PFAS-Containing Heat Transfer Fluids Used in Semiconductor Manufacturing

Semiconductor PFAS Consortium Heat Transfer and Thermal Test Fluid Working Group

July 26, 2023

Acknowledgments: The Semiconductor PFAS Consortium would like to acknowledge the contributions of the Semiconductor PFAS Consortium Heat Transfer and Thermal Test Fluid technical working group for their efforts to compile this information.

This publication was developed by the Semiconductor PFAS Consortium Heat Transfer and Thermal Test Fluid technical working group. The contents do not necessarily reflect the uses, views or stated policies of individual consortium members.

Also published in the Semiconductor PFAS Consortium white paper series:

White Paper	Background on Semiconductor Manufacturing and PFAS
Case Study	PFOS and PFOA Conversion to Short-Chain PFAS Used in Semiconductor Manufacturing
Case Study	PFAS-Containing Photo-Acid Generators Used in Semiconductor Manufacturing
Case Study	PFAS-Containing Surfactants Used in Semiconductor Manufacturing
White Paper	PFAS-Containing Fluorochemicals Used in Semiconductor Manufacturing Plasma-Enabled Etch and Deposition
White Paper	PFAS-Containing Materials Used in Semiconductor Assembly, Test and Substrate Processes
White Paper	PFAS-Containing Wet Chemistries Used in Semiconductor Manufacturing
White Paper	PFAS-Containing Lubricants Used in Semiconductor Manufacturing
White Paper	PFAS-Containing Articles Used in Semiconductor Manufacturing

About the Semiconductor PFAS Consortium

The Semiconductor PFAS Consortium is an international group of semiconductor industry stakeholders formed to collect the technical data needed to formulate an industry approach to perfluoroalkyl and polyfluoroalkyl substances (PFAS). Consortium membership comprises semiconductor manufacturers and members of the supply chain, including chemical, material and equipment suppliers. The consortium includes technical working groups, each focused on the:

- Identification of PFAS uses, why they are used, and the viability of alternatives.
- Application of the pollution prevention hierarchy to (where possible) reduce PFAS consumption or eliminate use, identify alternatives, and minimize and control emissions.
- Development of socioeconomic impact analysis data.
- Identification of research needs.

This data will better inform public policy and legislation regarding the semiconductor industry's use of PFAS-containing materials and will focus research and development efforts. The Semiconductor PFAS Consortium is organized under the auspices of the Semiconductor Industry Association (SIA). For more information, see www.semiconductors.org.

AGC Chemicals America	Georg Fischer	Samsung Austin Semiconductor
Analog Devices Inc.	GlobalFoundries	SCREEN Semiconductor Solutions Co., Ltd.
Applied Materials Inc.	Henkel	Senju Metal Industry Co. Ltd.
Arkema	Hitachi High-Tech America	Shin-Etsu MicroSi
ASML	IBM	Skywater
BASF	Intel Corp.	Solvay
Brewer Science	JSR	STMicroelectronics
Central Glass Co. Ltd.	KLA	Sumitomo Chemical Co. Ltd.
Chemours	Lam Research	Texas Instruments Inc.
DuPont	Linde	Tokyo Electron Ltd.
Edwards	Micron Technology	Tokyo Ohka Kogyo Co. Ltd.
EMD Electronics	Moses Lake Industries	TSMC
Entegris	NXP Semiconductors	Zeiss
Fujifilm Electronic Materials	Robert Bosch GmbH	

Table of Contents

Executive Summary

This white paper identifies the applications of PFAS-containing fluorinated heat transfer fluids used in the semiconductor manufacturing process, specifies the application-specific use requirements, and discusses the viability of non-PFAS alternatives in those applications and potential areas of research and development (R&D).

In process chiller equipment, liquid fluorinated heat transfer fluids and fluorinated refrigerants are used in complementary closed F-HTF loops and refrigerant cycles to meet operational temperature requirements in semiconductor manufacturing processes such as dry-etch, thin-film deposition and device test applications. This white paper focuses on the dry-etch process because it is the application with the most complex and stringent technical requirements for heat transfer fluid performance in semiconductor manufacturing.

While dry etch is the focus, all heat transfer fluid applications have specific manufacturing requirements. Many semiconductor manufacturing process steps require strict temperature controls to ensure the production of consistent, nanometer-sized device structures. Semiconductor manufacturing operations require very precise levels of control, as even the smallest amount of contamination, imprecision or impact on reliability can result in product defects and a loss of performance.

F-HTFs and fluorinated refrigerants have a unique ability to meet multiple performance requirements at once – possessing high boiling points / low pour points, low kinematic viscosity at working temperatures, and electrical nonconductivity as measured by low dielectric constants and high-volume resistance.

Currently, there are no viable non-PFAS alternatives for some specific semiconductor applications, given their inability to simultaneously provide the required boiling points and pour points. Non-PFAS alternatives increase the potential for catastrophic process contamination issues, may be less stable during use, and may require additional health and safety considerations from toxicity and/or flammability.

