SEMI Europe

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Question 7 SEMI Use Case Examples

Introduction

The unique properties simultaneously afforded by PFAS materials in terms of chemical resistance, temperature resistance, flexibility, low coefficient of friction, purity, non-flammability, etc., have led to thousands of applications in semiconductor manufacturing, where precision and purity of a wide range of highly complex equipment and a broad array of chemicals are required to deliver the exacting specifications demanded of advanced circuitry. The semiconductor industry has a long history of working toward more environmentally benign solutions including compliance with regulations on restricted materials. However, the ubiquitous nature of the applications space of PFAS in this industry, coupled with the lack of suitable alternative materials, makes substitution of PFAS an exceedingly difficult challenge, one whose magnitude cannot be overstated.

This response illustrates the numerous use cases of PFAS in semiconductors and the challenges posed when seeking alternatives by citing several examples where substitutions were evaluated but found to be insufficient. This is by no means intended by an exhaustive review of either all the applications of PFAS in semiconductor manufacturing, nor on the evaluations of alternatives. Rather it is meant to illustrate the expansive dependency that this multi-hundred-billion-dollar industry has on this unique class of materials and how, despite wide-ranging efforts, alternatives do not meet the criteria required for safe and capable replacement. The examples below are arranged based upon the application space in which the PFAS material is used. For a more exhaustive description of the use of PFAS in the semiconductor industry, please see "The Impact of a Potential PFAS Restriction on the Semiconductor Sector", an SIA PFAS Consortium-commissioned summary prepared by RINA, available on the SIA website[1] or attached to this Annex XV consultation submittal.

Ultrapure Water Systems

Ultrapure water (UPW) is one the many materials essential to semiconductor manufacturing and UPW systems are fundamental components of any chip fabricator, or Fab, infrastructure. Metal or organic contaminants must be avoided to prevent defectivity that can compromise performance, yield, and reliability. Pipes, valves, fittings and seals composing UPW systems are required to bridge performance in terms of purity[2], mechanical properties[3], flame retardancy[4], chemical resistance, safety and reliability. This requires the use of fluoropolymers, like poly(vinylidene fluoride) (PVDF), poly(terafluoroethylene) (PTFE), perfluoroalkoxy copolymer (PFA), and fluoroelastomers such as Fluorine Kautschuk Material (FKM) and FFKM. Poly(propylene) (PP) and poly(vinyl chloride) (PVC), among other organic polymers, have been evaluated as replacements, but do not meet the purity, chemical resistance, and lifetime

[1] "The Impact of a Potential PFAS Restriction on the Semiconductor Sector"; https://www.semiconductors.org/the-impact-of-a-potential-pfas-restriction-on-the-semiconductor-sector/

[2] SEMI F57- Specification for Polymer Materials and Components Used in Ultrapure Water and Liquid Chemical Distribution Systems

[3] ISO 10931- International Standard for PVDF Piping Systems

[4] ANSI/FM 4910-2013 (2021), American National Standard for Cleanroom Materials Flammability Test Protocol, https://www.fmapprovals.com/products-we-certify/products-we-certify/cleanroom-materials

required.[5,6] Feasible substitutes have yet to be identified and there is no publicly available information on the status of research and development (R&D) processes and the required time for substitution.

Chemical cleaning and Delivery Systems

Many chemicals including acids (hydrogen fluoride, hydrogen chloride, nitric acid, sulfuric acid), base (Aqueous ammonium, ammonium hydroxide) and oxidizing agents (Hydrogen peroxide, APM, HPM, SPM) are among many chemicals used in semiconductor manufacturing. As such, the equipment capable of processing and delivering liquid chemicals are fundamental components of any chip fabricator, or Fab, infrastructure. In employing such equipment, metal or organic contaminants must be avoided to prevent defectivities that can compromise performance, yield, and reliability. Pipes, valves, fittings and seals composing these systems are required to be constructed with materials which are corrosion resistant against these strong chemicals. poly(terafluoroethylene) (PTFE), perfluoroalkoxy copolymer (PFA), and fluoroelastomers such as FKM and FFKM can be used for those applications. Non-fluorinated materials are not available without the generation of the debris which is derived from the chemical corrosion. Feasible substitutes have yet to be identified and there is no publicly available information on the status of research and development (R&D) processes and the required time for substitution.

