have informed the use of fluorocarbons. Invention is needed to find alternatives because silica compounds ($SiO_2$, SiN, etc.) are the foundation of semiconductor device structures and tuneable silicon layers require a specific and tuneable ratio of carbon and fluorine to etch.

For chamber cleaning, fluorine ions and radicals are necessary; non-PFAS alternatives are either potent greenhouse gases or extremely reactive and toxic and PFAS by-products are created if residual carbon is present.

A fundamental re-design of semiconductors and the equipment, processes, and chemicals to make them would be needed if HFCs and PFCs are no longer available for plasma etch and chamber cleaning processes. As such the following timelines are estimated (at a minimum) to implement alternatives after a feasible invention is identified:

- Dry etching **more than 15 years** to qualify each specific etch type and **additional implementation time if alternatives are found.**
- Chamber cleans **more than 10 years** for each specific type.

Perfluorocarbons (PFCs) and hydrofluorocarbons (HFCs) are critical process gases used within semiconductor manufacturing and have played a critical role in the evolution of semiconductor device technology to its current level of development. PFCs and HFCs are used in dry etching and other process operations due to their chemical stability and as their reactivity in plasma. Table 6-1 below summarises these operations, the current substances used, the status of alternative and the timescale to develop them. Plasmas and other specialised semiconductor process operations can convert stable gases into radicals and ions without the need for reactive gases to be stored and transported within semiconductor manufacturing facilities.

As many of these PFCs and HFCs are greenhouse gases, which are currently subject to separate regulation, the semiconductor industry has worked for over 30 years (and continues to work) to develop best practices to minimise PFC and HFC emissions. However, alternatives to PFCs/HFCs have not yet been found and the search is proving especially challenging for the etching of the insulator in the semiconductor device structure.

## 6.1 Dry Etching

While wet etches and cleans are used to indiscriminately remove metal, insulators, polymers, or defects; plasma or “dry etching” is used to **remove or chemically change very specific elements on the surface of the wafer**.

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In the manufacture of recent logic semiconductor devices, there are more than 100 distinct plasma etching process steps. Many of these process steps use PFAS gases. Some etching processes use PFAS as primary gas(es), whist others use PFAS as an additive. Each of these process steps has a different purpose and different requirements to be achieved, therefore many different combinations of PFAS are used.

Plasma etching is directional, making it possible to target the specific, microscopic features needed to be removed or chemically changed. The desired combination of anisotropic/isotropic etching and protective layer formation can be obtained by using plasma of PFAS gas(es) or a gas mixture containing PFAS gas(es). These etching processes are indispensable steps in the production of semiconductor devices.

In the semiconductor industry today, very high aspect ratios are required to enable increasingly demanding device densities. This means that plasma processes must be able to etch out smaller and smaller gaps. Especially where etching the insulator of the semiconductor device structure, it is important to have the interaction between C/CHF/CF deposition and F etching, when controlling the dissociation ratio of PFAS molecular radicals by plasma. By using directional etching of F while protecting any material that is not intended to be etched or otherwise altered during the etching process, using a deposited layer consisting of C and F, it is possible to etch the intended shape.

The physical and chemical reactions on the wafer are dependent on the type of gases, the flow rate of gases, the chamber pressure, the power, and other highly controlled and highly specialised chemical, and chamber conditions. Changing any one of these parameters can change the overall profile of the device structure being formed by the plasma etch process. The gases used for a specific etch must be selective for the material to be removed or changed. For instance, gases such as $CF_4$ alone will etch both silicon and silicon dioxide, so $CF_4$ needs to be combined with other gases (like hydrogen) so that it etches only the silicon dioxide.

## 6.2 Plasma Cleaning

Even with the highly controlled, selective use of PFCs and HFCs, some by-product deposition or dielectric layers previously deposited may occur on the sidewall of semiconductor equipment chambers. This deposition in both plasma etching and chemical vapour deposition chambers, if not cleaned periodically, can result in contamination of the wafer and the ultimate scrapping of functional semiconductors.

Periodic PFC cleaning and conditioning of chambers is used to optimise product yield. PFCs and HFCs are used due to their relative stability in storage and gas transfer as well as their ion reactivity in plasma. The gases used to clean internal equipment surfaces must be reactive enough to clean the chamber, but not so reactive as to damage it. Common PFAS gases used for plasma cleaning and conditioning include, but are not limited to: $C_2F_6$, $C_3F_8$, $CF_4$, and $C_4F_8$. In the early 2000's and the implementation of 300mm wafer size and associated tool development, $NF_3$ chamber cleans were implemented for much of the 300mm semiconductor industry, replacing $C_2F_6$ and other PFC cleans.

## 6.3 Chemical Vapour Deposition/Atomic Layer Deposition of Organometallics

Deposition of many metal-containing films (including, but not limited to oxides, nitrides, and pure metals) required for current and future semiconductor process nodes relies on organometallic precursors containing polyfluorinated compounds as ligands. This is especially prevalent in late transition metal deposition precursors. The presence of fluorine in the molecules serves several important roles. First, the presence of fluorine atoms in organometallic compounds reduces the intermolecular dispersion force

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and thereby increases the volatility (lowers boiling temperature) significantly, allowing the precursor to reach the chamber where it will react to form films containing the metal of interest. The presence of fluorine in these ligands also influences the stability and reactivity of these materials. Fluorine containing ligands have a strong impact on the electron density at the metal centre and can stabilise a molecule sufficiently to allow easy transport to the chamber while leaving the molecule reactive enough to interact with other co-reactants resulting in the film of interest.

## 6.4 Other critical uses of PFCs and HFCs

Gas-cluster ion beam is a technology used for nano-scale modification of semiconductor surfaces through infusion or deposition. This technology is used to develop the necessary electrical properties of the wafer through surface modification. Current stability gases used in gas-cluster ion beam include, but are not limited to, $CF_4$ and $CF_3$.

Assembly, test, and packaging steps connect the semiconductor die to the semiconductor package. These steps include bonding, cleaning, and preparing the package to ensure electrical connectivity. Future advanced assembly, test, and packaging operations (including such processes as through silicon via and wafer stacking) are currently in the invention and research and development phase. PFC and HFC gases, such as but not limited to $CF_4$, are used, and may be used in next generation assembly, test, and packaging operations.

**Table 6-1 Examples of the manufacturing processes using PFC and HFC gases.**

| Processing need/ function | Example substances | Alternative or replacement status | Timeline to develop |
|---|---|---|---|
| **Dry etch** | $CHF_3$; HFC-23; Trifluoromethane; $CH_2F_2$; $CH_3F$ | There are no viable substitutes for fluorocarbon chemistries at present. These chemistries provide both thermodynamically favourable reactions for patterning silicon and its dielectrics and selectivity to carbon-based masking materials.<br>Attempts to separate these components (e.g., using hydrocarbons and separate fluorine sources) introduce additional safety concerns and likely form PFC by-products.<br>Alternative molecules containing C and F which do not fit into the PFAS definition may have complicating factors such as high global warming potentials and low destruction/removal efficiencies. | 15+ years for each specific etch type (for example: oxide etch, nitride etch, silicon etch, hardmask etch, etc.) **with additional time to implement each solution** |
| | $CH_2FCF_3$; HFC-134a; 1,1,1,2-tetrafluoroethane | | |
| | $C_5F_8$; PFC-1418; Octafluorocyclopentene | | |
| | $C_4F_8$; PFC-318; Octafluoro-2-butene | | |
| | $C_4F_6$; Hexafluoro-1,3-butadiene | | |
| | $C_3F_8$; PFC-218; Octafluoropropane | | |
| | $CF_4$; PFC-14; Carbon tetrafluoride | | |
| **Chamber cleans (for deposition and etch chambers)** | $C_2F_6$; PFC-116; $C_4F_8$; Hexafluoroethane | $NF_3$ has been implemented as an alternative due to its high utilisation efficiency but can create $CF_x$ by-products when there is residual carbon. | 10+ years for each specific cleaning type |
| | $C_3F_8$; PFC-218; Octafluoropropane | | 10+ years[50] |

[50] The alternative would require redesign of tools, existing semiconductor equipment and manufacturing processes which is why such a development timeframe is needed.

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| Processing need/ function | Example substances | Alternative or replacement status | Timeline to develop |
|---|---|---|---|
| | $CF_4$; PFC-14; Carbon tetrafluoride | | 10+ years[50] |
| **Pre-clean/seasoning** | $CF_4$; PFC-14; Carbon tetrafluoride<br>$C_4F_6$; Hexafluoro-1,3-butadiene | The process needs exactly the same gas combinations and mix ratio to the etching step following the process. | 5 years |
| **Assembly test and packaging** | $CF_4$; PFC-14; Carbon tetrafluoride | Replacements investigated, but not viable.<br>Other replacements may be possible but need further investigation. | 10+ years |
| **Gas cluster ion beam** | $CF_4$; PFC-14; Carbon tetrafluoride<br>$CHF_3$; HFC-23; Trifluoromethane | Replacement may be possible with $NF_3$, $SF_6$, $O_2$, Ar, further investigation needed. | 10+ years |
| **Organometallic precursors** | Metal HFAC<br>Metal TFAC<br>Others | The presence of fluorine in these ligands also influences the stability and reactivity of these materials. Evaluations in progress but do not meet required process performance; further investigation is needed. | Indeterminate |
| **Self-assembled monolayer and small molecule inhibitors[51]** | Polyfluorinated hydrocarbons | This is in the research stage. Lack of access to these molecules will limit innovation. | Indeterminate |

PFC and HFC gases have been used in the semiconductor industry for decades following many years of intensive development to optimise processes. These gases are and have been a critical component for manufacturing semiconductors due to their relative chemical stability during storage and transfer and relative chemical reactivity during plasma ion generation.

PFC and HFC emission reductions have been a committed goal of the semiconductor industry for over 30 years.[52] PFC and HFC emission reductions have been achieved through the development of industry best practices[53] such as: chemical recipe optimisation, chemical replacements, point of use abatement, and lower emitting remote plasma cleans. Semiconductor manufacturing was one of the first industries to establish global voluntary reduction targets for these PFCs when in 1999 the WSC agreed to reduce absolute PFC emissions by at least 10% by the end of 2010 having as a baseline the 1995 emissions. By 2010, emissions were reduced 32% below the baseline, surpassing the 10% reduction target. The WSC again committed to a voluntary PFC agreement in 2010 with a time horizon up to 2020 and reports on progress publicly in the WSC annual joint statement. However, during these 30 years of investigation,

[51] This is not discussed previously as it is in the research phase.

[52] World Semiconductor Council (WSC) Joint Statement, April 1999, http://www.semiconductorcouncil.org/wp-content/uploads/2016/04/PFC-Reduction.pdf

[53] World Semiconductor Council (WSC) PFC Best Practices Guidance, September 2012, http://www.semiconductorcouncil.org/wp-content/uploads/2016/07/Final_WSC_Best_Practice_Guidance_26_Sept_2012.pdf

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the industry has not identified safe and effective alternatives for all PFC and HFC gas uses. Given this, it is believed the elimination of HFCs and PFCs would require a fundamental re-design of semiconductors to a non-silicon base material as well as redesign of the processes and equipment used to make them. Replacing silicon with another material will not necessarily result in elimination of the need for HFCs and PFCs.

While the use of $C_2F_6$ in chamber cleaning has been replaced in many applications with $NF_3$, the semiconductor industry operates a variety of fabs with tools that may not always have the capability to upgrade to an alternative gas. It is important to note that this transition to $NF_3$ was the result of over 15 years of development which was initiated in 1997 and now has become the industry standard whenever possible. The cost implications of such a transition are high with the costs per chamber ranging from ~$60K to $400K and a semiconductor manufacturing fab containing hundreds of chambers for thin film (etch and deposition) processes.

Even with this transition, PFAS by-products are still produced when carbon containing precursors are used in the dielectric deposition and emitted due to the reaction and recombination of fluorine with carbon and hydrogen to create PFC and HFC by-products. Owing to the resilient nature of many chamber residues, highly reactive fluorine (the most electronegative atom) is required for chamber cleaning which is why alternatives still rely on the inclusion of fluorine. As such, although this does resolve in some ways the reliance on PFAS substances, it still involves PFAS if the end-to-end system is considered.

## 6.5 Environmental Considerations in PFCs and HFCs

As discussed above, the use of PFCs and HFCs is essential for plasma etching, plasma cleaning, and other low volume critical applications, their uses balance the process need for high chemical and ion reactivity with the need for safe and effective manufacturing. The industry's commitment to reduce greenhouse gas emissions has successfully reduced PFCs and HFCs emissions through a combination of process optimisation, substitution, and abatement. Implementation has required companies to invest time and funds to identify and research prospective changes to HFC/PFC chemicals, to design, test and implement process and equipment modifications, and to identify, test and design increasingly effective abatement systems. Although this process has proven effective at mitigating the impact of emissions, it has not proven effective in eliminating PFCs and HFCs from the manufacturing process.