Based on Semiconductor PFAS Consortium member surveys, current applications of fluorinated heat transfer fluids operate within closed-loop systems to prevent potential exposure during normal equipment operation. Some heat transfer fluids are released to the air from temperature control loops during maintenance tasks or leaks that may occur from fittings that require replacement. The semiconductor industry continues to test and implement equipment and operational control improvements to minimize and mitigate fugitive heat transfer fluid losses.

1.0 Introduction

Multiple chemistries and materials that fall within the definition of PFAS are imperative in highly precise and sensitive semiconductor manufacturing processes that build features of minute sizes, as exact replicates of each other, numbering in the billions, over the entire surface of a silicon wafer. For more information, see the Semiconductor PFAS Consortium white paper, "Background on Semiconductor Manufacturing and PFAS."

A heat transfer fluid is a liquid or gas that moves heat between high- and low-temperature sources and sinks to provide temperature control (see Appendix A for more terminology). The semiconductor manufacturing process employs heat transfer fluids in both cooling and heating applications to provide precise temperature control for specific manufacturing operations and to enable the testing of semiconductor chips within finished electronic products.

Selecting a heat transfer fluid that is incapable of achieving all of the performance requirements may result in imperfections that negatively impact semiconductor manufacturing process yields, or the ability to determine the appropriate functionality of semiconductor chips within expected conditions in finished electronic applications. Each manufacturing step in the semiconductor manufacturing process must be virtually perfect, with yields well above 99%, and there may be several hundreds of process steps in the manufacture of each advanced semiconductor device. Without very high yields at each step, the semiconductor manufacturing process would fail to produce functional and economically viable products.

1.1 Objectives

In this white paper, we discuss the use of heat transfer fluids, the applications of fluorinated fluids meeting the definition of a PFAS-containing material that are critical for semiconductor manufacturing operations, and the viability of potential non-PFAS alternatives. The high persistence, bioaccumulation potential and potential toxicity of some compounds designated as PFAS-containing materials drives this discussion. This white paper also discusses release potentials from the use of fluorinated heat transfer fluids and the environmental and safety controls in place that reduce those potentials.

Several efforts to develop regulatory restrictions are currently underway that intend to limit the use of PFAS-containing materials to only those deemed essential to the functioning of society. Borrowing from a concept embedded within the Montreal Protocol, essential uses are described as those that are necessary for "health or safety or other highly important purposes for which alternatives are not yet established" (Cousins, et al. 2019).

Although regulatory definitions of PFAS differ – as described the Semiconductor PFAS Consortium white paper, "Background on Semiconductor Manufacturing and PFAS" – the Semiconductor PFAS

Consortium has defined the scope of materials described in this white paper to include all chemistries and materials that contain molecules with -CF_2- and/or -CF_3 groups.

The uses of heat transfer fluids covered in this white paper are those used in process modules and process equipment chillers that most directly support semiconductor manufacturing and testing applications, for which the use of fluorinated heat transfer fluids is unique and highly specialized. These include (1) F-HTFs used in the HTF loop and (2) fluorinated refrigerants used in the refrigerant cycle in process equipment chillers, as shown in Figure 1. The HTF loop transfers heat between process module equipment and the process equipment chiller, while the refrigerant loops act as a heat sink within the process equipment chiller to transfer heat between the process module and the facility chiller systems. Facility chillers; condenser loops; cooling towers; and heating, ventilation and air-conditioning indirectly support manufacturing and testing applications but are outside the scope of this paper.

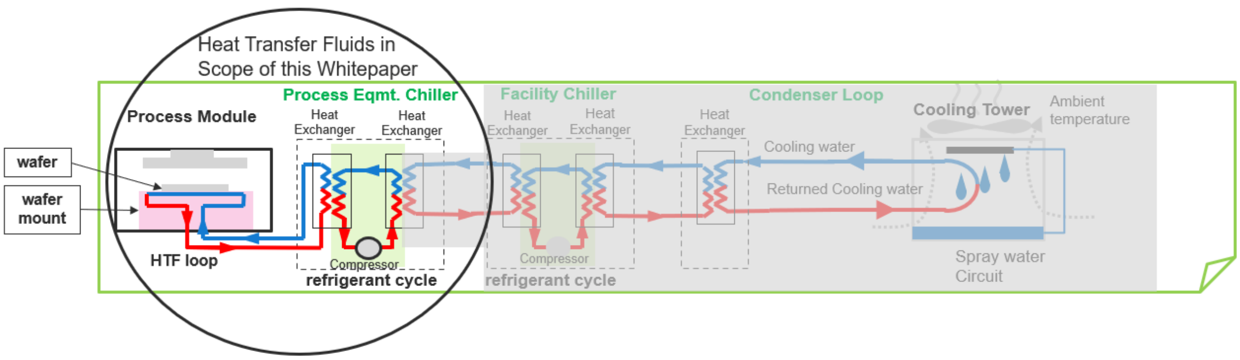


Figure 1: The focus of Heat Transfer Fluids described in this white paper.

Rather than comprehensively listing each individual application, this white paper covers the two most common applications across all semiconductor manufacturing - HTFs and equipment level refrigerants (as described in Figure 2). Process steps such as dry etch and device testing may have HTF and/or refrigerant applications. It is likely that we have not captured certain highly specialized applications here, including critical uses in analytical laboratory applications that are necessary to support manufacturing operations, or those within future manufacturing applications currently undergoing R&D.