Heat Transfer Fluids

Fluorinated heat transfer fluids (HTF), along with fluorinated refrigerants, are used in semiconductor manufacturing to provide precise temperature control in numerous processing and testing steps. HTFs are commonly used in plasma processing such as dry etch and thin-film deposition, where to be compatible with the materials of construction of the equipment chambers, the materials must be electrically non-conductive, as well as being appropriately non-toxic, non-flammable and not subject to inducing contamination issues[1] across a wide range of operating temperatures that require precise control.[7] Currently, non-PFAS alternatives, such as synthetic hydrocarbon oils, silicone oils, or ethylene glycol/de-ionized water mixtures cannot simultaneously meet these performance attributes.[8,9,10,11,12] Similarly, non-PFAS alternative

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[5] Burkhart M, Wagner G and Klaiber F, "Leaching Characteristics of Polyvinylidene Fluoride and Polypropylene," Ultrapure Water, May/June 1997: pp 30-33

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

[7] 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

[8] DOWTHERM™ J Heat Transfer Fluid. https://www.dow.com/en-us/pdp.dowtherm-j-heat-transfer-fluid.25619z.html#overview .

[9] "SYLTHERM™ XLT Heat Transfer Fluid Technical Data Sheet." DOW https://www.dow.com/en-us/document-viewer.html?docPath=/content/dam/dcc/documents/en-us/productdatasheet/176/176-01468-01-syltherm-xlt-heat-transfer-fluid.pdf

[10] "Technical Data Sheet DOWSIL™ ICL-1000 Fluid ." DOW. https://www.dow.com/documents/en-us/productdatasheet/11/11-42/11-4298-01-dowsil-icl

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

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

refrigerants, such as carbon dioxide or ammonia, cannot support the low-temperature operating points, have low energy efficiency, and are toxic or flammable.[13] For more detailed discussion of the use PFAS as HTFs for use in the semiconductor industry, see the SIA PFAS Consortium White Paper on the SIA website.[14]

Lubricants

PFAS 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 PFAS lubricants 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. Currently no alternatives are known to exist, as alternatives such as silicon-based lubricants do not offer the necessary technical performance. 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.[15] 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 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 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 are limited in the applications they can be used in. Silicone-based oils and lubricants are also very contaminating[16] and could lead to productivity loss.[17] For more detailed discussion of the use PFAS as Lubricants for use in the semiconductor industry, see the SIA PFAS Consortium White Paper on the SIA website.[14]

Photolithography Applications

There are multiple applications of photolithography that require the use of PFAS materials due to the unique attributes these materials provide that cannot be replicated with other chemistries by nature of the unparalleled strength of the carbon-fluorine bond and the strong electronegativity of fluorine. For example, photoacid generators (PAGs) are essential components of chemically amplified resists, which are materials used to define the fine circuitry of all advanced semiconductor chips. Six non-PFAS photoacids are listed in Appendix E of Annex XV, which upon detailed investigation prove not to be suitable for high resolution imaging as the

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

[14] https://www.semiconductors.org/pfas/

[15] Example of Factory Mutual approved vacuum lube - https://www.approvalguide.com/productDetail?productid=110777

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

[17] The Impact of a Potential PFAS Restriction on the Semiconductor Sector" - Section 9.1 https://www.semiconductors.org/the-impact-of-a-potential-pfas-restriction-on-the-semiconductor-sector/

results are significantly inferior to the performance shown by PFAS containing PAGs, showing faster photospeed, poorer feature quality, and excessive top-loss,[18] or acute toxicity.[19] For in depth description of the use PFAS as in PAGs for use in photolithography, see the SIA PFAS Consortium PAG White Paper and PFOS/PFOA Case Study on the SIA website.[14]

Another lithographic application requiring PFAS involves their use in top-antireflective coatings (TARCs). TARCs represent the largest product group by volume, accounting for more than 50% of PFAS use in lithography. TARCs are used to suppress reflectivity, which can compromise image integrity. PFAS materials are used as the provide the appropriate optical properties, specifically very low refractive index at the imaging wavelength. A non-PFAS alternative considered was the use of silica nanoparticles[20], but this failed for practical reasons at high volume manufacturing sites.

Other lithographic applications using PFAS include their use as surfactants in photoresists and bottom-antireflective coatings (BARCs); high contact angle barrier layers in immersion lithography, both as immersion topcoats or in topcoat-free photoresists[21]; and as photo-imageable poly(benzoxazoles) and poly(imides), used in packaging. For an exhaustive review of these applications, included attempts at identifying alternatives, see the SIA White Paper on Surfactants[14], as well as the aforementioned RINA white paper[1] attached to this Annex XV submittal.