The adoption of point of use (POU) technologies on many tools using PFCs and HFCs has reduced the potential hazard exposure risk to employees and has reduced greenhouse gas emissions. With the implementation of WSC PFC best practices in new fabs – including remote plasma clean and POU abatement- many facilities have needed to expand other treatment systems, such as wastewater, fluoride, and exhaust to meet the required standards for wastewater and air toxics. Some POU technologies use fuel-burning processes to abate PFCs and HFCs, creating additional nitrogen oxides, carbon monoxide, and other air pollutants from combustion in exchange for a reduction in PFCs and HFCs. Process and abatement alternatives often require a full safety, health, and environmental impact review to understand additional implications to employee and community safety and health. Viable alternatives often require coordinated efforts between material suppliers, equipment suppliers, device manufacturers, and environmental safety and health professionals to determine the overall environmental impact of even a small change.

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# 7 HEAT TRANSFER FLUID USES

**Summary:** Two types of fluorinated heat transfer fluids are used in semiconductor manufacturing processes and semiconductor device test applications: liquid fluorinated heat transfer fluids (F-HTFs) and fluorinated refrigerants. These two types of fluorinated heat transfer fluids are used in tandem within corresponding heat transfer fluid (HTF) loops and refrigerant cycles to meet operational temperature requirements in semiconductor manufacturing processes like dry etch or thin film deposition and semiconductor device test applications, of which dry etch is the predominant and most complex use with stringent manufacturing process requirements.

To date, non-PFAS alternatives have not been identified. For F-HTFs the performance characteristics require the material to be electrically non-conductive, to be compatible with all materials of construction including sensitive electrical components, suitable toxicity/flammability, and to not cause catastrophic process contamination issues. Fluorinated refrigerants work in tandem with F-HTFs and must remain in a gaseous or liquid form to remain pumpable and useful for temperature control.

As such, suitable, non-PFAS-containing substitutes for the majority of uses would need to be invented and those invented may not enable ready plug-and-play substitution. When a plug-and-play substitute is not available it would drive a complete redesign of manufacturing and support equipment. New equipment designs may also require invention, may drive additional space and/or facilities that could result in a reduction of available manufacturing space and/or expense, that could impact global competitiveness.

- For the small percentage of applications in which glycol / water alternatives can be substituted and refrigerants within process equipment chillers from **8 to more than 14 years** are required to substitute PFAS in HTF for semiconductor manufacturing processes.
- Where no alternatives have been invented for the remainder of semiconductor manufacturing processes such as dry etch applications (70 – 100% of cases), there is an **unquantifiable time to invent** an alternative, followed by from **5 to more than 15 years** required.
- Invention of a PFAS-free thermal test fluid hasn't started and time to do this cannot be quantified. Once **invented**, it will take from **8 to more than 14 years** to implement and if the thermal test equipment needs redesign to accommodate the new method longer.

Most F-HTF uses involve closed but not hermetically sealed systems where fluorinated long-life seals and optimised equipment minimise evaporative losses during normal operation. Small amounts of emissions are expected from HTF loops during maintenance tasks such as changeout of parts that require replacement, from filling and draining, as well as from any leaks that may occur upon failure of the couplers, seals or gaskets used within the loop systems. Waste is typically collected during operation and end of equipment life for recovery and reuse or thermal destruction.

Heat transfer fluids can be differentiated into two categories based upon their manner of absorption or extraction of heat from the substances to be cooled or heated:

- **Fluorinated heat transfer fluids** (F-HTFs) are used within closed loop systems between specialised semiconductor manufacturing process modules and process equipment temperature control systems that require either heating or cooling to achieve temperature control across a very broad temperature range (-80°C to +125°C) within very tightly controlled setpoints.[54] HTFs remain

[54] Reference: Tuma, P., & Tousignant, L. (2002). Reducing Emissions of PFC Heat Transfer Fluids. https://multimedia.3m.com/mws/media/122381O/reducing-emissions-of-pfc-heat-transfer-fluids.pdf

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in liquid phase in most cases and cool or heat by exchanging heat through use of simple heat exchangers that are part of the closed loop system. Classes of F-HTFs include:

- Perfluoropolyethers (PFPEs)
- Perfluorocarbons (PFCs)
- Hydrofluorocarbons (HFCs)
- Hydrofluoroethers (HFEs)
- Hydrofluoroolefins (HFOs)
- Fluorinated Ketones
- Other Fluorinated Liquids

- **Fluorinated refrigerants** are used in the refrigeration cycle of process equipment chillers and temperature control units to provide a heat sink often well below ambient temperatures (as low as –80°C). In most cases refrigerants undergo a repeated phase transition from a liquid to a gas and back again with the use of evaporators and condensers integrated into a hermetically sealed cooling loop. [55] Classes of fluorinated refrigerants currently in use within the process equipment chillers used and temperature control units, in support of semiconductor manufacturing include:
  - PFCs
  - HFCs
  - HFOs
  - Fluorinated Ketones
  - Other Fluorinated Liquids

Heat transfer fluids (F-HTFs) fulfil a number of different uses including[56]:

- Manufacturing processes where temperature setpoints must be maintained ranging from -60°C to 125°C and material must remain pumpable across this entire range. For most applications, only one stable temperature set point is required but this must be held within tight tolerances, such as +/- 0.1°C for dry etch, with corresponding cooling capacities of up to several kilowatts.
- Performance and thermal testing at various stages of the semiconductor devices development, to ensure device integrity and to test their ability to effectively operate within the finished electronic end products. Including:
  - Burn-in testing: Burn-in is a part of the end of line test done after package assembly. The part is placed in a socket and an electrical signal is applied to stress and heat up the part. The test is designed to find infancy failures, which are screened out and scrapped.
  - Thermal shock testing: Also known as hermetic seal testing. Parts are shocked at a cold or high temperature to simulate use conditions or shipping, or to accelerate failures that enable better understanding of the longevity of a part in expected use conditions.
  - Device reliability testing: Parts are cycled from low temperature to high temperature to simulate their use in the field, over tens to thousands of cycles. The HTF is required for this to take place in a temperature-controlled environment. Reliability testing is used to certify products for the lifetime use condition of multiple years, through a test protocol that can be achieved over a timeline of a few of weeks or months.

To support the complex requirements of semiconductor manufacturing, specific combinations of physical and chemical properties are required to be met simultaneously from the HTFs. The need to

[55] ANSI/ASHRAE Standard 34-2019, Designation and Safety Classification of Refrigerants.

[56] https://www.epa.gov/sites/default/files/2016-02/documents/pfc_heat_tranfer_fluid_emission.pdf page 2

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meet all requirements at once often requires selection of fluorinated heat transfer fluids, as similar capabilities are not found in non-PFAS alternative fluids. For example and as outlined in Table 7-1 below, certain dry etch processes, which require cooling of an electrostatic chuck very near an active plasma, will need an HTF that possesses a high boiling point, high thermal conductivity, and high resistivity in order to maintain the proper functioning of the wafer chuck, as well as the stability of the plasma. Similarly, an HTF that is used in semiconductor test applications, requires the following: a high boiling point, a low pour-point, low kinematic viscosity at low temperature and high specific heat to enable the test operational temperature range.

The following provides information on specific HTF applications.

**Heat Transfer Fluid (F-HTFs) in Process Equipment Chillers:** Temperature control for many semiconductor manufacturing steps is achieved through use of individual process equipment chillers which are roughly the size of a small home appliance and are part of the support equipment packages connected to each piece of semiconductor manufacturing equipment in a fab. Process equipment chillers pump HTF through the plumbing loops embedded in the process chambers to either remove or add heat to the system.

A semiconductor manufacturing facility may have well in excess of 1000 process equipment chillers all using PFAS F-HTF[57] which is circulated through the wafer mounts during the process. Through the years of development of semiconductor technology, it was necessary to replace water-based lower boiling point non-F-HTFs with higher boiling point F-HTFs. F-HTFs are capable of achieving all required performance requirements whilst avoiding the generation of imperfections that negatively impact the yield of the semiconductor manufacturing process. They also enable the determination of the appropriate functionality of the semiconductor devices within the conditions expected to be encountered within the end use applications. Part of the drive to convert to F-HTFs was their stability, inertness, reduced flammability risk, lower impact to manufacturing tooling and reduced requirement to replace materials during normal operation.

**Dry etch manufacturing equipment:** To meet precise temperature requirements within the manufacturing chamber, any alternative would need to avoid interfering with equipment performance or the manufacturing process, while maximising the lifetime of the manufacturing equipment. The process equipment side of the HTF loop usually has mechanical joints for maintenance of process equipment and formation of flammable vapour is possible under fault conditions. The electrical equipment and wiring within the process equipment may need to satisfy electrical design requirement for hazardous (classified) locations, such as NFPA 70.[58] Due to this the development of future non-PFAS utilising systems will likely require significant redesign timelines for development and implementation as outlined in Section 6.1.

**Testing applications of semiconductor devices:** Precision manufacturing processes necessitate the frequent use of test instrumentation to ensure that these processes are performing as required, and that the final semiconductor devices perform correctly and remain reliable across a range of environmental conditions. In some test applications it is necessary to electrically test a completed semiconductor device over varying conditions to assure that it can perform as required under different temperature conditions.

[57] Taken from EPA publication "Uses and emissions of liquid pfc heat transfer fluids from the electronics sector" available at Uses and Air Emissions of Liquid PFC Heat Transfer Fluids from the Electronics Sector | US EPA (1/11/2022)

[58] The US national electrical code, which is the benchmark for safe electrical design, installation, and inspection to protect people and property from electrical hazards.

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Certain types of semiconductor device test applications also employ temperature stressing to assure that the different materials of construction are mechanically compatible.

**Refrigerants within process equipment chillers**: Process equipment chillers currently make use of fluorinated refrigerants within their compressor systems to act as a heat sink and as heat-transfer agents between the manufacturing process and the facility chiller system. Operation of process equipment at the operational temperature set points requires complementary capabilities between the F-HTF in the HTF loop and the refrigerant in the refrigerant cycle. The most critical performance requirement of the refrigerant is to enable the lowest operational setpoint, while avoiding a catastrophic phase shift to solid form (the refrigerant must remain in a gaseous or liquid form to remain pumpable and useful for temperature control). Other performance requirements which need to be optimised include the energy efficiency of the chiller, size of the equipment, and avoiding introducing new safety and worker exposure risks.

It is important to note that **no HTF remains in the finished semiconductor device**. In any case HTFs[42] have the benefits of being odourless, non-flammable, non-explosive, evaporate cleanly and exhibit very low toxicity based on current understanding, which results in easier safe usage and storage. Due to the demanding environments HTF operates in, only specifically tailored fluorinated compounds are able to offer the required performance in many of the applications and there are very few manufacturers of HTFs for semiconductor industry applications.

The following tables shows examples of both types of PFAS HTFs. This table does not exhaustively describe the whole Semiconductor industry as it is limited to information provided by the Semiconductor PFAS consortium members.

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Table 7-1 Examples of HTFs utilising PFAS.

| PFAS use area | Typical PFAS Used | Role of PFAS | Status of alternatives | Timeline to develop | Concern of alternative |
|---|---|---|---|---|---|
| F-HTF in process equipment chillers (except high energy dry etching) | 3-ethoxy-1,1,1,2,3,4,4,5,5,6,6,6dodeca-fluoro-2-(trifluoromethyl)-hexane, Perfluoroalkanes, perfluoroethers and tertiary perfluoroamines,[59] Perfluorotributylamine, Hydrofluoroolefins[60] such as ethoxytridecafluoroheptene isomers: (Z)-1,1,1,4,4,4-Hexafluoro-2butene, Mixtures of perfluoro-polyethers (PFPEs)[61] | Suitable viscosity at lowest operating temperature, low dielectric constant that supports direct cooling of energised equipment by immersion, low vapour pressure, thermally stable, low toxicity, non-flammable, no affinity for hydrocarbon-based compounds, metal, and plastic compatibility. | In certain applications EG/DI combinations are being investigated. | Invention/Fundamental Research – 2-5+ years, Demonstration – 2 years, Integration – 2 years, HVM – 2-5 years. **Total** from **8 to more than 14 years.** | Materials compatibility and potential corrosion over time. |
| F-HTF in high energy dry etch manufacturing equipment | Ethoxy-nonafluorobutane $CH_2FCF_3$; HFC-134a; 1,1,1,2-tetrafluoroethane | Suitable viscosity (up to -80°C), low dielectric constants that support direct cooling of energised equipment by immersion, high volume resistance, thermally stable for operational temperature range (-50°C to +80°C) for long periods, chemical inertness, low vapour pressure, low toxicity, non-flammability, no affinity for hydrocarbon-based compounds, metal, and plastic compatibility. | Invention is needed for alternative. | Research – unknown, Demonstration – 2+ years; if unsuccessful, return to invention/fundamental research, Integration – 2+ years; if unsuccessful, equipment change may be required (additional 1 year + repeat integration), HVM – 2-5 years. **Total: Invention from 5 to more than 15 years.** | Dielectric property change may affect plasma conditions, which can require extensive process development for each application, followed by adjustment of process conditions. Possible design change of electrode assembly, the chiller and other critical parts of the process chamber may be required. For example, a high flammability alternative would require any equipment used in |

[59] Including 3M™ Novec™ 7XXX series Engineered Fluid range and 3M™ Fluorinert™ Electronic Liquid FC-3283/ FC-40/ FC-43/ FC-70/ FC-770/ FC-7000/ FC-7100/ FC-7200/ FC-7300/ FC-7700

[60] Sold as Chemours Opteon™ SF10.

[61] Including Solvay™ Galden™ range of HTF, including HT 80/ HT-110/ HT-135/ HT-170/ HT-200/ HT-270/ D02-TS, Solvay™ Fomblin™ 14/6 25/6, 16/6.