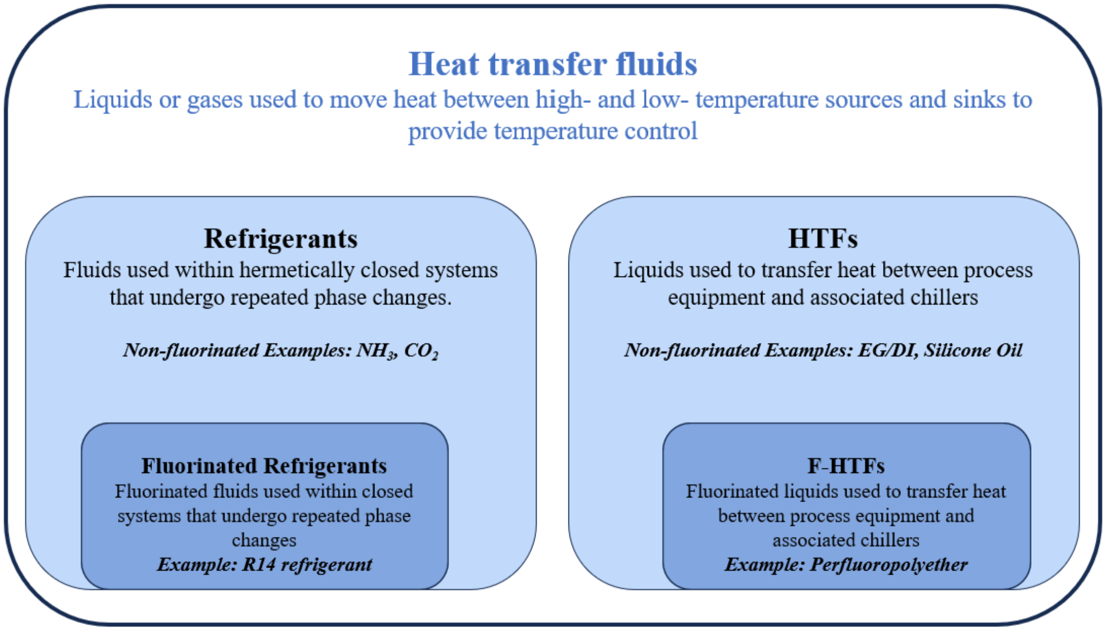


Figure 2: Heat transfer fluids and terminology as used in this white paper.

1.2 Fluorinated Heat Transfer Fluids Used in the Semiconductor Manufacturing Process

Based on their manner of absorption or extraction of heat from the substances to be cooled or heated, it is possible to classify heat transfer fluids into two categories:

- F-HTFs are used in closed-loop systems between specialized semiconductor manufacturing process modules and process equipment chiller systems. These chillers require either heating or cooling to achieve a specific temperature within very tight ranges beyond the reach of many water- and hydrocarbon-based fluids, while simultaneously ensuring appropriate heat capacity, viscosity, high dielectric strength, chemical inertness, stability and the material compatibility required to safely support semiconductor manufacturing processes. HTFs remain liquid in most cases and cool down or heat up through the use of simple heat exchangers that are part of the closed-loop system (Tuma and Tousignant 2002). F-HTF classes 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 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 (ASHRAE 2019). Fluorinated refrigerant classes include:

- PFCs.
- HFCs.
- HFOs.
- Fluorinated ketones.
- Other fluorinated liquids.

1.3 Critical Performance Requirements Met by F-HTFs in Semiconductor Manufacturing

Semiconductor manufacturing facilities require the installation and continuous operation of hundreds to thousands of process equipment and associated cooling systems. The temperature set points required for the successful completion of manufacturing steps can range from –60°C to +120°C. Most applications require only one stable temperature set point, but it must be held within a tight range, such as ±0.1°C for dry etch, with corresponding cooling capacities as high as several kilowatts (Nieman 2016). Some applications require a single HTF with more than one temperature setpoint, where each HTF must be controlled within a tight temperature range. Equipment installations must be reliable and easy to service, in order to minimize downtime.

The semiconductor manufacturing process also requires the completion of device testing applications at various stages in order to ensure device integrity and its effective operation within finished electronic end products. Semiconductor device testing can require the same –60°C to +125°C operational temperature range to appropriately stress the device and simulate conditions to which the final product may be exposed.

Supporting the complex requirements of semiconductor manufacturing requires heat transfer fluids to meet specific combinations of physical and chemical properties simultaneously. This need to meet all requirements at once often requires fluorinated heat transfer fluids, as similar capabilities have not been found in non-PFAS alternative fluids.

For example, as outlined in Table 1, certain dry-etch processes that require the heating and/or cooling of a wafer held in place by an electrostatic chuck near active plasma will need an HTF that possesses a high boiling point, a low pour 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 used in semiconductor testing must enable a wide operational temperature range requiring a high boiling point and a low pour point, as well as low kinematic viscosity at low temperatures and a low dielectric constant.

