European
Semiconductor
Industry
Association

Per- and polyfluoroalkyl substances (PFAS)

ESIA comments on Annex XV restriction report

Brussels, 2 June 2023

General Comments

Introduction

The semiconductor industry is very reliant upon many applications of materials (solids, liquid, and gases) falling under the definition of PFAS as set out in the EU REACH PFAS restriction proposal (any organic chemical with a perfluorinated methylene group (-CF2-) and/or perfluorinated methyl group (-CF3) moiety). Those materials are used in manufacturing process chemistries, in specific semiconductor functional layers and packages, semiconductor manufacturing equipment, semiconductor manufacturing infrastructure, and support equipment in addition to the semiconductor device.

Many of those uses are very specific for the sector and are determined by the special physicochemical properties of PFAS giving low surface tension, stability and chemical compatibility, inertness, purity, chemical and permeation resistance, a wide range of temperature stability, a low coefficient of friction, electrical properties, bacterial growth resistance, nonflammability, and a long service life (>25 years).

The Semiconductor Manufacturing Process

Table A.49 in Annex A to the restriction proposal sets out uses and properties of PFAS in the semiconductor industry. Based on the significant amount of work performed by the semiconductor industry since the submission to Royal Haskoning, a lot of additional uses of PFAS have been identified. In light of this, ESIA would like to clarify that table A.49 is not complete. Therefore, please check the attached Excel file for an update table. We continue to refine this dataset and will submit an updated version at a later stage.

There Is No “Digital” Without Chips

Today’s society is highly digitalized with even further plans by the EU Commission to advance the digital transformation through the Digital Decade plan. Should the semiconductor manufacturing process not be granted an appropriate derogation that covers the semiconductor manufacturing ecosystem including its supply and value chains as illustrated in the attached file “Updated Annex A Table A.49”, then the EU’s ability to achieve its six priorities – A European Green Deal, A Europe Fit for the Digital Age, An Economy that Works for People, A Stronger Europe in the World, Promoting our European Way of Life, A new Push for European Democracy will simply collapse. It is worth noting that if such a comprehensive derogation is not granted to the Semiconductor industry, it is more than likely that the ability to manufacture or indeed import semiconductors will cease once the entry into force and associated transition timeframe expires.

The Need for Legal Certainty

The Semiconductor industry needs legal certainty so not to hamper future investment in the EU and therefore keep and maintain the highly specialized employment prospects of those who work within the industry. The European semiconductor sector accounts for ca. €53.81 billion total billing, which amounts to a market share of ca. 9.28% of the worldwide semiconductor sector. The European semiconductor industry directly employs around 200,000 people and has one million indirect employees.

Competitive Disadvantage

Due to the long time required for developing, industrializing, and marketing new semiconductor devices, the proposed PFAS restriction will also have an unwanted effect on current R&D efforts. Semiconductor devices and manufacturing processes being developed today with current PFAS containing materials will be ready to be placed on the market some ten years from now. Should the restriction come into force as it is structured today, additional development effort will be needed to redirect the R&D process to try to replace PFAS materials, therefore putting the EU semiconductor industry at a competitive disadvantage, compared to industry located in other jurisdictions that do not have a comparable PFAS regulatory roadmap.

For most of the industry’s uses of PFAS, the ability to intercept the current R&D endeavours to remove PFAS will not be successful as most uses have no known PFAS alternatives. Accordingly, this would need fundamental R&D activities in a collaborative manner due to the extremely complex functions PFAS compounds perform within the semiconductor industry.

Substitution Timelines

Due to the many uses of PFAS within the semiconductor industry, the industry has attempted to group uses into three distinct substitution timeframes. Please refer to the ESIA’s response to Q7 for more details. Generally, it takes 5 to 25 years to develop, qualify, and implement alternatives.

PFAS Emissions in the Semiconductor Industry

Photolithography: The ESIA response concerning the industry's PFAS emissions focused on photolithography and emission from uses of gaseous perfluorocarbons. According to a US Semiconductor Industry Association (SIA) survey (see RINA paper attached, p. 41), it is estimated that in 2021 PFAS emissions arising from 2248kg of PFAS use in photolithography use per annum in the EU resulted in a worst-case scenario 1161kg of PFAS emissions.