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| PFAS use area | Typical PFAS Used | Role of PFAS | Status of alternatives | Timeline to develop | Concern of alternative |
|---|---|---|---|---|---|
| | | | | | its proximity to meet specialised safety standards such as Class 1 division 2 under NFPA 70. |
| Testing applications of semiconductor devices | Perfluoroamine,[62] Perfluorotributylamine,[63] PFPE based testing fluids designed for specific test conditions[64] | Suitable viscosity (up to -40°C), low dielectric constants that support direct cooling of energised equipment by immersion, high volume resistance and its long-term stability, thermally stable for the entire operational temperature range (-40°C to +120°C), low toxicity, non-flammability, chemical inertness, low vapour pressure, no affinity for hydrocarbon-based compounds, metal, and plastic compatibility. | Invention is needed for alternative. | Invention/Fundamental Research – 2-5+ years, Demonstration – 2 years, Integration – 2 years, HVM – 2-5 years. **Total: from 8 to more than 14 years.** | Possible design change of tester head assembly, chiller and other critical parts of the process equipment may be required. For example, a high flammability alternative would require any equipment used in its proximity to meet specialised safety standards such as Class 1 division 2 under NFPA 70. |
| Refrigerants within process equipment chillers | $C_2HF_5$; HFC-125; Pentafluoroethane[65], $CH_2FCF_3$; HFC-134°; 1,1,1,2-tetrafluoroethane, $C_3H_3F_5$; HFC 245fa; Pentafluoropropane, R407C | Refrigeration capability that can cool the HTF by heat exchange to lower than -50°C with a cooling capacity of at least 7kW. | $CO_2$, $NH_3$ $C_3H_8$, and Feasibility studies of $N_2$ chillers required. | Invention/Fundamental Research – 2.5+ years, Demonstration – 2 years, Integration – 2 years, HVM – 2-5 years. **Total: from 8 to more than 14 years.** | $CO_2$ refrigerant chiller doesn't satisfy cooling capacity, as operational temperature is very close to the triple point. Therefore, a fluctuation of pressure control can result in vapor-solid phase transition (refrigeration failure). $NH_3$ is flammable and toxic, which requires containment |

[62] Such as 3M™ Fluorinert™ Electronic Liquid FC-3283.

[63] Such as 3M™ Fluorinert™ Electronic Liquid FC-43.

[64] Including , Galden® D02-TS, D02, D03, D05, 3M™ Novec™ 7500/7100 Engineered Fluid and Solvay Galden® PFPE HT-135.

[65] Such as Chemours FE-25™, Fike Ecaro-25®.

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| PFAS use area | Typical PFAS Used | Role of PFAS | Status of alternatives | Timeline to develop | Concern of alternative |
|---|---|---|---|---|---|
| | | | | | and exhaust abatement, so cannot be located near the production facility. It also is less efficient at temperatures below -30°C. $C_3H_8$ is flammable and inefficient at very low temperatures and again cannot be used near the production facility. |

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## 7.1 Alternatives

To date, no non-PFAS alternatives have been identified which can be used in dry etch and semiconductor test applications, due to the required performance characteristics of electrical non-conductivity, compatibility with all materials of construction (including sensitive electrical components), non-flammability, all within the operational range that is required for the manufacture and test of semiconductor products.

### 7.1.1 Alternatives to Liquid HTF

The most promising available non-fluorinated HTFs that have been considered for use in semiconductor manufacturing operations include synthetic hydrocarbon oils, silicone based HTFs and glycol ether and deionised water (EG/DI) combinations.

#### Synthetic Hydrocarbon Oils

Synthetic hydrocarbon oils have kinematic viscosity values that are much higher than the F-HTFs that are currently in use. This leads to an inability to maintain tight temperature tolerances at the upper operational temperature limit currently required. Residues of these HTFs can cause contamination of the fab environment, leading to a decreased process yield. Flashpoints are also much lower and have the potential to drive significant changes to equipment chiller designs owing to safety requirements.

#### Silicone-based HTFs

Silicone-based heat transfer fluids are inert and have many unique properties like extreme stability against thermal oxidation, low freezing points, wide operating temperatures, good dielectric strength, favourable environmental properties, and low toxicity. Whilst silicone-based fluids have many advantageous properties for use as an alternative HTF, they are non-viable for use in semiconductor manufacturing processes such as dry etch. This is due to their ability to cause catastrophic contamination issues when they vaporise or to result in residual deposits on surfaces which in turn contaminate the very sensitive processes associated with the semiconductor manufacture.[66] This issue has already been reported in other industries, which have needed to scrap parts that have become contaminated with silicone oil residues.[67] These accidental transfers, in the order of a few drops of fluid, are most likely to occur during the performance of certain maintenance activities like the changeout of replaceable parts connected to the chiller loop. If silicone oils were used to replace the current F-HTFs in dry etch applications, these accidental transfers could result in the need for extensive cleaning and significant downtime in order to complete chamber rebuilds and replace contaminated parts.

#### Ethylene Glycol and Deionised Water (EG/DI) Combinations

Mixtures of EG/DI are commonly used as HTFs within semiconductor applications. However, where F-HTFs are currently in use, they have been selected because EG/DI is not able to meet boiling point and pour point requirements to support the operational temperature ranges. In addition, EG/DI mixtures have been observed to exhibit a reduction in resistivity during use; this makes the control of the etch and deposition processes increasingly difficult. This can lead to a catastrophic interaction with the plasma or an electrical short circuit due to contact with the wafer chuck. Residues of EG/DI HTFs within the process chamber can cause contamination of the fab environment, leading to decreases in die yield. Use of these HTFs also requires special design considerations to avoid aggressive corrosion of the sensitive semiconductor manufacturing equipment.

[66] https://www.rdworldonline.com/please-help-us-determine-the-source-of-the-silicone-contamination/

[67] The Removal of Silicone Contaminants from Spacecraft Hardware, 2002, https://apps.dtic.mil/sti/pdfs/ADA410311.pdf

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Additional information on alternatives to liquid HTF can be found in the 'PFAS-Containing Heat Transfer Fluids (HTF) used in Semiconductor Manufacturing Whitepaper' outlined in Table 1-2.

### 7.1.2 Alternatives to Refrigerants

Process equipment chillers currently make use of fluorinated refrigerants within their compressor systems to act as a heat sink and as heat-transfer agents between the manufacturing process and the facility chiller system. Currently available non-fluorinated refrigerants include carbon dioxide and ammonia which have the following concerns:

- Limited operational ranges that do not meet the required operational temperature for dry etch and semiconductor test applications (–60°C).
- Less energy efficient compared to PFAS refrigerants, and in order to provide a similar level of cooling, more chilling capacity would need to be installed, requiring significantly more space and higher energy consumption.
- Ammonia based refrigerant chillers are required by ANSI/ASHRAE Standard 34 safety classification rating of $B_2L$ to be installed in a separate building with ammonia monitoring and other controls, such as a pressure relief valve and associated abatement.

Additional information on alternatives to liquid HTF can be found in the 'PFAS-Containing Heat Transfer Fluids (HTF) used in Semiconductor Manufacturing Whitepaper' outlined in Table 1-2.

## 7.2 Environmental Considerations for use of F-HTFs

F-HTF is bought by the semiconductor manufacturer when they install and commission the equipment and requires periodic replenishment. As designed, the F-HTFs used within the chiller and test equipment are contained with intent to minimise release during use and are accessed and maintained only by trained and/or certified technicians. Prior to the initiation of maintenance activities, the HTF contents of the chiller and associated equipment is drained into collection containers that are managed either for direct reuse, or for reclaim. If any HTF fluid is required to be managed as a waste, the fluid is incinerated at appropriately certified waste management facilities.

Small amounts of emissions are expected from HTF loops during normal operation of the chillers and heat exchangers, with the exact amount dependent on the process operating temperature. Emissions are also possible during maintenance tasks such as changeout of parts that require replacement, from filling and draining, as well as from any leaks that may occur upon failure of the couplings, seals or gaskets used within the loop systems. Due to the relatively high vapour pressure of the HTFs that are used in semiconductor manufacturing and testing applications, the HTF that escapes containment is released to the air. Overall, the industrial emissions of F-HTF are actively minimised to reduce greenhouse gas emissions and reduce manufacturing costs. Data from the US EPA on emissions across the electronics manufacturing industry from 2014-2021 shows that more than 70% of reporting facilities claimed less than 1 tonne per year of emissions, which is equivalent to less than 2 kilograms of F-HTF per year per piece of equipment (assuming 500 individual closed-loop systems per facility).

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# 8 ASSEMBLY, TEST, PACKAGING AND SUBSTRATE MATERIALS USES

**Summary:** As packaging becomes more and more complex due to decreasing semiconductor device size, increased processing speed, and/or increased packaging complexity, the combination of material properties required to meeting these challenges are often only found in the fluorinated hydrocarbon family. Changes to assembly packaging materials range in their complexity, but unlike other uses due to their interface with both the silicon die and the end customer product, additional customer product change notification/ requalification processes need to be followed (minimum average product requalification is 1-2 years, with some applications such as aerospace, military, or automotive requiring 6+ years).

The following timelines are estimated to find or implement PFAS free alternatives:

- Packaging fluxes **more than 5 years,** to find and implement alternatives.
- Surfactants from **10 to more than 18 years**, to find and implement alternatives, with many suppliers being single source which may cause suppliers to exit the market.
- For a few older die attach adhesive applications alternatives can be expected in the very near future (1+ year). However, for most adhesives and encapsulants it is expected to take from **10 to more than 13 years** to find and implement alternatives.
- However, for the vast majority of package related uses of adhesives, in MEMS and Thermal Interface Materials System (TIMS), die overcoats, encapsulants and underfills, die passivation and substrate polymer there are no viable alternatives to the PFAS being used. For some of these technologies, alternatives have been sought for 18 years without success. For these uses it is likely that alternatives will take **more than 20 years** to find viable alternative chemistries or technologies and 6 years to implement.

There should be no release of PFAS during normal use of consumer or other end products, for those that include PFAS containing semiconductors. The concentrations of PFAS in assembly, testing, and packaging (ATPS) chemistries are low (parts per billion range) and any releases are anticipated to be minimal and only at the end of the product's useful life, during electronics recycling or disposal. Some of the electronic reclamation processes are thermal and may cause a break-down of PFAS, but this would require further investigation.

A semiconductor package encloses one or more semiconductor devices or integrated circuits protecting the device from the environment. The package connects the semiconductor to the printed circuit board (PCB), dissipates heat and provides protection from the surrounding environment particularly from moisture, shock/vibration, dust, etc. Semiconductor packaging is the process of assembling integrated circuits into final products, individual integrated circuit components are fabricated from semiconductor wafers, and these are then diced into integrated circuit die and tested.

Assembled packages go through multiple package types, to form three dimensional integrated circuits. Older technologies still use subsequent thermal and chemical steps to produce, therefore thermal and chemical stability in the assembled package are important. Semiconductor packaging technology evolves quickly and there are lots of different technology levels on the market at any one time, including dual in-line packaged assembly like wire bond ball-grid assembly and flip-chip technologies as illustrated schematically in Figure 8-1 and Figure 8-2.

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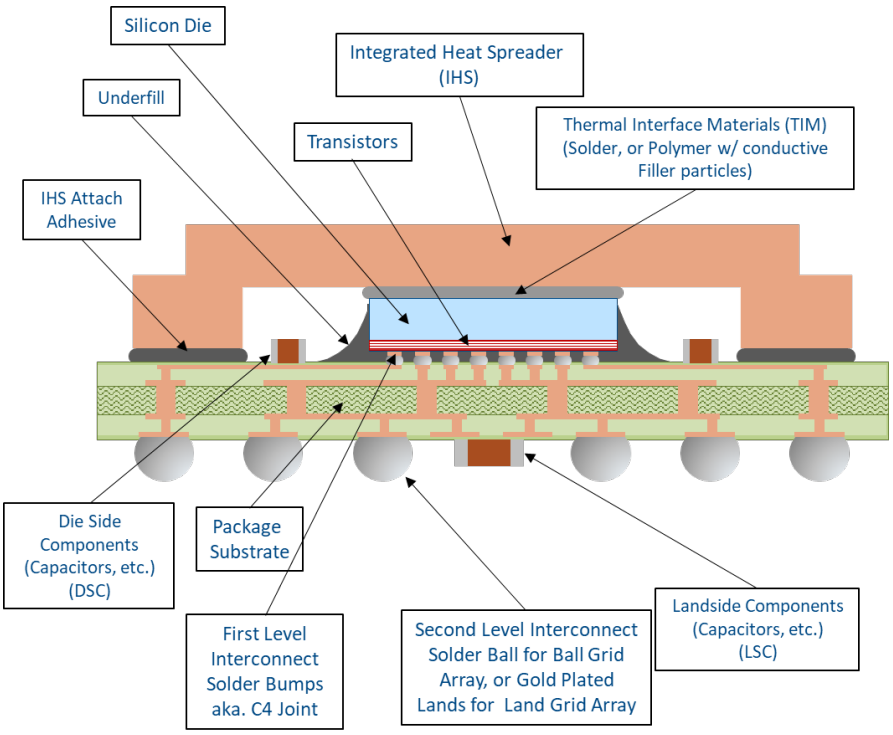


**Figure 8-1 An example package, with many other configurations possible.**

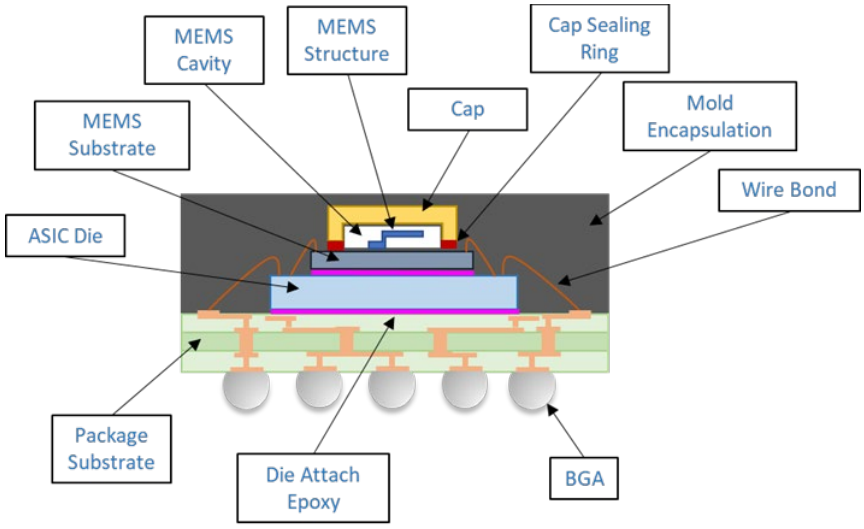


**Figure 8-2 An example MEMS package.**

Packaging has developed over time, as outlined in Figure 8-3 and Figure 8-4, with all of these packaging types still supported by current manufacturing practices.