Table 1 lists the critical performance properties that must exist simultaneously. The Potential Non-PFAS HTF Alternatives section covers additional performance considerations and properties.

Table 1: Material properties of F-HTFs that support the semiconductor manufacturing performance properties required for representative dry-etch and test applications.[1]

Material Properties	Dry Etch[2]	Test Applications
Balancing Boiling Point[3] with Pour Point[4] (A range of operational temperatures that can be as high as 135°C or as low as –80°C)	135°C	135°C
	–80°C	–80°C
Kinematic Viscosity	Acceptable viscosity at the required lowest operating temperature, which can be approximately 0.7 centistokes (cSt) at 90°C Approximately 1.9 cSt at –20°C	Acceptable viscosity at the required lowest operating temperature, which can be less than 15 cSt at –60°C
Dielectric Constant at 1 kHz	≤ 1.92	< 6
Volume Resistance	>1 × 10^6 ohm-centimeter (Ω-cm)	not applicable

[1] Material properties including kinematic viscosity, dielectric constant and volume resistance must be met across all temperature ranges.
[2] Assumes the most demanding dry-etch applications.
[3] Generally, the boiling point of an HTF must be approximately 15°C higher than the highest operational set point.
[4] Generally, the pour point of a fluid must be approximately 20°C lower than the lowest operational set point.

The operation of process equipment at operational temperature set points requires complementary capabilities between the HTF in the HTF loop and the refrigerant in the refrigerant cycle. The most critical performance requirement of the refrigerant is the ability to maintain the lowest operational set point while avoiding a catastrophic phase shift to a solid form, as the refrigerant must remain in a gaseous or liquid form to remain pumpable and useful for temperature control. There are other physical and chemical properties to consider, as discussed in the Currently Existing Non-PFAS Alternative Refrigerants section and shown in Figure 5.

1.4 The Role of the C-F Bond and the Unique Properties of F-HTFs

Fluorination dramatically affects the physical properties of organic molecules. The fundamental properties of the fluorine atom are responsible for these effects, particularly its high electronegativity and ionization potential and low polarizability. Fluorine's extreme electronegativity results in a strongly polarized bond with carbon ($^{d+}$C-F^{d-}), which means a partially ionic character and thus increased strength of the C-F bond (14 kcal/mole higher than the C-H bond) (Clot, et al. 2011). Because of such polarization, the C-C bonds in a perfluorinated molecule also become stronger compared to those of the hydrogenated analogs.

The extreme chemical and thermal stability typical of perfluorinated fluids are caused by the high strength of the C-F and C-C bonds in the molecule and the shielding effect of the negatively charged fluorine atoms. Also, the nonflammability typical of perfluorinated fluids is a consequence of the extreme chemical stability, since flammability is the potential behavior of a substance to react with oxygen.

Although the C-F bond has a polar character, the fluorine atom itself – small and very electronegative – has very low polarizability, which means that it is less chemically reactive. The practical consequences are weak intermolecular interactions, low surface energy and pronounced dielectric behavior. Perfluorinated aliphatic compounds (PFCs, PFPEs) have the lowest dielectric constant and surface tension of any liquid at room temperature; they can wet any surface (Marchionni, Ajiroldi and Pezzin 1996).

The intermolecular interactions are so weak in perfluorinated fluids that they can be considered nearly "ideal" liquids, remaining liquid and pumpable across a range of temperatures required in semiconductor manufacturing – temperatures where nonfluorinated HTFs tend to become solid or gaseous. For example, the boiling points of PFCs are close to those of hydrogenated counterparts with the same number of carbon atoms, despite the much higher molecular mass of the former. Even the vaporization enthalpies (ΔH_v^{298}) of PFCs are slightly lower than that of hydrocarbons with the same number of atoms in the chain. In PFPEs, the vaporization enthalpy becomes even lower as the oxygen-to-carbon ratio increases (Marchionni, Ajiroldi and Pezzin 1996).

Weak intermolecular interactions affect other critical physical characteristics of these fluids, such as viscosity and pour point. Perfluorinated fluids are characterized by very low viscosity and low pour points, in combination with a relatively high boiling point (Smart 2001). The intermolecular interactions are so low that even fluids with relatively high molecular weights (and boiling points) do have low viscosity at low temperatures and a very low pour point. The higher the boiling point and the lower the pour point, the wider the operational range of the fluid. In this view, perfluorinated fluids do have very wide liquid operational ranges, a premium characteristic for many applications.

Another unique characteristic of perfluorinated fluids is their combination of hydrophobic and oleophobic properties; that is, the nonmiscibility both with water and organic (hydrogenated) molecules. This unique combination is again explained by the low polarizability and the shielding effect of negatively charged fluorine atoms. The oleophobicity of PFCs and PFPEs is an important characteristic for heat transfer applications, since these fluids do not easily solubilize contaminants, do not swell elastomers and plastics used in cooling-loop circuits, and do not solubilize the additives of such polymers (Krafft and Riess 2015). In other words, PFCs and PFPEs are compatible with almost all materials used to build equipment and circuits. Additionally, the hydrophobic character protects the fluid from water absorption, which helps stabilize performance, including resistivity and conductivity.