Seals and Gaskets

Fluoroelastomers, such as FKM and FFKM, are well known industry standard choices for vacuum seals in semiconductor processing equipment, due to their broad resistance to plasma, aggressive chemistries, and high temperature requirement that are inherent in efficient semiconductor manufacturing processes. Lifetime of seals made from proposed substitute materials such as EPDM or silicone for 'in-chamber' sealing applications will be dramatically reduced due to the increased etch rates, particle formation, permeation, outgassing and general incompatibility with common semiconductor processing conditions. In the best case, implementing the proposed alternatives will result in equipment that is in a constant, unsustainable state of repair, with negative impacts on manufacturing yields, both driving significant cost increases and reducing competitiveness. At worst, proposed alternatives are completely incompatible with application conditions, and pose serious safety concerns for Fab operation. Performance of fluorinated elastomers compared to such alternatives is well

[18] Y. Suzuki and D.W. Johnson, Proc. SPIE 3333, 735 (1998); DOI: 10.1117/12.312350
[19] US Patent 3,853,943 (1974), Example C
[20] US Patent 2007/0072112 A1
[21] D.P. Sanders, Chem. Rev., 2010, 110, 321-360.

documented in literature for over 40 years.[22,23,24] We know of no non-fluorinated elastomeric sealing materials in production, early development, or even research that could come close to matching the overall performance of fluorinated elastomers as seals in wafer processing equipment.

Gases for Plasma Deposition and Etch

Perfluorocarbons (PFCs) and Hydrofluorocarbons (HFCs) are used in thin film deposition, plasma etch/wafer clean, and chamber cleaning steps in the semiconductor manufacturing process. Silicon and its compounds are the basis of the manufacturing of semiconductors. PFCs and HFCs are unique in their ability to react with silica compounds in predictable, controllable, and selectable ways. It must be noted when discussing alternatives, that the uses described above are broad terms to describe a process, but in actuality, each use in the semiconductor manufacturing process is unique (e.g., 100+ different instances alone of plasma etching for one device) and can require different material(s) or compositions to meet the performance requirements.[1] Currently non-PFAS alternatives simply do not exist. The proposed alternatives, nitrogen trifluoride (NF_3) or sulfur hexafluoride (SF_6) often used in conjunction with various hydrocarbons (C_xH_y) or fluorine (F_2) gas, create significant environmental or safety concerns. First, using the alternatives in these processes creates PFAS byproducts which is antithetical to the intent of this regulation. Additionally, mixing an oxidizer (NF_3) with a flammable (hydrocarbons) creates an additional fire safety risk. Moreover, NF_3 and F_2 are toxic and present worker safety concerns.[25,26] Finally, NF_3 and SF_6 possess high global warming potentials (GWP) and are subject to regulation under the EU F-Gas regulation (517/2014).[27]

Articles

Articles is a broad term used to describe various components or 'parts' of more complex systems or equipment used in semiconductor manufacturing. This far-reaching definition includes simple components such as tubing, containers, gaskets, valves and filters, to more complex, integrated parts such as capacitors, robots, sensors, or power supplies. These are just a few of the hundreds of articles that are used in semiconductor manufacturing equipment, in the infrastructure of the Fab itself, or in the supply chain of the various materials used in Fabs. PFAS materials play an indispensable role in many articles, as they provide the unique combination of properties required to deliver the precise control essential to chip manufacturing. Particularly critical to many articles is that these attributes are retained for the duration of a Fab's existence or, in the

[22] Wang, S., & Legare, J. M. (2003). Perfluoroelastomer and fluoroelastomer seals for semiconductor wafer processing equipment. *Journal of Fluorine Chemistry*, *122*(1), 113–119. https://doi.org/10.1016/S0022-1139(03)00102-7
[23] R. N. Peacock; Practical selection of elastomer materials for vacuum seals. *Journal of Vacuum Science and Technology* 1 January 1980; 17 (1): 330–336. https://doi.org/10.1116/1.570380
[24] Kenneth M. Pruett. (2005). *Chemical Resistance Guide for Elastomers III: A Guide to Chemical Resistance of Rubber and Elastomeric Compounds* (III). Compass Publications.