Use of gaseous perfluorocarbon compounds (plasma etch and CVD chamber cleaning): In terms of the emissions of gaseous perfluorocarbon compounds (PFCs), the amount of PFC emissions that come within the definition of PFAS set out in the restriction proposal into the air is estimated to be 12,892 kg in 2022. To ascertain the concentration of PFAS that is contained in the typical wastewater from a semiconductor manufacturing facility (fab), some collaborative research was undertaken with Cornell University. For the study wastewater samples from three fabs in the United States were collected. The sum concentrations of the target PFAS in the diluted discharge samples from each fab were 623, 394, 376 ng/L (Paige Jacob, Krista A. Barzen-Hanson, and Damian E. Helbling Environmental Science & Technology 2021 55 (4), 2346-2356 DOI: 10.1021/acs.est.0c06690). Please refer to Q5 for more detail.

Question 1

***Sectors and (sub-)uses**: Please specify the sectors and (sub-)uses to which your comment applies according to the sectors and (sub-)uses identified in the Annex XV restriction report (Table 9). If your comment applies to several sectors and (sub-)uses, please make sure to specify all of them.*

ESIA answer

The semiconductor sector is relying upon several application of materials (solids, liquid, and gases) falling under the definition of PFAS, therefore our comments are related to the following uses and sub uses identified in Table 9.

Electronics and semiconductors (Annex E.2.11.) Semiconductors Wires and cables / Coating, solvents, and cleaning / Electronic components / Heat transfer fluids / Advanced semiconductor packaging / Photolithography

Applications of fluorinated gases (Annex E.2.8.) Refrigeration / Insulating gas in electrical equipment

Question 5

***Proposed derogations – Tonnage and emissions**: Paragraphs 5 and 6 of the proposed restriction entry text (see table starting on page 4 of the summary of the Annex XV restriction report) include several proposed derogations. For these proposed derogations, information is requested on the tonnage of PFAS used per year and the resulting emissions to the environment for the relevant use. Please provide justifications for the representativeness of the provided information.*

ESIA answer

The ESIA response below is focused on photolithography emissions and emissions from uses of gaseous perfluorocarbons.

Photolithography

PFAS-based technologies have been used in the semiconductor industry to develop smaller and more advanced products as they enable cutting-edge developments in photolithography.

Photoacid generators (PAGs) are essential components of the Chemically Amplified Resists (CARs) which are used in advanced photolithography. When exposed to ultraviolet (UV) light, they generate strong acids. The chemistry requires sulfonium or iodonium- salts with PFAS-type anions. The solubility change of the photoresist is caused by the super acids which are created by the strong electronegativity of the fluorine atom. All PAGs that have been demonstrated to be successful are fluorinated. **Top antireflective coatings (TARCs**) need a very low refractive index, low surface energy and outstanding barrier properties. Fluorinated acrylate / methacrylate / styrene-based copolymers provide these properties. **PFAS surfactants**' unique properties, i.e., very low surface tension and a combination of hydrophobic and oleophobic behaviour, are used in numerous photolithographic materials. Fluorinated acrylate / methacrylate / styrene-based copolymers provide **immersion top coatings** with the necessary low surface energy, outstanding barrier properties and a lack of intermixing with the photoresist.

Key photolithography uses of PFAS and technical criteria

Photoresists and BARCs – PAGs

- Function: Precursor for the photoacid catalyst needed for CARs and BARCs.
- Types of compounds used: These chemicals are complex and to obtain the required performances they contain several lower chain length PFAS.
- PFAS provide: Strong electronegativity of Fluorine atom in the complex resist/chemical matrix allows for controlled generation of strong acid upon exposure to UV light.

Photoresists – polymers

- Function: Control pattern profile in extreme ultraviolet (EUV).
- Types of compounds used: lower chain length PFAS polymer.
- PFAS provide: Increases absorbance, improves the dissolution properties, increases resolution.

Top antireflective coatings

- Function: Control of thin-film interference effects in resists.
- Types of compounds used: water and developer soluble PFAS polymers.
- PFAS provide: High fluorine content is needed to achieve the low refracting index needed to effectively suppress film interference effects.