In summary, the success of fluorinated fluids in many applications within the semiconductor industry depends on the combination of multiple properties provided by fluorine. The positive attributes found in fluorinated heat transfer fluids will be difficult to find in non-PFAS alternative fluids. Liquid F-HTFs are integral to many semiconductor operations, and finding suitable nonfluorinated alternatives would require invention and equipment redesign.

1.5 History of F-HTF Use in the Semiconductor Industry

Figure 3 is a timeline of the use of F-HTFs in the semiconductor manufacturing process. Before the 1970s, process chillers used nonfluorinated HTFs such as deionized water or ethylene glycol/deionized water (EG/DI). F-HTFs were introduced into semiconductor device testing applications in the 1970s and 1980s. In the 1990s, there was an additional need to cool wafers against increasing heat loads during semiconductor processing. F-HTFs have the unique performance characteristics to be used in proximity to components such as electrostatic chucks (which hold wafers in place during processing), higher-power radio-frequency sources in manufacturing processes, and new design features in the semiconductor device itself.

Initially, the transition from liquid EG/DI to F-HTFs in the process equipment chillers that serve dry-etch and test applications led to inadvertent increases in F-HTF emissions from equipment leaks, because device manufacturers made these changes without adequately considering the need for any additional upgrades to minimize leaks from chiller pumps, seals and connectors. The lower surface tension of liquid F-HTFs compared to water resulted in these leaks, which equated to emissions to air. Process equipment chiller systems are now comprehensively designed to minimize fugitive losses (U.S. EPA 2006).

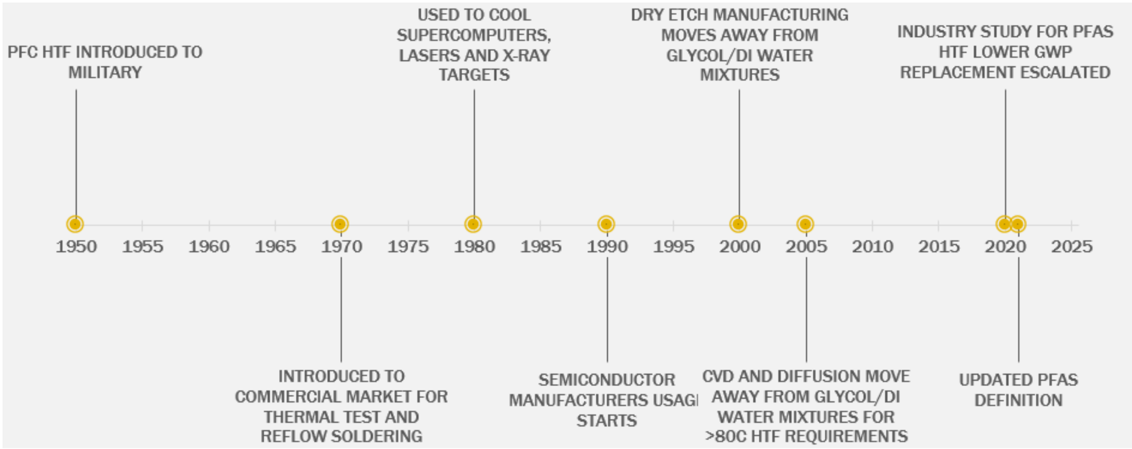


Figure 3: A timeline of the use of F-HTFs in semiconductor manufacturing to help meet critical temperature control requirements.

2.0 Applications for F-HTFs in Semiconductor Manufacturing

F-HTFs used in process equipment chillers are predominately associated with dry-etch semiconductor manufacturing equipment and semiconductor device testing applications. Process equipment chillers are integrated into larger heat transfer systems that involve heat transfers through facility chiller and cooling tower systems.

2.1 Process Equipment Chillers and TCUs Used in Semiconductor Wafer Fabrication

As stated in the Critical Performance Requirements Met by PFAS HTFs in Semiconductor Manufacturing section, semiconductor manufacturing and test processes require a narrow temperature control window with minimal variation over time and across the surface of a wafer. Dry-etch tools, for example, may require ±0.1°C stability to a set temperature over a wide range of possible temperatures within the dry-etch process chamber in order to prevent damage to the wafer from the heat of the plasma (Nieman 2016). The cooling capacities required to achieve these exacting levels of temperature control can exceed 10 kW (34,121 BtU/hr) for each individual process chamber. To put this in perspective, the 10 kW of cooling capacity required per process chamber is approximately the same cooling requirement as more than 15 commercial kitchen refrigerators (Welbilt 2023); (Avantco 2023).

The use of individual process equipment chillers, which are roughly the size of a small home appliance and are part of support equipment packages connected to each piece of semiconductor manufacturing equipment in a fab, help achieve precise temperature control. Process equipment chillers pump HTFs through plumbing loops embedded in process chambers to either remove or add heat to systems. The HTF then transfers that heat either from or to a thermal reservoir outside the fab in a multistage process shown in Figure 4. In some cases, process equipment chillers are embedded within larger temperature control units (TCUs) that contain an additional refrigeration cycle that uses fluorinated refrigerants.