[25] https://echa.europa.eu/brief-profile/-/briefprofile/100.029.097
[26] https://echa.europa.eu/brief-profile/-/briefprofile/100.029.049

[27] https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32014R0517

case of consumable parts, that they last as long as possible to avoid frequent replacement, which is costly, time-consuming, and waste-generating. A detailed overview of the wide-ranging use of PFAS in articles used in semiconductor manufacturing can be found in SIA PFAS Consortium Articles White Paper on the SIA website.[14]

A prime example illustrating the necessity of PFAS use for articles is in the handling of specialty chemicals. Hundreds of chemicals are used in today's semiconductor manufacturing processes.[28,29] Impurities such as particles, metal ions, and organic contaminants can lead to yield and reliability problems.[30] Contamination control is critical in proactive and predictive yield management, especially in high volume manufacturing (HVM) in the semiconductor industry to drive down cost.[31] The strict requirements for clean chemicals, as well as compatibility issues, necessitated the selection and use of the robust and clean filters available. Specifically, electronic grade, concentrated 96% sulfuric acid is a high purity chemical used for cleaning and etching applications in semiconductor manufacturing. The acid is typically heated from 90 to 150 °C and filtered continuously. Because of the high temperature, strongly acidic and oxidizing environment, only fluorocarbon PTFE membrane can withstand the aggressive acid, and as such, PTFE has been the workhorse in the industry for this application.[32,33,34,35] Currently, there is no known commercially available membrane filter that can replace PTFE membrane for this type of application.

[28] Kim S, Yoon C, Ham S, Park J, Kwon O, Park D, Choi S, Kim S, Ha K, Kim W. Chemical use in the semiconductor manufacturing industry. Int J Occup Environ Health. 2018 Jul-Oct;24(3-4):109-118. doi: 10.1080/10773525.2018.1519957. Epub 2018 Oct 3. PMID: 30281405; PMCID: PMC6237170.

[29] Misra, A., Hogan, J., and Chorush, R. (2002) Handbook of chemicals and gases for the semiconductor industry. Ch2. Wafer Cleaning Chemicals. Published by Wiley. ISBN: 978-0-471-26385-2

[30] IRDS (2021) International roadmap for devices and systems, 2021 update, yield enhancements. IEEE. https://irds.ieee.org/images/files/pdf/2021/2021IRDS_YE.pdf

[31] Libman, S., van Schooneveld, G., Wilcox, D., Marion, B. (2021) Enabling Advanced Semiconductor Yield via Proactive Technology Management - an overview of the IRDS research work and future roadmap, as well as SEMI standard and future focus areas. Presented at Ultrapure Micro 2021 conference

[32] Takakura, T. and Tsuzuki, S., "Particle removal efficiency evaluation of filters in 150 °C sulfuric acid", presented at the 75th JSAP Autumn Meeting, pp. 17P–A14-6, 2014

[33] Takakura, T. , Tokuno, K., Tsuzuki, S., Yamazaki, K., Tomotoshi, A. and Teshima K., "Particle reduction in high temperature sulfuric acid using PTFE membrane filter and low pulsation bellows pump," 2018 29th Annual SEMI Advanced Semiconductor Manufacturing Conference (ASMC), Saratoga Springs, NY, USA, 2018, pp. 117-120, doi: 10.1109/ASMC.2018.8373148.

[34] Masashi Nose, Takehito Mizuno, Shuichi Tsuzuki and Toru Numaguchi, "Particle removal performance of 20nm rated filters for advanced wet chemical cleaning," 2007 International Symposium on Semiconductor Manufacturing, Santa Clara, CA, USA, 2007, pp. 1-3, doi: 10.1109/ISSM.2007.4446893.

[35] Takakura, T. and Tsuzuki, S. "Particle removal efficiency evaluation of filters in IPA," 2016 International Symposium on Semiconductor Manufacturing (ISSM), Tokyo, Japan, 2016, pp. 1-4, doi: 10.1109/ISSM.2016.7934541.

Summary

The examples provided here are only a tiny fraction of the myriad use of PFAS in semiconductor manufacturing. Not mentioned explicitly, but also critical to this industry are applications as surfactants and in liquid chemistries for cleaning, wet-etching, or metal plating; uses in packaging technology as adhesives, release layers and encapsulants; as well as uses in chemical transport and delivery, mask making, etc. More extensive discussion on these applications and more can be found in the series of White Papers produced by the SIA PFAS Consortium.[14] Each application has their own unique requirements, for which PFAS materials have been chosen because of the unique attributes of these materials. While replacements have been evaluated, more often than not, materials cannot be found that have the combination of attributes to be suitable substitutions. The references provide evidence to this effect and are complemented by significant amounts of confidential or unpublished information from representative companies that is sensitive to their individual business objectives.