Immersion barriers

- Function: Protection of the resist from immersion liquid and of the exposure tool from contamination. Prevent water film pulling and resist component leaching in immersion topcoats.
- Types of compounds used: Spin-on barriers: Water insoluble and developer soluble PFAS polymers with fluorinated side chains. Embedded barriers: oligomeric or low molecular weight polymeric highly fluorinated compounds. Fluoroalcohol methacrylate polymers with high water contact angles (in the order of >90°).
- PFAS provide: Barriers that are soluble in casting solvents, insoluble in water but soluble in developer, and that sow no intermixing with photoresists. Hydrophobicity and control of contact angle, inert under 193nm radiation, and transparency.

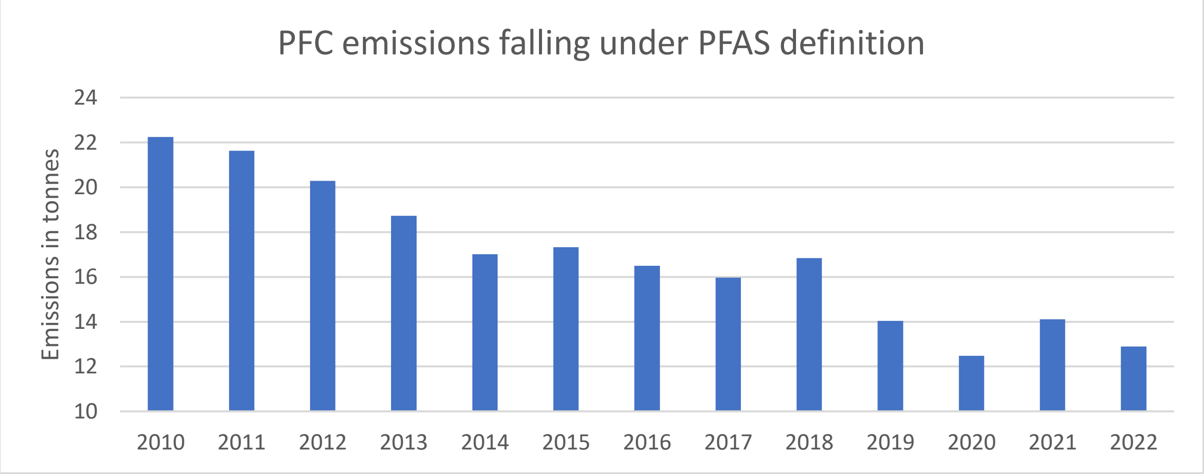
Dielectric Polymers [Polyimides (PI) / polybenzoxazoles (PBO)]

- Function: Provide electrical, thermal, moisture, chemical, and mechanical protection for the semiconductor device.
- Types of compounds used: Water-insoluble PFAS polymers.
- PFAS provide: PFAS groups attached to the polymer backbone provide solubility in environmentally friendly casting solvents and enable aqueous development.

Overall, it is estimated that the total PFAS used for photolithography described above in Europe amounts to 2248 kg per year (see RINA paper attached). The estimated emissions amount to 1161 kg.

Perfluorocarbon compounds (PFC) emissions

Use of gaseous PFCs (plasma etch and CVD chamber cleaning, deep reactive ion-etching). In terms of the emissions of gaseous PFCs, the amount of emissions into the air that fall under the proposed REACH PFAS restriction definition was quantified at 12.892 kg in 2022.



Wastewater

Regarding PFAS emissions into wastewater, there are no industry wide measurements yet. However, a 2021 peer-reviewed study published in "Environmental Science & Technology" collected and analysed wastewater samples from three fabs in the United States (Paige Jacob, Krista A. Barzen-Hanson, and Damian E. Helbling Environmental Science & Technology 2021 55 (4), 2346-2356 DOI: 10.1021/acs.est.0c06690). The authors found that the sum totals of the PFAS concentrations in the downstream samples from the three fabs are 0.623 ± 0.024, 0.394 ± 0.018, and 0.376 ± 0.024 µg/L, respectively. These are the concentrations in the wastewater measure prior to dilution in a receiving water system or with municipal wastewater and are relatively low compared to other known sources of PFAS emissions to the environment. These wastewater limits, which would never be consumer by humans, are close to the same levels as a drinking water specification. Please note that the EU PFAS drinking water directive parameter values stand at: PFAS Total = 0.50 µg/L (totality) and Sum of PFAS = 0.10 µg/L (potable water).