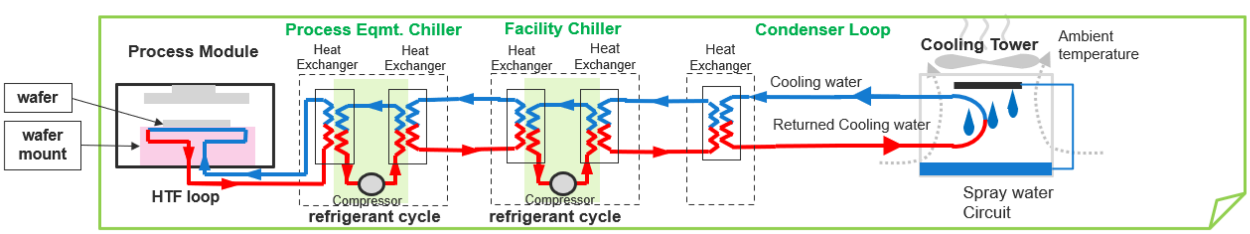


Figure 4: Complete heat transfer systems include process equipment chillers, facility chillers and condenser loops.

2.1.1 Typical Integration of Process Equipment Chillers with Facility Chillers and Condenser Loops

Process equipment chillers connect to a facility-scale chiller, and ultimately to cooling towers, through a series of closed-loop heat transfer systems. Process equipment chillers (illustrated in Figure 5) associated with semiconductor manufacturing equipment often require integration into facility cooling systems to enable the capture, transfer and elimination of waste heat generated from wafer manufacturing processing to the outside environment. These chillers also typically have a refrigeration circuit to bring HTFs to very low temperatures.

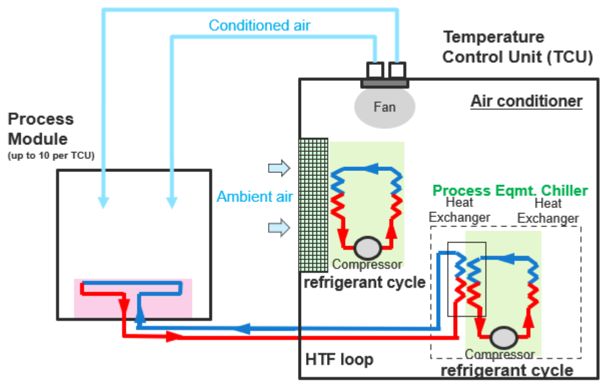


Figure 5: A TCU uses heat transfer fluids to provide conditioned air to process equipment.

As mentioned in the F-HTFs Used in the Semiconductor Manufacturing Process section, a refrigeration loop moves refrigerant through a cycle of compression and expansion (often converting it between liquid and gas phases) to transfer heat to reach temperatures well below ambient (as low as –80°C in a typical fab). The choice of refrigerant is based on the lowest necessary temperature, heat capacity and temperature range, as well as safety-related characteristics that allow the installation of chillers close to process tools to achieve the necessary level of temperature control on the tool.

HTF flows between the process equipment chiller and the process tool to remove or add heat to and from certain parts of the wafer-processing chamber. Additional heat transfer loops can flow between facility chillers and condenser loops. Additionally, refrigerants contained in hermetically sealed systems with compressors in process equipment chillers and facility chillers act as a heat sink for the manufacturing process and enable the transfer of heat and cooling to other components of the larger heat transfer system.

2.1.2 TCUs Used in Semiconductor Wafer Fabrication

Manufacturing equipment (such as photolithography material coaters and developers) requires an additional layer of specialized temperature control and air conditioning supplied by a TCU. A TCU is a combination of a refrigeration unit, which supplies temperature- and humidity-controlled air to process equipment, and a process equipment chiller. A single TCU may have to provide conditioning for large volumes of air (up to 100 m^3/min) and maintain highly precise temperature control (~25°C with ±0.05°C) and humidity (±0.1% relative humidity) across as many as 10 process modules.

The TCU contains an additional refrigerant cycle, in addition to the HTF loop and refrigerant cycles associated with its embedded process equipment chiller. Cleanroom ambient air temperatures and humidity exceed the variability requirements for the process module supported by the TCU, and therefore need additional cooling and humidity control. This additional refrigerant cycle also uses fluorinated refrigerant.

2.2 HTFs in Dry-Etch Applications

The dry-etch semiconductor manufacturing process uses partially ionized gases in the form of a plasma to aid in the creation of semiconductor features through the selective removal of solid materials from targeted areas on a wafer's surface. Dry-etch processes are required for the etching of semiconductor materials that cannot be effectively etched with other processes, such as those using wet chemicals. Dry-etch manufacturing is a main manufacturing application and has the most complex, stringent manufacturing process requirements for HTFs in semiconductor manufacturing.