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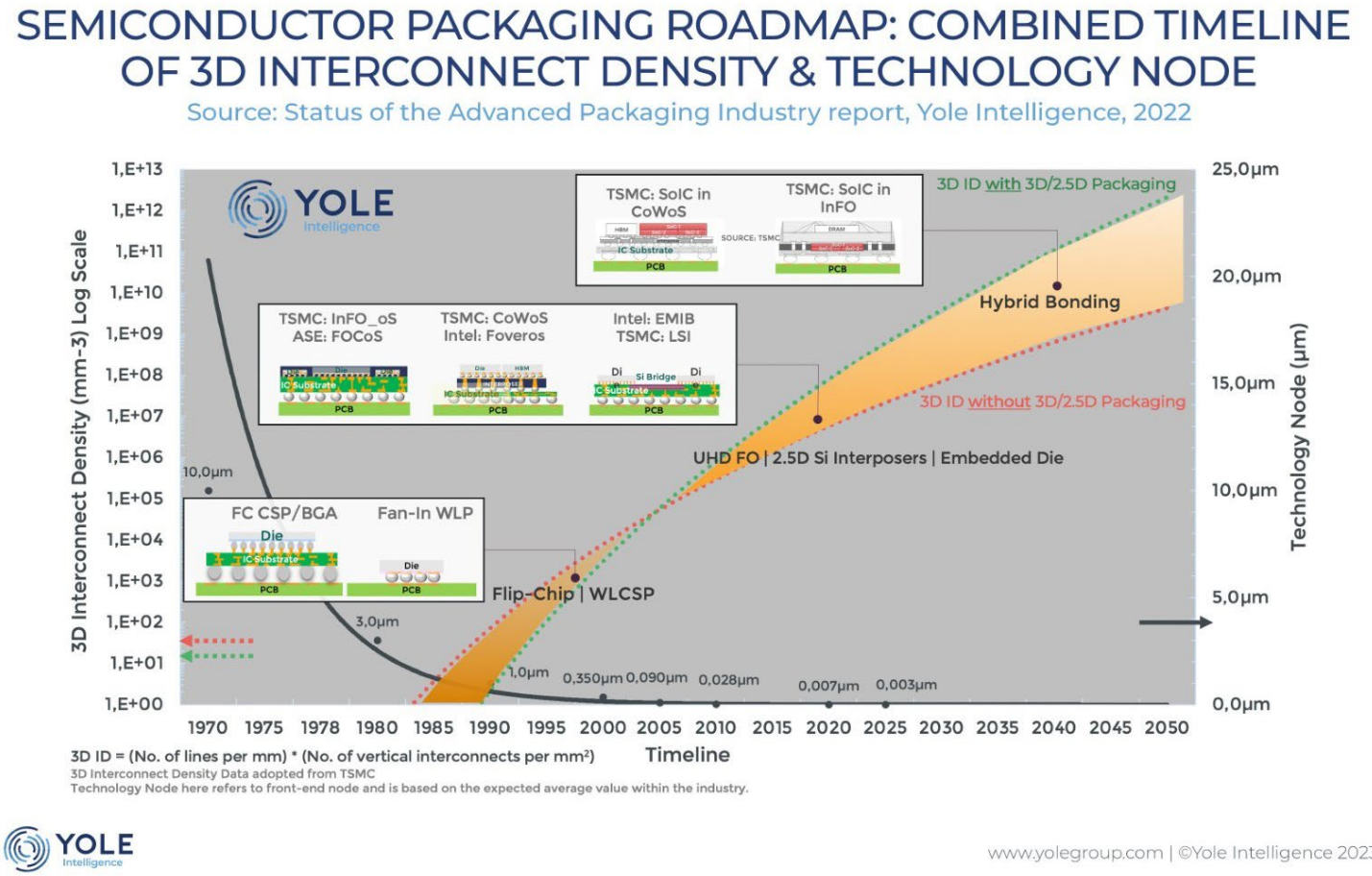


**Figure 8-3 Timeline for the semiconductor packaging showing the complexity of packaging increasing over time.**

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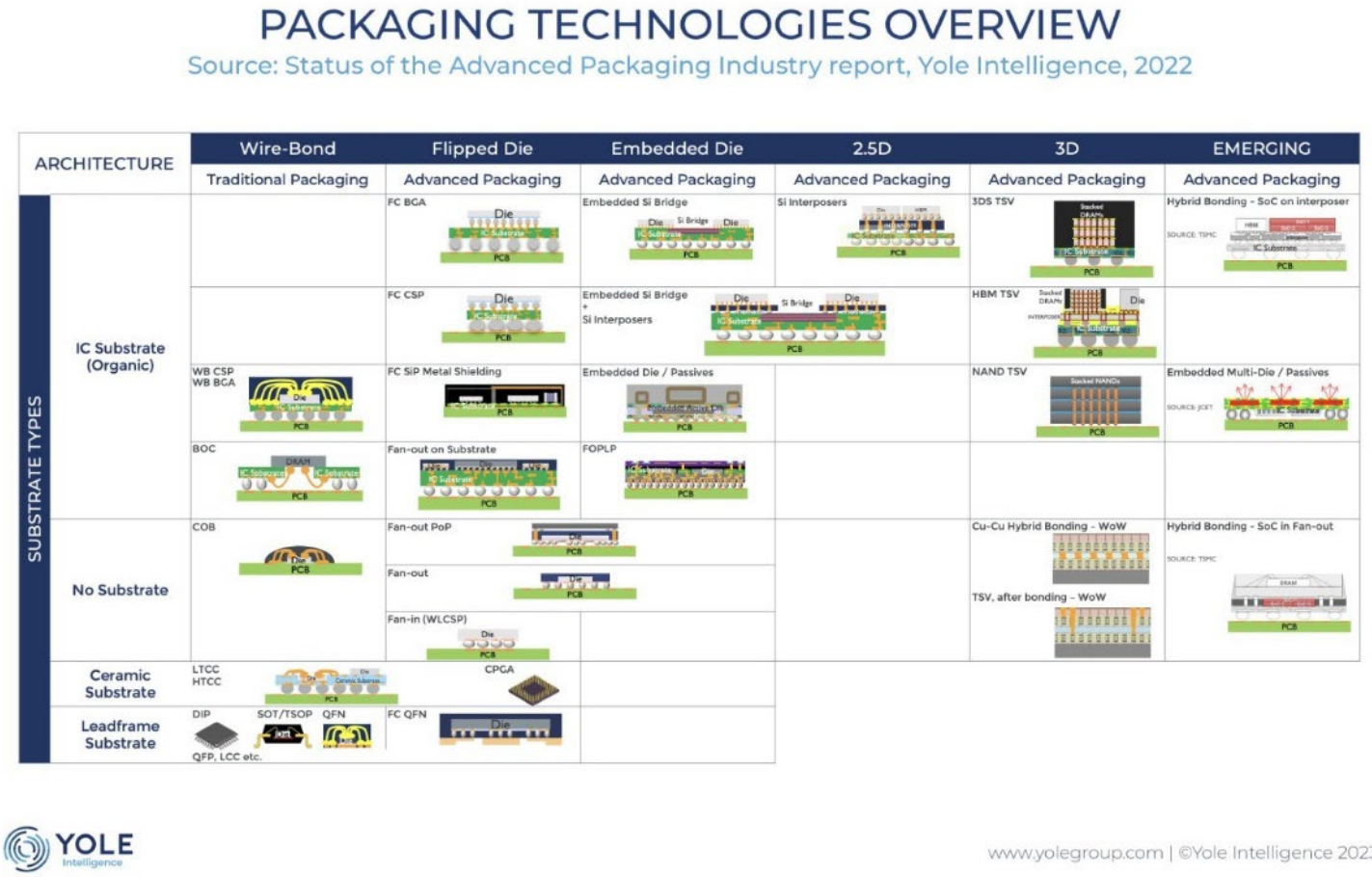


Figure 8-4 Status of the Advanced Packaging Industry including multiple types of packaging and materials.

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Assembly, Test, Packaging, and Substrate use PFAS in many applications, across multiple process steps, including:

- **Substrate polymers,** including core, build-up, or dielectric materials. These enable high speed signalling between components of a module or an assembly. This is turn enables specific functions within a larger completed package to be met, like on-chip memory, accelerators, controllers, and chip-to-chip interconnections. PFAS provide low dielectric constants, high thermostability, chemical inertness (to acids, bases, and solvents), and low moisture absorption, low electric permittivity / dielectric loss, low water absorption, and low coefficient of thermal expansion (CTE)[68]. These materials are required to be photo-imageable to meet the required high-resolution requirements for chip-to-chip interconnects, PFAS properties typically found in photolithographic chemistries are used and further discussed in Section 4.

  Core dielectrics currently use fully-imidized polyimide and polybenzoxazoles which have to have a pendant PFAS group on the polyimide backbone to be soluble in organic coating solvents. Without the presence of PFAS groups on the polyimide backbone, advances in semiconductor packaging technology will be delayed by decades or never materialise.

- **Assembly materials – coatings**
  - **Die overcoat / adhesive** to provide hermetic sealing for moisture sensitive applications and chemical resistance.
  - **Die attach adhesives** to attach silicon die to packaging substrates or leadframes, while helping to mitigate stress on the die and encapsulant. PFTE/PFAS in the epoxy anti- bleed out agent in die attach glue is important to control the amount of epoxy (adhesive) bleed beyond the peripherals of the die mounted to the frame/substrate.

- **Encapsulants** (hermetic or molding) to provide environmental and mechanical isolation via the following properties: heat conductivity due to a low CTE across a wide temperature range without a glass transition temperature. Electrically insulated, and hydrophobic to avoid void related failures.[69]

- **Underfills** to reduce stress on solder joints and increase the durability and longevity of the assembled package compared to an assembled package without underfill. Underfills must have high mechanical strength, low CTE and generally contain ~50% silica materials with the remainder being polymeric materials such as vinylidene fluoride-propylene hexafluoride copolymer and tetrafluoroethylene-propylene copolymer. The polymer must have high viscosity to ensure homogeneity and low volatility to minimise void formation. Surfactants utilising PFAS are also used to ensure compatibility of the additive with the resin system as well as helping to control resin bleed out.

- **Surfactants** used in defoaming or foam promotion, thin films and spin coating applications require surfactants to adjust the surface energy of the solution the surfactant is added to. They are also used in temporary bonding / mechanical debonding processes. Surfactants can play many rolls within a formulation, such as lowering surface tension, behave as wetting agents, foaming agents,

[68] These properties are referred to in patents from the University of Electronic Science and Technology of China (CN107474312B), Jiangxi Tieno Technology Co Ltd (CN106604536B, Intel (US 11, 348,897 B2), and Taiwan Semiconductor Manufacturing Company Ltd (TSMC) (US 10,261,248 B2).

[69] A common failure mechanism for encapsulants is void creation caused when water absorbed by the encapsulant expands during heating caused by operation of the semiconductor, as demonstrated by: Thompson, Dane & Tentzeris, Manos & Papapolymerou, John. (2007). Experimental Analysis of the Water Absorption Effects on RF/mm-Wave Active/Passive Circuits Packaged in Multilayer Organic Substrates. Advanced Packaging, IEEE Transactions on. 30. 551 - 557. 10.1109/TADVP.2007.898637.

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defoaming agents, or dispersants. Surfactants can be used to improve the coat quality of solution processed films. Surfactants can also be added to cleaning solutions including resist strippers and temporary adhesive cleans to improve the cleaning efficiency.