Question 7

***Potential derogations marked for reconsideration – Analysis of alternatives and socio-economic analysis**: Paragraphs 5 and 6 of the proposed restriction entry text (see table starting on page 4 of the summary of the Annex XV restriction report) include several potential derogations for reconsideration after the consultation (in [square brackets]). These are uses of PFAS where the evidence underlying the assessment of the substitution potential was weak. The substitution potential is determined on the basis of i) whether technically and economically feasible alternatives have already been identified or alternative-based products are available on the market at the assumed entry into force of the proposed restriction, ii) whether known alternatives can be implemented before the transition period ends (taking into account time requirements for substitution and certification or regulatory approval), and iii) whether known alternatives are available in sufficient quantities on the market at the assumed entry into force to allow affected companies to substitute.*

A summary of the available evidence as well as the key aspects based on which a derogation is potentially warranted are presented in Table 8 in the Annex XV restriction report, with further details being provided in the respective sections in Annex E.

To strengthen the justifications for a derogation for these uses, additional specific information is requested on alternatives and socio-economic impacts covering the elements described in points a) to g) in question 6 above.

ESIA Answer

General Information on Substitution Timelines in the Semiconductor Industry

Semiconductor technology development cycles often take a long time. Because of the complexity of the products and associated production processes, a major innovation can take years to bring to market. Manufacturers of electronic devices, working in conjunction with their materials and equipment suppliers, must typically proceed through multiple stages of research, technology integration, prototyping, and manufacturing ramp-up to achieve a process change effectively. One technology development cycle typically takes around 10 years from fundamental research to production ramp-up.

Many materials are unique and have specific technical requirements making it extremely challenging to find a viable alternative. For many of the uses of fluorocarbon-containing materials by the semiconductor manufacturing industry, no known alternatives exist. Moreover, alternative substances need to be invented before they can be qualified. The indicative timelines to develop, qualify, and implement alternatives fall into the following broad categories.

If a non-PFAS alternative exists and is available, and no alterations to the infrastructure are necessary and it is demonstrated that the alternative provides adequate performance for a specific application, it typically takes **3 – 4 years** to perform the required manufacturing trials, recertification and successfully implement the alternative into high-volume manufacturing.

Where a non-PFAS alternative is available, but it is necessary to make alterations to manufacturing tools, products, processes, or facilities before the alternative can be introduced successfully, it may take **3 – 10 years or more** to successfully implement the alternative.

For certain applications, it is currently not possible to show that a PFAS-free alternative has the same specific properties. In such cases, it is necessary to invent and synthesize new chemicals, and/or develop alternative approaches to semiconductor device manufacturing providing the required electrical and computational performance. Given that inventing new chemicals is an open-ended process without a specified timeline or guarantee of success, it may take **5 to more than 25 years** to find suitable alternatives which then can be implemented.

It is possible that in some cases it is found that a PFAS-free alternative is not able to provide the necessary chemical function. Where it is not possible to invent a PFAS-free alternative, it may be necessary to abandon the integrated circuit device structure and replace it with an alternative device structure that has the same performance. In some cases, the use of non-PFAS alternatives is prevented by the fundamental laws of chemistry and physics.

Photolithography

The semiconductor industry has been researching PFAS-free alternatives for 25 years. There may be some instances where substitution is possible, in most photolithography applications, PFAS-free materials have been found to be unsuccessful or ineffective. For many applications it would be necessary to reinvent potential PFAS-free alternatives. Identifying and implementing is a lengthy process that involves academic research, material supplier research, development (validation), scale-up, and subsequent efforts by the semiconductor manufacturer to demonstration (verification), integration, implementation, and scale-up to high-volume manufacturing. Even though all PFAS uses have their specific challenges and timelines for development, it will take **15 to more than 20 years** to develop PFAS-free alternatives for most of the photolithography uses, while for photoacid generators (PAGs), it is expected that this process takes **more than 25 years**.