2.2.1 Essential Performance Requirements for HTFs in Dry-Etch Applications

In dry-etch applications, both HTFs and process equipment chillers help achieve precise temperature control. Dry-etch HTF performance requirements include:

- Temperature control. HTFs and chillers control temperature within a tight variability range of ±0.1°C.
- Thermal performance specifications. These specifications dictate the ability to achieve an operational temperature maximum of 120°C and a minimum of –60°C.
- Chemical performance specifications. Current process chiller designs that support dry-etch manufacturing equipment require low kinematic viscosities throughout the operational temperature range to ensure effective flow, and to achieve a temperature variability range of ±0.1°C. HTFs must also be compatible with construction materials such as aluminum, stainless steel, copper, brass, FKM fluoroelastomers and ethylene propylene diene monomer rubber.
- Electrical conductivity characteristics. A high dielectric constant and volume resistance ensure the proper function of critical electrical components located in manufacturing process chambers such as the electrostatic chuck and the wafer anode, which require near-zero electrical conductivity. In addition, effective control of the plasma used in dry-etch processes requires stable electrical conductivity.
- Safety performance characteristics. Current process equipment chiller designs use nonflammable HTFs with installations located in occupied manufacturing areas compliant with building and fire-code requirements, as well as industry process equipment safety guidelines such as the SEMI S2 Environmental, Health, and Safety Guideline for Semiconductor Manufacturing Equipment.

2.3 HTFs in Semiconductor Device Testing Applications

Precision manufacturing processes necessitate the frequent use of test instrumentation to ensure that manufacturing processes are performing as required, and that the final semiconductor devices perform correctly and remain reliable across a range of environmental conditions.

Some test applications require the electrical testing of a completed semiconductor device to ensure that it can perform under different temperature conditions. Certain semiconductor device test applications employ temperature stressing to confirm that different construction materials are mechanically compatible.

There are three general types of testing applications important to the semiconductor manufacturing process:

- Burn-in testing. Burn-in is a test performed after package assembly. The semiconductor device is placed in a socket and an electrical signal is applied to heat and stress the device. This test is designed to find device failures, which are screened out and scrapped.
- Thermal shock testing, also known as hermetic seal testing. The semiconductor device is shocked at a cold or high temperature to simulate shipping or operational conditions, or to accelerate failures that enable better understanding of the longevity of a device in expected conditions.

- Device reliability testing. The semiconductor device is cycled – tens of thousands of times – through a low- to high-temperature range to simulate customer use. Reliability testing ensures that the semiconductor device will remain operational throughout the final product's expected lifetime.

2.3.1 Essential Performance Requirements for HTFs in Semiconductor Device Testing Applications

HTFs used in semiconductor test equipment have specific performance requirements related to chemical, thermal and electrical compatibility. They must be compatible (noncorrosive, nonreactive) with the construction materials used in the distribution network of the testing equipment and nonconductive to protect sensitive semiconductor circuitry. HTF performance requirements include:

- Chemical and thermal stability. HTFs must be stable throughout testing operations and applied stressors.
- Thermal performance specifications. The ability to achieve an operational temperature range of 125°C maximum (in a stable state) and –60°C minimum (for extreme cold testing).
- Chemical performance specifications. HTFs must be compatible with construction materials of testing distribution systems (which include aluminum, stainless steel, copper, brass and elastomers such as fluorosilicones, and ethylene propylene diene monomer rubber), while also possessing viscosity – the ability to flow effectively throughout the temperature ranges specified above, and with a low temperature dependence.
- Electrical conductivity characteristics. The HTFs used in semiconductor test applications must have low electrical conduction characteristics in order to prevent impacting the circuitry of the semiconductor device being tested, which includes high electrical resistivity, high volume resistance and low dielectric constants.
- Safety performance characteristics. Current process equipment chiller designs use nonflammable HTFs with installations located in occupied manufacturing areas compliant with building and fire-code requirements, as well as industry process equipment safety guidelines such as the SEMI S2 Environmental, Health, and Safety Guideline for Semiconductor Manufacturing Equipment.

2.3.2 F-HTFs in Semiconductor Device Testing Applications

In semiconductor test applications, F-HTFs have a unique ability to simultaneously provide all required performance characteristics. HTFs used in semiconductor test applications must be compatible with the construction materials of chiller and testing fluid distribution systems, as well as the semiconductor device being tested.

F-HTFs can meet the required high boiling point, low pour point, low kinematic viscosity and low dielectric constants required in semiconductor testing. F-HTFs are also nonflammable and inert to common construction materials, including most metals and fluorinated and nonfluorinated polymers. They have the required electrical properties to avoid the buildup of static electricity and conduction of electrical currents used by testing equipment electrical systems, as well as the semiconductor products being tested (P. E. Tuma 2001).

3.0 Potential Non-PFAS HTF Alternatives

As shown in Tables 2 and 3, to date there are no non-PFAS alternatives that satisfy all dry-etch and semiconductor test application performance requirements. Semiconductor HTFs must be simultaneously (1) electrically nonconductive, (2) compatible with all construction materials including sensitive electrical components and (3) to be nonflammable and useful within the operational range required for the manufacturing and testing of semiconductor products.