- **Temporary bonding / mechanical debonding**: an adhesive/release layer pair or single layer material (with appropriate bond strength) providing support to the wafer which is mechanically de-bonded after processing. The release layers for mechanical release typically have very low surface tension. Fluorinated polymers are one class of polymers which fit this description. After debonding the surfaces are cleaned, the cleaner may include a surfactant in its formulation.
- **Laser release layers:** either as a film or mold release sprays use PFAS such as PTFE or ETFE. These provide UV light sensitivity, thermal stability, aid in photoacid generation efficiency and the removal of the adhesive from the wafer or other piece cleanly.
- **Thermal interface material (TIM)** act as a heat conduit between the package (silicon die) and a heat spreader. Good coverage, consistency, and longevity of the material are necessary to withstand high temperatures and multiple thermal cycles.
- **Packaging of microelectromechanical systems (MEMs)** for surface energy modification of MEMS for anti-stiction purposes.
- **Packaging adhesives** (either thermal or UV curable) to improve adhesion between dielectrics and low roughness copper without having to resort to roughening surfaces which introduces low insertion loss. Types of adhesive include paste, film, or wafer.
- **Packaging fluxes** to assist with connecting the die to substrate, with different types of flux used depending on the joining technology in use. With PFAS used as a surfactant in ultra-low residue flux[70] and thermocompression bonding flip chip copper pillar joining, using a specialist copper pillar flip chip flux, but not ball—attach processes or pin attach processes where alternatives to PFAS are routinely used. PFAS-containing surfactants provide heat resistant, void solder resistance[71] and have wetting properties that control spread ensuring package reliability and yield.
- **Memory component packaging** may use PFAS processing steps listed in the manufacture of some products. Additionally, PFAS may be present in manufacturing equipment.
- **Die passivation** as part of the back end of line bumping process[72] in that the photo imageable dielectric is used both to help pattern the bumps and remain on the die to protect the interlayer dielectric (underlying electronics within a die).

As technology is moving to faster signal processing the use of PFAS components is expected to grow, as no other manufacturable material currently exists with the same electrical properties for dielectric constant and insertion loss.

Specifically, as the signalling frequency increases the conductor length becomes even more critical; higher losses require lower insertion loss materials. This is mainly because PCB conductor lengths are long and signal loss increases with longer travel distances. Fluorinated components offer best in class electrical properties for dielectric constant and insertion loss. It may also be the case that in certain packaging applications, where high speed signalling is needed on the core or on package architectures such as package on package or interposers where the material used is a glass reinforced epoxy matrix, PFAS containing components may be needed to mitigate the risk of signal loss.

[70] As discussed by various patents including KR100985004B1 and IBM's DE2137329A1.

[71] As discussed in Arakawa Chemical Industries Ltd Patent CN101090797B.

[72] Solder bumps deposited on chips pads situated on the top side of a silicon wafer during the final wafer processing step.

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## 8.1 Impact of change

Packaging materials have interactions with both the silicon die and the end customer product, so if substances are changed the following additional steps would be required:

1. Alternative process will require notification of change for each product for each customer. As the assembly process is the interaction between the fab and the end product, it is possible that there could be dies and passivation materials from multiple fabs or multiple motherboards and second level interconnect materials. This creates extensive complexity as a change in one assembly material could require testing across multiple silicon die vendors or multiple second level interconnect vendors/customers. Typical notifications require at least one year prior to any change, due to the contractual requirements and the necessity of the end customer to determine impacts within their processes and/or products, but certain market segments such as aerospace, military, and automotive could require longer change notification or more extensive testing.
2. In some applications, PFAS substances allow for reduced consumption of material (as in coating on a silicon wafer or other substrates). However, if increased volumes of material are needed this will increase cost/wafer and possibly increase waste.
3. In some applications, PFAS substances improve film coating uniformity when coated on a silicon wafer (or other substrates). If the alternative is not able to achieve the same level of uniformity, the process tolerance might suffer. Increased sample volumes may be required during testing or new processes may need to be developed. Ultimately this could lead to loss of yield and scrap.
4. New analytical methods may need to be developed to analyse the presence of alternatives. This will add cost and time to product development. It is also possible that new tooling or methodology developments, will also need to be added.

Table 8-1 indicates the status of alternatives for identified packaging uses and estimated timelines for the development of the alternatives.

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**Table 8-1 Examples of the packaging products utilising PFAS.**

| Substance | Function | Quantity | Status of alternative | Concern of alternative | Timeline to develop |
|---|---|---|---|---|---|
| PTFE (including versions FEP, PFA, AF, and PTFE 30 | Main polymer substrate and build up dielectric material | >0.1% | Replacement known & viable for some formulations but not all.<br>Alternatives are not available in cases where one or more of the functional quality characteristics is not met such as adhesion, dielectric constant, ability to process. | Lower dielectric characteristics, low Coefficient of thermal expansion, low electric permittivity / dielectric loss, and low water absorption.<br>Quality, reliability, form, fit, function in some material changes. Hazards from alternatives. | 10+ years depending on chosen replacement technology |
| Fluorinated-ethylene propylene | TIMs | <0.1% | No viable alternatives have been identified. | Tear resistance, high tensile strength + incorporation of highly thermally conductive fillers such as carbon nano tubes, metals, ceramics into different resin systems may require unique compatibility that only fluorinated-ethylene propylene has. | 10+ years |
| Perfluoroalkyl Alcohols, Fluorine Resins | Additive fluxes | <0.1% | Replacement marketed by flux manufactures in 2020 which needs to be evaluated by manufacturers.<br>After two years of research one candidate flux is now being tested by a chip packaging company, to see if it will perform adequately and has a sufficiently low failure rate. | Quality, reliability, thermal stability, wetting.<br>Some flux alternatives are halogenated and so have other hazards which could prove to be **regrettable substitutions**. | 4-5+ years |
| Fluorinated Pressure Sensitive Adhesives | Additive in adhesive | None as it is a processing aid and not included in the final product | Replacement known & viable for some formulations but not all, with more information outlined below this table. | Difficulties finding a surfactant with low surface energy performance.<br>For one alternative: inadequate chemical resistance, thermal stability. For the other alternative there are the same concerns as well as inadequate photoactive properties. | 10-13+ years depending on technical challenges. |
| Die overcoat / encapsulant | | Unknown | No known viable alternative. | | 15+ years |

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| Substance | Function | Quantity | Status of alternative | Concern of alternative | Timeline to develop |
|---|---|---|---|---|---|
| $PFH_xA$ as per relevant dossier presented to ECHA by the European Semiconductor Industry Association 6th September 2021 or perfluoropolyethers | Anti-stiction purposes and surface energy modification in MEMS[73] device | <0.1%. <1kg/year of PFAS in products sold globally. | No known alternative | After >18 years of work, and >$30M, it was determined that non-PFAS alternatives do not exist that meet the performance requirements | 20+ years |
| Adhesive (UV curable adhesives, die attach adhesives) containing PTFE | Surface energy modification in adhesives | <0.1%. <1kg/year of PFAS in products sold globally.<br>In final component PFTE is estimated to range between 0.01 % and 1.4 % | No known alternative | After >18 years of work, and >$30M, it was determined that non-PFAS alternatives do not exist that meet the performance requirements: low dielectric constant; low dielectric loss; high adhesion too low roughness Cu pre and post stress testing [74] | 10+ years |
| PTFE/ Polyvinylidene fluoride (PVDF)/ tooling and fixturing adhesive. | Die attach adhesive and Epoxy Anti Bleed Out agent | None as it is a processing aid and not included in the final product | Testing ongoing. Viable alternative available for all formulations | Time will be required to roll out the alternative technology to all tooling and fixturing uses. | 8+ years to develop – 1 year remaining to implement |
| Trifluoroacetic anhydride in polyimide, polybenzoxazole, and other epoxy-based passivation | Die passivation | In final component the PFAS substance is estimated to be <500 ppm | No known alternative | Non-PFAS alternatives do not exist that meet the performance requirements (Thermal and chemical stability, photo imageable, dielectric, good wetting) | 10+ years |
| Surfactant / defoaming agent | | Unknown | Replacement may be possible & plan in place to evaluate | Quality, reliability, form, fit, function. | 4+ years |
| Additive in defoaming agent-PFTE | Underfill | 0.01% | Replacement possible, to start the detailed evaluation this year | Quality, reliability, form, fit, function. | 4+ years |

[73] MEMs are made up of components between 1 and 100 micrometres in size and usually are made up of a central processor and several components that interact with the surroundings like microsensors. MEMS chips are often packaged together with an application-specific integrated circuit chip stacked together inside the plastic package, so that one package has the sensor and the circuitry, saving space and cost.

[74] A highly accelerated method of electronic component reliability testing using temperature and humidity as the environmental parameters.

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Supply chains for some of the specialty chemicals that are of concern, such as low surface energy surfactants, are currently limited to typically just a few, or a single-source supplier, or the end-user actually makes these chemicals themselves. It is expected that once restrictions are in place that suppliers may stop making the intermediates necessary and/or the end product, or they may increase the cost to cover these more limited/restricted materials. For example, Semiconductor PFAS Consortium members purchase a commonly used surfactant, where over the past 10 years the demand from other industries has diminished such that the semi-conductor industry is now the sole user of this surfactant. Research and development efforts to replace the surfactant were not successful.

PTFE is an additive in some die attach adhesives to provide for added specificity in the polymerisation to perform the function of limiting the area of the flow of the adhesive or bleed control. These PTFE “Antibleed agents” control the amount of epoxy bleed beyond the peripherals of the die mounted to the leadframe/substrate. This is important to prevent spread of the epoxy to adjacent critical areas such as wirebond pads which will lead to product failures such as wire non-stick on pad, spread on die top resulting in prevention of mold compound adhesion and subsequent void and delamination on the package. The PTFE also promotes flatness of the die and uniform adhesive thickness. For some specific die attach adhesive applications in packaging, alternatives have been under investigation since 2014 and some appear to work and appear to be viable. For this specific application, the alternative is expected to be used in production in the near future (1 year +).

## 8.2 Environmental considerations for PFAS packaging materials

There is no foreseeable release of PFAS substances during normal use of consumable products or other end products. Moreover, the concentrations of PFAS in ATPS chemistries are low (parts per billion range) and any release is expected to minimal and only at the end of the product’s useful life. This release would occur only during electronics recycling or disposal. Some of the electronic reclamation processes are thermal and may cause a break-down of PFAS, but this would require further investigation.

There has not been a large-scale investigation in the waste streams across the assembly / test / packaging / substrate supply chain for the broad definition of PFAS that we are using within this paper. As most PFAS materials have not been regulated, there have not been the same tracking of PFAS molecules through manufacturing use to finished semiconductor products as there have been for other regulated or traced ATPS compounds. Further investigation and research in this area will be needed.

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# 9 PUMP FLUIDS & LUBRICANTS USES

**Summary:** PFAS lubricants are critical for use in semiconductor manufacturing, and currently no viable alternatives are known to exist for many critical applications. As such it is expected that **more than 10 years** would be required to substitute PFAS lubricants in general applications and **more than 25 years** for lubricants used in photolithography.

Potential silicone-based alternatives have a high likelihood of being **unsuitable substitutions** due to the high likelihood for increased failure rates and inability to meet critical performance requirements, like inertness when used in harsh conditions and low off-gassing and particle generation when used in manufacturing areas and processes where maintaining the highest standards of cleanliness is of paramount importance. Also, a switch to a relatively more reactive alternative is likely to result in:

- Mechanical system and seal failures that affect **human health and safety** within the workplace, and environmental releases of toxic/dangerous chemicals from the manufacturing process.
- **Additional energy consumption** of the machinery they are used in would be required due to their decreased performance.
- Reduction in the lifetime of such lubricants so **increased raw material and processing energy** would be required to manufacture additional quantities of lubricants when compared to PFAS lubricant use.

Overall volume of PFAS lubricants used within the semiconductor manufacturing industry is small, with expected minimal impact to human health and safety, and minimal exposure to the environment through reuse, recycling, and proper waste management.

Any substitution effort would require significant resourcing over an extended and indeterminate amount of time, at significant expense that could impact the local (i.e., EU, US, and US States) semiconductor industry's global competitiveness. Some substitutions would require extensive redesign and retrofit of semiconductor manufacturing equipment to an extent that would be cost-prohibitive for semiconductor manufacturers.

Solid and liquid lubricants are used to reduce friction and wear between surfaces and as a sealant to prevent the ingress of foreign materials into the lubrication clearance zone. Semiconductor manufacturing requires high-performance lubricants, many of which are PFAS-based, to prevent the creation of particles within cleanrooms and the extreme physical environments present in the manufacturing environments, as well as remaining inert, non-off gassing, and UV stable. PFAS lubricants are critical for use in semiconductor manufacturing, and currently no viable alternatives are known to exist, alternatives such as silicon-based lubricants do not offer the necessary technical performance.

In many cases the lubricants are exposed to demanding environments for over 10 years, so long term reliability is key. The overall volume of PFAS lubricants used within the semiconductor manufacturing industry is small and no lubricant will ever be on the semiconductor chip. As such the expected environmental exposure is minimal due to lubricant reuse, recycling, and proper waste management.