Wet Chemistries

PFAS-free alternatives for wet chemistries vary a lot from application to application and are influenced by the technology and application in which they are used. Often, an alternative that is suitable for one application is not suitable for another. Therefore, the timeline for implementing alternatives for wet chemistries ranges broadly from **3 to 15 years after a suitable alternative has been identified**.

Fluorocarbons Uses in Plasma Etch / Wafer Clean and Deposition

In the plasma, etch/wafer clean application, **no viable alternatives for fluorocarbon chemistries are known**, because of the basic chemistry and physics of etching silicon and its compounds, which are essential for fabricating semiconductors. For certain applications, PFAS-free alternatives have been identified, such as the use of nitrogen trifluoride in chamber cleans. However, these alternatives may produce emission by-products which contain PFAS, where carbon-containing films are present. However, these alternatives may not be suitable for all applications. In addition, some alternatives may give rise to further occupational health and safety concerns. Considering concerns regarding their global warming potential, the semiconductor industry has decreased the use of chamber clean gases that contain PFAS over the last 30 years. Even though fluorine-free alternatives meet the manufacturing needs, the industry has implemented best practices initiatives, reducing its air emissions of PFCs and hydrofluorocarbon compounds (HFCs) significantly.

To switch to fluorine-free alternatives, it would be **necessary to fundamentally reinvent semiconductor devices**, as it would require replacing silicon as the basis for semiconductor manufacturing.

Fluorinated Heat Transfer Fluids

To implement fluorine-free heat transfer fluids, it would be necessary to completely redesign semiconductor manufacturing-related equipment in the small number of applications in which these can be used. For the remaining applications, suitable alternatives offering the required technical performance have not been invented yet. For the small number of applications for which alternatives are available, implementation would take **8 to 14 years**. Substituting refrigerants in process equipment chillers would take a similar amount of time. For applications where no alternatives are currently known, these would have to be invented. Subsequently, it would take **another 5 to 15 years or more** to implement these alternatives. However, this timeline could be significantly longer depending on the number of cooling systems affected per manufacturing facility. Regarding PFAS-free thermal test methods, it would take 8 to 14 or more years, after an alternative has been invested, to implement it.

Semiconductor Assembly, Test, and Packaging

Depending on the use, implementing PFAS-free alternatives may take 5 – 20 years or more. For simpler uses like packaging fluxes, qualification and implementation of an alternative will likely take more than 5 years. For most package-related uses of adhesives, the semiconductor industry has been searching for alternatives for 18 years without success and it is expected to take **more than 20 years** to identify and implement.

Due to their interaction with both the silicon die and the end customer product, as well as to the environment, changes to assembly package materials make it necessary to notify the product change to the customer and requalify and approve the product, while keeping the required specifications for thermal chemical resistance. This requires additional time to the timelines mentioned above. It is required to start customer qualification activities **at least 1-2 years** before the change is implemented; some applications even require **more than 6 years**. In certain instances, the absence of viable alternatives is evident, leading to compromised safety and functionality of the end customer product.

Pump Fluids and Lubricants

Even though PFAS-free lubricants exist, they do not meet essential performance requirements, i.e., inertness under harsh conditions, low off-gassing, and low particle generation. These properties are critical due to the cleanliness requirements during manufacturing. Moreover, these PFAS-free alternatives have increased failure rates and human health and safety impacts. The substitution of PFAS lubricants in general applications is expected to take **more than 10 years** and it will take **more than 25 years** to replace lubricants used in photolithography because of the need for ultraviolet stability.

Articles

Potential non-PFAS alternatives would require total reinvention for many applications. It is expected to take **more than 15 years** to implement a suitable alternative if physically and chemically possible, depending on the material and its application. Given the complexity of the semiconductor supply chain, implementing PFAS-free alternatives requires efforts throughout the entire supply chain, which may overburden smaller partners in the supply chain.

Question 10

Analytical methods: Annex E of the Annex XV restriction report contains an assessment of the availability of analytical methods for PFAS. Analytical methods are rapidly evolving. Please provide any new or additional information on new developments in analytics not yet considered in the Annex XV restriction report.