## 9.1 Challenges with non-PFAS lubricants

It is important to keep in mind that PFPEs were introduced in semiconductor applications mainly because of safety reasons due to their stability and non-flammability. Any alternative would need to offer these same technical attributes, so as not to decrease the overall safety of these systems potentially causing safety incidents/explosions, injuries, and damage to manufacturing facilities. Specifically, non-PFAS lubricants generate more heat as the lubricant breaks down, which results in lost productivity via

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indirect routes of increased wear and loss of precision leading to increased defect rates. This has direct implications including reduced productivity and costs through machine downtime for maintenance, cleaning and relubrication activities and replacement of parts.

The production of semiconductors is undertaken in cleanrooms that are thousands of times cleaner than those used for manufacturing of medical devices. Due to this need and the high dimensional tolerances required, all moving mechanisms within manufacturing cleanrooms and within the semiconductor manufacturing equipment itself must be lubricated. Lubricants also ensure that maintenance intervals are minimised, and the lifetime of moving parts is extended to the maximum possible.

PFAS-based lubricants also have negligible evaporation loss which plays an important role in applications such as vacuum applications. Other PFAS-free alternative cannot offer such very low outgassing performance, which would lead to contamination of the semiconductor wafer during production processes and therefore a decrease in yield. In addition, the more an alternative outgasses, the shorter the lifetime of the grease due to its degradation and the increased heat generation and energy consumption. The biggest issue is the potential for generation of particles / contaminants. Any friction arising from insufficient lubrication causes particle generation, and this results in a reduced yield. Each stage in the process must be virtually perfect with yields above 99%, because there may be hundreds of process steps used to manufacture each advanced semiconductor device. Without those very high yields, semiconductor manufacturing would fail to produce functional and economically viable products.

Increased mechanical failures of moving parts, resulting in an increased need for maintenance and shorter lifetimes of semiconductor manufacturing equipment, and a need to update semiconductor manufacturing equipment designs to incorporate additional redundancy and allow access to removable parts. This is due to the fact that all known non-PFAS-containing alternatives would provide lesser performance than the PFAS-containing lubricants currently in use.

The following table provides an overview of PFAS-containing lubricants used in semiconductor manufacturing and support equipment, all of which would require more than **10 to more than 25 years** to develop a PFAS free alternative that meets all technical performance requirements.

**Table 9-1 Examples of the products utilising PFAS lubricants.**

| Substance | Function | Status of alternative | Concern of alternative |
|---|---|---|---|
| PFPE Oil | Very low outgassing properties, and no outgassing of hydrocarbon compounds. Provides a viscous, hydrodynamic film that is sufficient to support the load and separate ball from the raceway in bearing applications, enabling high endurance performance.[75] Any lubricant used within the dry vacuum pump system may mix with the chemically reactive, oxidative process materials and/or corrosive process materials. UV stability for photolithography applications. | Currently, no non-PFAS-based oils and greases are known to be viable for use in dry vacuum pump applications.<br>PFPE is the sole option to be used for the base oil of ferromagnetic fluid used in the ferromagnetic fluid sealed rotation feedthrough. | No known substitute, as all available substitutes are associated with lesser performance, including outgassing, chemical inertness, and thermal stability characteristics.<br>Where PFPE greases are used the components are considered 'lubricated for life'. |

[75] https://www.dupont.com/molykote/perfluoropolyether-pfpe.html/

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| Substance | Function | Status of alternative | Concern of alternative |
|---|---|---|---|
| PFPE with PTFE micropowders and/or thickeners, grease | Provides a viscous, hydrodynamic film that is sufficient to support the load and separate ball from the raceway in bearing applications, enabling high endurance performance. Any lubricant used within the dry vacuum pump system may mix with the chemically reactive, oxidative process materials and/or corrosive process materials. Robots for manufacturing use this grease to provide for immediate and accurate responses without jerkiness, as required for high precision, due to performance requirements that include excellent stability and absence of gum formation, a very low coefficient of friction. | The PTFE micropowder is a thickener for which there is no known substitute, as it is a self-lubricating solid that slides against each other with very little friction, without becoming a source of particulate contamination. | No known substitute |
| Multiple-alkylated cyclopentane based greases with PTFE thickener | Used to lubricate linear guides, slides and ball screws requiring low vapour pressure, non-flammability, and high stability. | No known substitute for PTFE as self-lubricating solids that slide against each other with very little friction/particle generation. | No known substitute |
| PTFE polymers and polymer plastics with PTFE additives | Solid lubricants utilised in pure polymer form, or additives in polymers and coatings or surface treatments that provide low friction coefficients in applications that require low particle generation, chemical inertness and high stability and excellent stick-slip characteristics | Currently no viable substitutes that have the ability to provide the required lubrication within the semiconductor applications that require use of these solids | No viable substitutes, as available solid lubricant alternatives require very dry conditions that are not provided within semiconductor manufacturing environments |

The amount of any of the above listed substances in the manufacturing equipment is not known but estimated to be <0.1% w/w in most instances. In the worst-case applications such as ferromagnetic fluid sealing applications and certain dry vacuum pumps, there could be a maximum of 5% w/w in the manufacturing equipment.

The best potential PFAS-free alternatives are believed to be silicone-based oils and lubricants, however these have a limited temperature range when compared to PFAS alternatives, they are prone to off gassing, and have compatibility issues with some elastomers. As such, this is limited in the applications they can be used in. Silicone based alternatives also have the disadvantage of producing lens contamination in lithography as they decompose under UV irradiation and form a film on optical components particularly lenses. This leads to significant loss in optical transmission which severely lowers the productivity (by 10%) within a few weeks of use and increases the number of scrap wafers. Such a productivity loss has a negative impact to overall manufacturing production and reduces competitiveness in the global marketplace.

It is also worthwhile noting that D4-, D5-, and D6-ring siloxanes could be included in those silicones, which are classified as SVHC under the REACH Regulation due to their classification as Persistent, Bio accumulative and Toxic-substances. A change from PFAS-based lubricants to silicone might therefore

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be considered a **regrettable substitution**. Moreover, the increase in expected failures and the number of scheduled maintenance processes is likely to subject operators to a higher probability of exposure to the lubricant used.

As yet a PFAS-free viable alternative does not yet exist, and so a fundamental technology development would be needed in either the lubricant-containing equipment and/or lubricant itself. This is especially true of the lubricants used in photolithography as a fundamental change in the airborne molecular contamination load would be required. This change would require several years and significant expense to complete fundamental research, to qualify new designs, and to implement the use of non-PFAS lubricants. Once a promising alternative is invented/identified, the estimated timeline of qualification is expected to be at least 10 years but in the majority of applications 25+ years. For the more technically demanding applications, such as lubricants used in high vacuum applications with elevated temperatures, or reactive chemical/gas processes a fundamental technological development would need to occur within the advised timelines so there is some uncertainty with these estimates. It is possible that in some applications all PFAS-free alternatives will only offer reduced technical performance and increased environmental impacts and increased maintenance would always be observed if an alternative is used.

The overall mass quantity of PFAS-containing lubricants used within the semiconductor manufacturing process is very small. Semiconductor PFAS Consortium members estimate that on average 200ml of lubricant/oil per pump, and 100 g of grease per tool per year is used. However, this is not localised but rather virtually all contact points between moving parts make use of PFAS-containing lubricants and therefore the number of uses is estimated to be in the many tens of thousands within a semiconductor fabrication facility. Even if a number of these uses are less technically demanding and therefore a non-PFAS containing substitute may be possible, the reliability of such uses still needs to be ensured as it could result in catastrophic manufacturing losses.

The process of substituting lubricant would potentially require extensive cleaning with special solvents and the rebuild of up to 3000 pieces of complex machinery in each fabrication facility. It is also expected to significantly increase the requirement for maintenance activities, estimated to be a 3-fold increase or more.[76] As such, the resulting increase in waste would be expected to rise by a similar amount. Due to the increase in maintenance requirements, a higher proportion of down time for semiconductor manufacturing equipment is expected which against the backdrop of increasing demand would not be acceptable. The only way to maintain the same production volume would be to increase the quantity of production equipment and clean rooms, which in turn uses more energy, utilities etc. and the $CO_2$ emission per semiconductor device would then be higher.

## 9.2 Environmental Considerations in Lubricants

Liquid PFAS lubricants are only used in closed systems and do not need to be replenished as often as other lubricants as they are designed to be long-lasting. There are instances, such as PFPE greases where the lubricant does not need to be replaced throughout the life of the equipment. As such the potential exposures for most lubricants are limited to product damage, or at end-of-life.

There are some liquid lubricant uses which require changing periodically, with some being between 1-2 years but others only after 10 years+. During oil change, the liquids are pumped via a closed system into a tote/drum with negligible emissions. Liquid wastes are collected and sent for recycling. All PFAS

[76] Based on estimations made by Semiconductor PFAS Consortium membership.

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containing solid wastes involving lubricants are treated by incineration at specialist facilities capable of dealing with halogens and destroying PFAS.

### Relative impact of alternatives

Based on the currently available alternatives discussed above, even in the limited applications where PFAS-free alternatives could be used, it is expected that **additional energy consumption** of the machinery they are used in would be required due to their decreased performance. There is also the consideration that the lifetime of such lubricants is also generally decreased, so **increased raw material and processing energy** would be required to manufacture additional quantities of lubricants when compared to PFAS lubricant use.

It is also worthwhile highlighting that thanks to their stability, all of the PFPE oils can be easily recycled and reused (reducing almost to zero emission into the environment). There are in fact readily available market options which provide a recycling service for PFAS pump oils, with progressive research into improvements in the quality of the recycled products.

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# 10 ARTICLE USES

**Summary:** The PFAS substances most commonly present within articles used within the semiconductor industry are PVDF, PTFE, FKM, FFKM, PCTFE, ETFE, PFA, and PFA-CF.[77] As the number of applications that use fluoropolymer articles are myriad, a more detailed review is outlined in the PFAS Consortium whitepaper "PFAS-Containing Articles used in Semiconductor Manufacturing" outlined in Table 1-2.

The semiconductor manufacturing process is unique in several ways. It is making the smallest dimension objects ever attempted by humans, using some of the most exacting chemical processes to build features 5 nm (5 billionths of a meter) in "width". The feature size of device elements in turn demands the lowest possible organic, inorganic, metallic or particulate contamination from the environment in which wafers and devices are processed. Semiconductor manufacturing and related equipment (SMRE) is equipment used to manufacture, measure, assemble, or test semiconductor products. Many individual component parts in SMRE, facilities equipment, and infrastructure are dependent on PFAS-containing articles to provide the required cleanliness and purity; chemical & permeation resistance; compatibility; inertness; temperature stability; low coefficient of friction; non-flammability; optical, mechanical and electrical properties; processibility; and bacterial growth resistance to manufacture semiconductor devices as listed in Table 10-1.

For most uses, **invention is required to develop suitable replacement materials**. A timeline cannot be assigned to the invention process; however, once potential replacements are identified, some may take up to **15 years or more to evaluate**, demonstrate, qualify, and implement in the full supply chain. Applications such as transport of ozonated ultrapure water (UPW), tubing used to transport chemicals, fittings, O-rings, valve seals, process chambers and tanks, pump wetted parts, filters and scrubbers, and various applications in electronics all fit into this category as an alternative has not been invented which is suited to the use. It is not a given that non-PFAS alternatives that have all the salient properties of PFAS would be found.

This section covers known fluoropolymers present in articles required for semiconductor manufacturing which are components of SMRE and semiconductor manufacturing facility equipment and infrastructure. SMRE are enormously complicated with a large, international supply chain.

The current leading-edge photolithography exposure tool as shown in Figure 10-1, is described by Dario Gil, a senior vice president at IBM, as "…definitely the most complicated machine humans have built."[78] The EUV tool, manufactured by Dutch firm ASML, contains 100,000 parts and two kilometres of cabling. A single fabrication facility (fab) manufacturing leading edge chips has multiple EUV tools as well as dozens of deep UV exposure tools. There are challenges in identifying which components contain fluoropolymers as the information may be held within the supply chain of Consortium members which can be many layers deep. Consortium members are starting to obtain information from their supply chain, but the depth and complexity of the supply chain, and a lack of disclosure requirements, hinder information gathering.

[77] Fluoroelastomers (FKM), perfluoroelastomers (FFKM), polychlorotrifluoroethylene (PCTFE), ethylene tetrafluoroethylene (ETFE), perfluoroalkoxy alkanes (PFA), and perfluoroalkoxyperfluoropropyl vinyl ether with carbon fibre filler (PFA-CF).

[78] The Tech Cold War's 'Most Complicated Machine' That's Out of China's Reach - The New York Times (nytimes.com)

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Figure 10-1 ASML Latest Extreme Ultraviolet Photolithography Exposure Tool.[79]

Fluoropolymer and other PFAS-containing articles are found in a wide variety of articles used by the semiconductor industry for the manufacture of semiconductors, examples of which are listed in Table 10-1. A more detailed review is outlined in the PFAS Consortium whitepaper “PFAS-Containing Articles used in Semiconductor Manufacturing” outlined in Table 1-2.

## 10.1 Required Characteristics

Fluoropolymers have multiple useful characteristics, but it is the simultaneous achievement of these properties that makes these materials critical for the safe and efficient manufacture of semiconductors. The following is a list of fluoropolymer properties which are important for semiconductor manufacturing:

- Purity
- Chemical and permeation resistance
- Temperature stability
- Coefficient of friction
- Non-flammability
- Optical properties
- Mechanical properties
- Contamination control
- Electrical properties
- Processability
- Bacterial Growth Resistance

One example is the use of perfluoroelastomers in high performance fluoroelastomer seals in semiconductor manufacturing equipment in gaps between mating surfaces to prevent contamination. These polymers are required to be resistant to a broad range of chemicals and high temperatures, as many of the seals are exposed to $O_2$ plasma, fluorine ($F_2$) plasma and/or $O_2/F_2$ mix plasma at temperatures of 200°C and higher. Technological advancements in semiconductor device

[79] Photo courtesy of ASML.

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manufacturing have only been made possible by utilising these and other highly reactive species, often at high temperatures. Fluoroelastomer seals also do not outgas even at these conditions and equipment cleanliness is maintained. Seals such as these are only used where necessary as these technical characteristics come with an associated increase in cost when compared to non-PFAS alternatives. Fluoroelastomer seals also are necessary to maintain the vacuum within semiconductor manufacturing equipment, which ensures safe removal of harsh chemicals and worker protection. Therefore, any potential alternative needs to be able to operate in such an environment without degradation, erosion, or loss of elastomeric properties over a reasonable interval of time to be considered a realistic alternative. Very few polymers are able to operate in these environments.

Another example is the use of PFA and PTFE in chemical tanks used in wet cleans and wet etch processing equipment. The manufacture of integrated circuits requires contamination removal and surface preparation to enable high yields. Aggressive chemicals, sometimes at high temperature are used in wet cleaning and etching. PFA and PTFE are used because they do not react with the chemicals, do not leach contaminants that can negatively impact yield, and are stable under process conditions including elevated temperature. The material must be compatible with the continual exposure of aggressive chemicals and not contaminate the system with particles, metals, or dissolved organics, during the life of the equipment. PTFE may be used in tubing, valves, spray nozzles and other components that contact the chemicals to prevent contamination and ensure chemical compatibility. In addition, PFA tubing is highly flexible and can be easily bent and routed, making it easier to design and implement in wet etch processing equipment.

Fire/explosion, fluid leakage and critical service interruption are the primary threats to safe and continuous fab operations according to FM Global, a leading insurer of semiconductor facilities world-wide.[80] Fluoropolymers used to meet technical performance requirements such as chemical compatibility while also mitigating fire and release risks. SEMI S14[81] and FM 7-7 are used by the semiconductor industry to mitigate fire risk. These standards reference other standards such as FM4910 and UL 94 to assess smoke generation and/or fire propagation. Examples where fluoropolymers are used for technical performance requirements and fire protection include:

- Ultrapure water (UPW) piping and tubing
- Wet bench construction materials.
- Fluoropolymer insulated wire and cable.
- Fluoropolymer and fluoropolymer-coated ductwork.
- Ultra-high purity (UHP) chemical distribution
- Process liquid heating systems.
- Valve manifold boxes.
- Hazardous production chemical liquid storage.

[80] As noted in FM7-7, “Fire and explosion hazards include combustible plastic construction materials (tools, ducts, and scrubbers)...”.

[81] SEMI S14 - Safety Guideline for Fire Risk Assessment and Mitigation for Semiconductor Manufacturing Equipment, S01400 - SEMI S14 - Safety Guideline for Fire Risk Assessment and Miti

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**Table 10-1** Examples of articles utilising PFAS where no alternatives have been identified to date.

| Substance | Function | Concern of alternative[82] | Timeline to develop |
|---|---|---|---|
| PVDF | In Lithium batteries: provide a thermal and electrochemical stability as a barrier. Excellent electrochemical stability, good wettability with electrolyte and acceptable binding ability between active materials and current collectors. | Information should be sought from lithium battery manufacturers; expected concerns include chemical resistance, heat resistance, and non-flammability. | Unknown |
| PTFE | In bearings: provide lubricity, chemical resistance, thermal resistance. | Chemical resistance, heat resistance, and cleanliness. | Unknown |
| PFAs or PTFE | Wet cleans and etch processing equipment such as tubing and fittings, Purity via low particle shed, surface smoothness, chemical resistance, thermal resistance. | Whether they can be maintained and if they will gain the necessary safety approvals. | >15 years |
| FKM, FFKM and PTFE | In wire insulation, O-rings, valve seal, abatement seals, sealing tape: elasticity, chemical inertness, resistance properties against power, dampness, temperature, heat, UV, and corrosion. | Chemical resistance, heat resistance, and non-flammability. | >15 years |
| PVDF, PTFE, PFA | In chemical storage and transportation (tanks, pumps, pipes, seal, gaskets etc), ultra-pure water systems including pumps and filters provides purity via low particle shed, surface smoothness, and is chemically resistant. | Chemical resistance and cleanliness. | >15 years |
| PTFE | In exhaust abatement / scrubber: chemical inertness, non-flammable. | Chemical resistance and heat resistance. | >15 years |
| PTFE/PFA/PCTFE, ETFE, PFA-CF, PTFE/PFA/PVDF | In Chemical dispense arm/nozzle assembly, wafer spin chuck, wafer splash guard, reclaim tank, IPA tank, solvent supply/measuring tank, chemical mixing tank, air/liquid separation box chemical mixing box wafer handling and effector coatings, valves, control, switching, regulating monitoring systems low pressure chamber, robot hand, lifters piping, automated material handling systems wafer carriers, UPW & Chemical Filters/housings; Purity via low particle shed, surface smoothness, chemical resistance, thermal resistance, resistance to permeation of chemical resistance and gasses. | Reduced durability and component lifetimes resulting in a significant increase in waste. | 5-15+ years depending on the application |
| PTFE | In potentiometer shims provides smooth motion. In potentiometer resistive inks: presumed to provide long term wear. In SMD tantalum capacitors provides a special mechanical/chemical barrier on the magnesium electrode. In liquid dielectric capacitors as dielectric films and electrolyte constituents provides long term chemical stability. | Information should be sought from potentiometer and capacitor manufacturers. | Unknown |

[82] Properties where it may be difficult to find an equivalent alternative, or factors that will increase development times, or possible consequences of an alternative.

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If the technical characteristics of a proposed alternative do not strongly align with the PFAS substance it is intended to replace, the requalification time is anticipated to be much longer; moreover, the replacement may fail entirely.

## 10.2 Alternatives

The specific application of the article informs the necessary technical requirements, which in turn inform the viability of potential alternatives. The following are key themes relating to technical performance that alternatives need to meet:

- **Cleanliness:** Alternative materials must offer the same level of cleanliness with specifications such as SEMI F57[83] outlining requirements. For example, ultra-pure water (UPW) systems need to operate to demanding specifications which include metals <0.05ppb, low ion contaminants (>19 Mohm/cm resistivity), total organic carbon <1.0 ppb, dissolved oxygen of <5 ppb, low particulate matter with no particles greater in size than 0.2 microns, and <10 particles/ml of particles greater than 10 nm diameter. The historic move from PVC to PVDF to meet these criteria took 47 years to fully complete (1948-1995).
- **High chemical resistance** as otherwise this could lead to chemical leakage, chemical damage to equipment and in operating conditions pose safety concerns for workers. For example, replacing PFA and FFKM seals would require a redesign of the tool which would either need to include a seal, where this would be exposed to the plasma, or would need to shield the seal from plasma exposure.
- **Heat resistance** as otherwise this could lead to piping components melting or deforming, resulting in chemical leakage and fire, e.g., silicon rubber replacing PTFE gaskets in turbo pumps could result in failure due to decreased heat resistance.

Replacing with PFAS-free alternatives is often incredibly challenging as often potential alternatives require more frequent replacement. For example, data collected by Consortium members has highlighted that the degradation of O-rings consisting of PFAS- free alternatives is higher than the currently used PFAS material. The use of such alternatives would result in increased waste generation, equipment downtime, and maintenance worker exposure to potential hazards. There is also the environmental concern related to any failures of the materials in service, resulting in a higher likelihood of negative environmental impacts and worker exposure due to unplanned releases of process chemicals.

In order for PFAS-free alternatives to be incorporated in semiconductor equipment, and especially fabs, it is important that the initial qualification is undertaken by the many layers of the supply chain. Although there may be PFAS-free alternatives advertised, until they have been evaluated in semiconductor applications described in this report, they cannot be determined to be viable alternatives. Extensive test data would be required to understand the impacts of material changes on the safe use, degradation potential and useful life of any articles. Without the development timescales outlined in Table 10-1, there is a greater probability of an alternative material failing whilst in use, which could have serious health and safety implications. Alternatively, if the replacement part is for a key piece of equipment in the device manufacturing process, it could impede the availability of many thousand end-use devices (chips) per day.

[83] F05700 - SEMI F57 - Specification for High Purity Polymer Materials an – semi.org

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### 10.2.1 Examples of unsuccessful PFAS-free article trials

The following are some examples of PFAS-free alternatives that have been researched and evaluated but do not offer suitable performance in the applications in which they were assessed, grouped by the failure type.

#### Decreased Cleanliness

- Sulfuric acid container made from high-density polyethylene (HDPE) leached particles over time, resulting in wasted chemical and product failure. PFA/PTFE lined containers eliminated the leached particle issue.
- IPA container made from HDPE leached high molecular weight organics into IPA causing a process issue and contaminating the tubing and process chamber.
- Polyvinylchloride (PVC) has been shown to shed particles, so is not suitable for use in SMRE.[84]
- One of the major properties of fluoropolymers is their low outgassing, which contribute to the clean environment required during photolithography. Without PFAS materials impurities are deposited on mirrors used during the processing of semiconductors. Only fluor- and silicon-based materials are able to meet the critical requirements necessary for these applications.[85]

#### Increased Failure/Safety Concerns

- PVC filter housing for the dilution of copper water increased failures by a factor of 2.5. Changed to PFA and zero failure rate was achieved with removal of the risk of chemical spill and safety concerns for the workers.
- Stainless steel was used for level indicator of ammonia waste transmitters, but this had a high corrosion rate, resulting in the overflow of the tank due to failure of the component. The part was substituted by a PFAS, and the failure rate was greatly reduced.
- The design of piping system to deliver organic amines was trialled however PFA was the only material that showed compatibility with organic amines and achieved zero failure rate.
- HDPE was investigated as a possible replacement for PTFE in tanks, tubing, and containers, however after 6 months it was found to start decomposing in 70% nitric acid, which leads to chemical leakage and an increased replacement rate.
- Pulse dampeners using nitrile or EPDM (ethylene propylene diene monomer) elastomers failed because of chemical breaching the diaphragm. By using fluoropolymers, i.e., PTFE, PVDF or PFA in the diaphragm the failure rate has been zero, eliminating both a contamination and failure mechanism.
- Non-PFAS elastomers have been used as O-rings and seals, by mistake, within mechanical and chemical/gas delivery systems. In some cases, these seals failed almost immediately and caused leaks due to their incompatibility with the gases and chemistries running through the lines. This has resulted in the requirement to disassemble the system and replace the O-rings, result in >10 days of lost production time to replace and requalify the system.

[84] Burkhart, Marty, Martin Bittner, Casey Williamson, and Andrea Ulrich, “A Scientific Look at Lab Quality Deionized Water Piping Materials”, Ultrapure Water, Nov 2003, p 36-41.

[85] Based on information on outgassing complied by NASA in relation to O-rings and gaskets. Outgassing Data for Selecting Spacecraft Materials Online | Outgassing (nasa.gov)

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Each of the above examples indicate that replacement can increase product safety risk and, more importantly, a risk to workers and the manufacturing facility. As such each use meets a safety need in production. For example, if the alternative non-PFAS substance used is combustible or does not have the appropriate heat resistance it will result in an unacceptable fire risk.

## 10.3 Environmental Considerations for Articles

Potential environmental impacts associated with articles occur primarily during the manufacture of raw materials, which is upstream of the semiconductor devices manufacture. There are also environmental impacts associated with the end of life of articles. Articles are reused and recycled when possible. In some instances, articles are contaminated during use with hazardous chemicals and, therefore, require management according to specific regulatory obligations. The industry will continue to act responsibly by taking advantage of circular economy opportunities as they arise.

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# 11 ENVIRONMENTAL IMPACT, END OF LIFE AND WASTE CONSIDERATIONS

The semiconductor industry works to understand the environmental impact of its manufacturing process and employs wherever possible appropriate engineering controls, abatement, and treatment systems to minimise emissions. In addition, the semiconductor industry undertakes process optimisation to reduce the amount of waste generated and disposed of at a regulated waste disposal facility.

The semiconductor industry has implemented where possible control and treatment technologies to reduce emissions and discharges of chemicals, including PFAS, used in semiconductor manufacturing processes. Typical environmental releases include emissions to air and water and disposal of hazardous or non-hazardous waste. Some PFAS-containing materials are sent off-site for treatment, such as incineration, or disposal in regulated solid waste disposal facilities. Semiconductor manufacturing facilities also have on-site abatement systems for air emissions and wastewater pre-treatment or treatment systems prior to discharging wastewater. The semiconductor industry continues to actively identify, test, and implement wherever possible improved process controls that reduce PFAS releases to the environment.

## 11.1 Air Emissions Control and Abatement

Manufacturing facility exhaust systems are designed to remove chemical vapours or gases and heat from equipment. The use of PFCs and HFCs is essential for plasma etching, plasma cleaning, and other low volume but critical applications, as their uses balance the process need for high chemical and ion reactivity with the need for safe and effective manufacturing. The chemistries used in photolithography have relatively low vapour pressure and as outlined in Section 4.6 the quantities of emissions from photolithography are extremely small.