ESIA Answer

Analytical tools and methods that are currently commercially available to detect PFAS in wastewater are believed to allow visibility to only a small fraction of PFAS constituents that are found in semiconductor manufacturing wastewaters. This is due to the limitations of current analytical method libraries, and the large number of PFAS species in use.

The industry has reviewed what it considers to be a short list of analytical techniques that can detect some PFAS species within semiconductor wastewater. However, it was not possible to identify an analytical method that would detect all PFAS in a comprehensive manner. Consequently, it is essential that further research is conducted to advance such analytical techniques noted below so that a more complete series of methods will be available to the semiconductor industry.

1. US EPA 537.1 (modified)
   The detectable PFAS was C4-C13 species. In semiconductor wastewater, the limit of detection was found to be ~1ppt. The primary gap highlighted with this method related to almost all the species included in the analytical library are not used in semiconductor manufacturing, with perfluorobutanesulfonic acid (PFBS) commonly being the only exception. The applicability of this method is limited mainly to the detection of PFAS by-products.

2. US EPA Draft 1633 (EPA method in development)
   The detectable PFAS was C4-C13 species. The limit of detection was ~ 1 ppt. This method is not yet commercially available.

3. US EPA Draft 1621 AOF (EPA method in development)
   The detectable PFAS for this method was the total organic fluoride content. The limit of detection was unknown but was assumed to be in the ~100-900 ppb range. The gap identified with this method for semiconductor wastewater was the fact that most short and ultrashort PFAS species will not be detected, as they must first adsorb to the GAC column, and most C1-C5 species adsorb in an inadequate manner, if at all.

4. Liquid Chromatography-High-Resolution Mass Spectrometry (LC-HRMS)
   A project supported by a grant from the Semiconductor Research Corporation (SRC) partnered with Cornell University to use the LC-HRMS method to complete an investigation of Fab wastewaters (Paige Jacob, Krista A. Barzen-Hanson, and Damian E. Helbling Environmental Science & Technology 2021 55 (4), 2346-2356 DOI: 10.1021/acs.est.0c06690). For this method there were ~30 PFAS with standards and ~1000 PFAS from a spectral software library without standards. The limit of detection was ~1-10 ppt for those PFAS species that have standards. In terms of gaps, the ~1000 PFAS derived from the spectral software library only allows for the positive identification of the structural category and or PFAS species, but not the numerical concentration. In addition, the availability of this analytical service is very limited, and analyses require many hours processing and review prior to making results available.

5. ^{19}F Nuclear Magnetic Resonance (NMR)
   The detectable PFAS represents a true total PFAS. The limit of detection appears to be ~1 ppt. With respect to the gaps with this method, the availability is very limited, and it is unknown whether access can be readily obtained. Also, sample throughput will likely be low, as each sample requires a six-hour run.

6. BS EN 14852
   The detectable PFAS for this method was total fluorine. The detection limit was 50 ppm. With respect to identified gaps, although the standard is commonly used in the semiconductor industry’s supply chain, the results are not reliable for solid materials or chemicals in the liquid form.

7. ISO 21675:2019
   Water quality: Determination of perfluoroalkyl and polyfluoroalkyl substances (PFAS) in water — Method using solid phase extraction and liquid chromatography-tandem mass spectrometry (LC-MS/MS) Detection limit is 10 ng/L (for drinking water), 20 ng/L (for wastewater).

For further information:

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ABOUT ESIA

The European Semiconductor Industry Association (ESIA) is the voice of the semiconductor industry in Europe. Its mission is to represent and promote the common interests of the Europe-based semiconductor industry towards the European institutions and stakeholders in order to ensure a sustainable business environment and foster its global competitiveness. As a provider of key enabling technologies, the industry creates innovative solutions for industrial development, contributing to economic growth and responding to major societal challenges. Being ranked as the most R&D-intensive sector by the European Commission, the European semiconductor ecosystem supports approx. 200.000 jobs directly and up to 1.000.000 induced jobs in systems, applications and services in Europe. Overall, micro- and nano-electronics enable the generation of at least 10% of GDP in Europe and the world.