The semiconductor industry has a history of commitment to reducing greenhouse gases and has successfully reduced PFCs and HFCs emissions through a combination of process optimisation, substitution, and abatement. The use of POU technologies on many tools using PFCs and HFCs has reduced the potential hazard of exposure to employees and has reduced greenhouse gas emissions. With the implementation of WSC PFC best practices in new fabs - including remote plasma clean and POU abatement- many facilities have needed to expand other treatment systems, such as wastewater, fluoride, and exhaust to meet the required standards for wastewater and air toxics.

Some POU technologies use fuel-burning processes to abate PFCs and HFCs, creating additional nitrogen oxides, carbon monoxide, and other air pollutants from combustion in exchange for a reduction in PFCs and HFCs. It is therefore especially important that process and abatement alternatives undertake a full safety, health, and environmental impact review to understand additional implications to employee and community safety and health.

In addition, tool PFCs and HFCs, F-HTF are also a potential small source of PFAS emissions to air. The F-HTFs used within chillers and test equipment are contained with intent to minimise release during use. Prior to any maintenance activities, F-HTF in the equipment is drained into collection containers that are typically managed for direct use or reclaim at the location of the F-HTF supplier. If any of the F-HTF fluid is required to be managed as waste, the fluid is typically managed for destruction by incineration or thermal destruction by certified waste management facilities. However, during this activity it is possible that small quantities of the F-HTF can be released into the air.

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## 11.2 Wastewater Treatment

Semiconductor manufacturing facilities generate organic and aqueous waste streams which are treated in accordance with local and federal waste and wastewater regulations. Historically, the majority of aqueous chemicals employed in fab manufacturing processes are discharged to an industrial wastewater drain system that conveys wastewater for treatment of specific regulated pollutants in accordance with local and federal regulations, and subsequently discharged to a publicly owned treatment works or surface water. Most PFAS are not regulated pollutants and therefore unless company specific provisions are in place, the wastewater from processes that use aqueous wet chemical formulations that contain PFAS would likely be discharged to the publicly owned treatment works without substantive removal of the PFAS. The industry is actively researching PFAS wastewater releases and treatment technologies.

Conventional precipitation-coagulation-clarification treatment processes that are typically used to remove dissolved metals and fluoride from semiconductor wastewater would not be expected to exert a high removal efficiency for soluble PFAS. However, partitioning of some PFAS to the biological waste solids can be anticipated, and may represent a significant opportunity for PFAS migration in the treatment processes. In general, the state of technology for PFAS wastewater treatment is immature, with significant improvements needed to increase the number and types of PFAS that can be cost effectively removed from wastewater.

## 11.3 Waste Disposal

Organic waste, including organic liquids containing PFAS, is typically segregated, collected, and containerised to be treated at an offsite licensed treatment and disposal facility, as a blended fuel by high temperature incineration or reprocessing.

Liquid PFAS lubricants are only used in closed systems and do not need to be replenished as often as other lubricants as they are designed to be long-lasting. As such the potential exposures for most lubricants are limited to product damage, or at end-of-life. For lubricants requiring replenishment, during oil change, the liquids are pumped via a closed system into a collection container with negligible emissions. Typically, liquid PFAS lubricant wastes are collected and sent for recycling so are not expected to enter waste disposal streams.

For articles and packaging, there should be minimal or no release of PFAS during normal use of the end product containing semiconductors. At the end-of-life of the product containing the semiconductor, or any parts replaced during the manufacture of semiconductors, would enter waste disposal streams where any PFAS contained therein could enter the environment. Articles are reused and recycled when possible. In some instances, articles replaced during the manufacture of semiconductors are contaminated with hazardous chemicals and, therefore, require management according to specific regulatory obligations so would not enter general waste disposal streams.

## 11.4 Environmental Impacts of Non-PFAS Use

It is worthwhile noting that if PFAS-based materials are substituted, there are some broad potential adverse environmental implications which are as outlined:

- If alternatives **decrease yield** even by very small percentages significant increases are required in semiconductor manufacturing facility size resulting in correspondingly increased chemical, water, and energy consumption, as well as waste generation.
- **Decrease in PFAS-free alternative performance would increase the consumption of parts and waste generation** for some uses. For example, some PFAS-free articles have an increased risk of

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release to air and water due to early article failure, increasing the number of leaks and the consumption of articles, as they need replacing more often. This loss of process integrity also results in process safety concerns due to loss of containment.

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# 12 SUMMARY OF FINDINGS

RINA has undertaken a process of data collection and analysis based on a survey of Semiconductor PFAS Consortium members and subsequent discussion and technical feedback. The evidence provided can be summarised as follows.

PFAS are used in chemical formulations, components of manufacturing process tools, facilities infrastructure, and packaging used to make the semiconductor devices that are integral to the modern world. The current semiconductor state of the art is critically reliant on the use of PFAS chemistry owing to the particular properties that these substances provide to enable the extremely demanding performance requirements of semiconductor devices to be realised. **Given their unique properties, it is going to be extremely difficult, if not impossible in some instances, to find viable alternatives without stepping back decades in technological advancement.** There are also environmental impacts with not using PFAS, such as the potential for decrease in yield and therefore and increase in chemical, water, energy consumption and waste generation. In addition, there is the potential for the decrease in performance of some PFAS-free articles to result in increased waste.

The following highlights key uses of PFAS and the estimated time to identify PFAS-free alternatives in each area. More detailed technical information can be found in the respective white papers and case study reports written by the Semiconductor PFAS Consortium (listed in Table 1-2).

- **Photolithography** – PFAS has been an enabling technology in the development of ever smaller semiconductors through cutting edge lithographic developments. PFAS are used in multiple processing steps including photoacid generators (PAG), antireflective coatings (TARCS), surfactants, and barrier layers. For each use type, there are significant technical challenges, many of which will require a new technological development to enable any alternatives to even be potentially viable.

  All successfully demonstrated PAGs are fluorinated and there are no universally applicable viable fluorine free alternatives for a vast array of lithographic materials. Current PAGs have been in development for 25 years, and alternatives are expected to take from **15 to more than 20 years** to reach production.

  TARCs previously used PFOS and PFOA, which industry moved away from to shorter chain PFAS when regulators identified them as a safer alternative. A high fluorine content is needed to achieve the low refractive index required for TARCs to work, so an **alternative solution needs to be identified**, after which qualification activities can start.

  There is a similar need for the invention of new materials offering the necessary technical parameters for immersion barriers and dielectric materials.

  It may be possible to find non-PFAS alternatives for less advanced surfactant applications using current known potential alternatives, however, for most advanced applications, a new material would need to be invented to meet the necessary technical requirements.

  Although each PFAS use has its own challenges and timelines for development, most uses are expected to take between from **10 to more than 13 years** to develop and qualify a PFAS-free alternative, with the exception of PAG's.

  Alternative solutions will not only have to offer highly demanding technical performance for their intended use, but also not affect subsequent processing steps. A further complicating consideration is that a one-for-one replacement in many of the PFAS uses is not deemed to be technically viable due to the changing technological challenges as the node size decreases. As such, qualification

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activities are likely to be limited to certain node sizes, with particular challenges at the smaller node sizes.

- **Wet Chemistry** – There are application-specific performance requirements, which may be product or company specific and essential applications which are not universally used by all manufacturers, fabs or products. PFAS are used in several types of formulations of photodevelopers, and etchants, at different steps in the semiconductor manufacturing process. The timeline needed to develop, qualify, and implement alternatives falls into the following four broad categories:
  - **3 to 4 years**: If an existing non-PFAS alternative is available and can be demonstrated to provide adequate performance for a specific application.
  - **3 to more than 15 years**: In some applications where existing non-PFAS alternative may be viable but requires tooling and/or process changes before it can be successfully introduced into HVM.
  - **Successful invention required (from 5 to more than 25 years**): where the invention of new chemicals, and/or development of alternative approaches to manufacturing the device are required, with no guarantee of success.
  - **No alternative achievable**: In some cases, it may ultimately be found that a non-PFAS alternative is not capable of providing the required chemical function and therefore an alternative semiconductor device structure would be required.
- **Fluorocarbon uses in plasma (or "dry") etch / wafer clean and deposition**– PFC and HFC are used in plasma (or dry) etch/wafer clean, deposition chamber clean, and organometallic precursors and cannot be substituted as extreme cleanliness is necessary to anisotropically etch features without damage. PFC and HFC emission reductions have been a committed goal of the semiconductor industry for over 30 years. However, cutting-edge semiconductor technology only exists because of the unique properties of these gases to perform specifically as intended in this environment. **Fundamental changes in semiconductor materials, device design and manufacturing processes are required for alternatives to be feasible. For the vast majority of uses 10-15 years after invention of new semiconductor materials, designs and processes** would be required to substitute **for each specific type** of PFC and HFC use.
- **Heat Transfer Fluids (HTF)** - Fluorinated HTFs are used as liquid fluorinated heat transfer fluids (F-HTFs) and fluorinated refrigerants which are used in tandem within HTF loops and refrigerant cycles to meet operational temperature requirements in semiconductor manufacturing processes like dry etch, thin film deposition and semiconductor device test applications. Similarly performing non-PFAS do not exist for most heat-transfer applications, due to differing working temperature ranges, viscosity, and dielectric properties.

  There are some PFAS-free HTF, such as glycol / water alternatives which can be used in a limited number of applications. However, it would require from **8 to more than 14 years** to substitute due to the need for equipment redesigns to ensure the ongoing safety of equipment making use of the HTF. A similar timeline from **8 to more than 14 years** is also required for the substitution of refrigerants within process equipment chillers. For over 70% of applications there is no currently viable alternative, so **an alternative would need to be invented**, after which from **5 to more than 15 years** would be required to implement this and ramp up to HVM.

  There are very few companies which manufacture thermal test fluids, which are manufactured to extremely high specifications. Invention of a PFAS-free thermal test method has not started and the time to do this cannot be quantified. However once invented, it will take from **8 to more than 14 years** to implement, or considerably longer if the thermal test equipment needs redesign to accommodate the new method.

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- **Assembly, Test, & Packaging Materials** - As packaging becomes more and more complex due to decreased size, increased processing speed, and/or increased packaging complexity, the combination of properties required are often only found in the fluorinated hydrocarbon family. Changes to assembly package materials range in their complexity, but unlike other uses, due to their interactions with both the silicon die and the end customer product, additional customer product change notification/approval steps are required (average 1-2 years, with some applications requiring 6+ years). The following timelines are estimated to implement PFAS free alternatives: **Packaging fluxes 5+ years**, **surfactants 18+ years**, with many suppliers being single source which may cause suppliers to exit the market, **encapsulants 13+ years**, and **adhesives and certain MEMS anti-stiction agents 20+ years** as alternatives have been sought for 18 years without success.

  It is important to keep in mind that the use of PFAS underpins fast signal processing requirements, so the need for PFAS components is expected to grow to limit signal losses; so additional PFAS uses are expected to be required to enable key technology developments within the semiconductor industry.

- **Pump Fluids & Lubricants** - PFAS lubricants are critical for use in semiconductor manufacturing, and currently no viable alternatives are known to exist. As such it is expected that **more than 10 years** would be required to substitute PFAS lubricants in general applications and **more than 25 years** for lubricants used in photolithography. Potential silicon-based alternatives have a high likelihood for increased failure rates and an inability to meet critical performance requirements, like inertness when used in harsh conditions and low off-gassing and particle generation when used in clean manufacturing environments. A more reactive lubricant is also likely to result in system and seal failures, ultimately resulting in health and environmental impacts as a result of, increased energy consumption of the machinery, and the more frequent replacement of the lubricant.

- **Articles** - Very many individual component parts in semiconductor manufacturing equipment are dependent on these substances to provide the compatible, inert, clean, temperature tolerant environment needed for the fluids used in the equipment. Fluoropolymer articles are key in supporting billion-dollar EUV semiconductor lithography machinery, plasma chambers, ultra-pure water system piping, and the multitude of electronic equipment and tools that support a manufacturing facility.

  Alternatives typically take **more than 15 years** to substitute, and it is not guaranteed that a non-PFAS alternative will be able to offer all the salient properties of PFAS.

It is worthwhile noting that the timelines outlined above have a significant degree of uncertainty. For many of the substances there are no alternative theoretical material chemistries to use as a basis for invention and a whole new area of chemistry and/or technology will be required. There are also concerns that a change process as large as designing out all PFAS has never taken place and the timelines are based on the time to undertake a single change. As highlighted above, there may be interactions between multiple stages in processing which will need to be explored. There will also be limitations on how many suitably knowledgeable people are available given the magnitude and complexity of the task at hand. As such, the timelines could easily be much longer than those estimated.

The semiconductor industry has, where possible, implemented control and treatment technologies to reduce emissions and discharges of chemicals, including PFAS, used in semiconductor manufacturing processes. Typical environmental releases include emissions to air and water and disposal of hazardous or non-hazardous waste. Some PFAS-containing materials are sent off-site for treatment, such as incineration, or disposal in regulated solid waste disposal facilities. Semiconductor manufacturing facilities also have on-site abatement systems for air emissions and wastewater pre-treatment or treatment systems prior to discharging wastewater. In addition, the semiconductor industry undertakes process optimisation to reduce the amount of waste generated and disposed of at a regulated waste disposal facility.

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