3.1 Potential Implications of Substituting Current F-HTFs with Non-PFAS HTF Alternatives

In the search for non-PFAS alternatives, there are several factors to consider, including:

- Whether an alternative non-PFAS HTF can meet operational specifications. The dry-etch and semiconductor testing applications that are the focus of this white paper have extreme operating temperature ranges of –60°C to 120°C. These operational temperature ranges require that HTFs remain pumpable throughout the temperature range, meaning that they must have an appropriately high boiling point of at least 135°C and a low pour point of –80°C or lower.
- Potential impacts to the stability of the manufacturing process. Dry-etch applications are extremely sensitive to changes in the electrical conduction properties of HTFs, requiring consideration of these characteristics:
    - Water solubility and volume resistance. HTFs that can absorb water can exhibit changes in resistance over time. The resistivity of the HTF must stay stable and at a level of near-zero conductivity. Industry experience has shown that HTFs containing water can exhibit reductions in resistance, which can affect the ability to control required manufacturing processes, such as those using plasmas. Therefore, HTFs containing or contaminated with water require frequent changeouts, which are associated with significant equipment downtimes.
    - Dielectric constants. HTFs with low dielectric constants ensure the proper functioning of electrostatic chuck systems, which rely on the ability to build up electrical potential to hold wafers. A loss of electrical potential on an electrostatic chuck leads to a loss of ability to hold the wafer close to the wafer mounts, and a loss of ability to control wafer temperatures within process temperature control variability limits. Using HTFs with low dielectric constants enables appropriate maintenance of the floating capacitance of the wafer electrode, as well as the ability to maintain stable plasma potentials, which are critical for controlling etch processes.
- The safety of process equipment and chiller installations. The HTFs that enable operation within the operational temperature limits required for semiconductor manufacturing exhibit great variability in their flammability characteristics. These differences can significantly affect the ability for process equipment chiller designs to comply with building and fire-code requirements, as well as industry process equipment safety guidelines (such as SEMI S2 and S14) (U.S. SEMI 2023). Most F-HTFs currently in use are nonflammable. Some non-PFAS alternative HTFs – suitable for use at the lower limits of the operating temperature range – have detectable flash points and flammable ranges in air that are likely to drive extensive design requirements for both process equipment and chillers. The process equipment side of the HTF loop usually has mechanical joints for the maintenance of process equipment. The formation of flammable vapor is possible under fault conditions, which would require electrical equipment and wiring within the process equipment to comply with electrical design requirements for hazardous (classified) locations, such as requirements documented within National Fire Protection Association (NFPA) 70. The use of flammable materials would limit the quantities of HTFs used and could require the placement of chiller units in nonoccupied areas and at distances prohibitive to semiconductor manufacturing processes.
- Impacts from process contamination. Certain HTFs carry the risk of direct contamination of the semiconductor manufacturing process to varying degrees. Certain HTFs – such as silicone oils - create silicon-oxide contaminants that can cause a near complete loss of die yield if not strictly and properly managed, resulting in extensive tool downtime to replace affected parts and eliminate sources of the contamination. See the Currently Existing Non-PFAS Alternative HTFs section for more detailed information on the contamination potential of alternative HTFs. In contrast, F-HTFs exhibit excellent chemical stability characteristics, and do not create contaminants that negatively impact the manufacturing process.

- Impacts on energy use. Several characteristics associated with HTFs help define the energy efficiency of the process equipment chiller designs that use them. The HTF must simultaneously optimize these characteristics to minimize energy use needs:
  - Kinematic viscosity. HTFs with lower kinematic viscosities require less energy to move through pumps.
  - Density. Higher-density HTFs generally enable higher-efficiency heat transfer. For example, F-HTFs have a uniquely high density (~1.6 to 1.8 g/cm^3) compared to other non-PFAS-containing materials, which are generally ~1.0 g/cm^3 or less.
  - Dielectric constant and volume resistivity. HTFs that provide low dielectric constants and stable resistivity reduce energy losses by providing a barrier from high fluctuating voltages and electrical leakage (U.S. EPA 2006).
- Space requirements. Space within semiconductor manufacturing environments is quite valuable and constrained, both in the cleanroom as well as in support facilities. Thus, it is advantageous to have space-efficient designs for manufacturing equipment in order to enable the installation of more manufacturing equipment per unit space and higher product throughput per factory. The SEMI E72 specification restricts the size of equipment like process equipment chillers in relation to larger packages of equipment for the purpose of ensuring space efficiency (U.S. SEMI 2023). From this perspective, there are certain characteristics associated with HTFs that help determine the space efficiency of process equipment chillers, including volumetric expansion coefficients, thermal conductivity and specific heat. HTFs with relatively lower volumetric expansion coefficients, higher thermal conductivity and higher specific heat enable the design of process chiller systems with smaller components, including tanks to contain the HTFs.

3.2 Timelines for Developing and Qualifying Alternative Process Chiller and Equipment Designs

The identification, development and implementation of alternative non-PFAS HTFs and refrigerants will likely require a considerable redesign of process chillers and associated semiconductor manufacturing equipment in order to continue meeting critical design parameters while accommodating lesser-performing HTFs. Design changes could require both foreseen and unforeseen impacts in the ability to meet critical process parameters such as operating temperatures and operational stability, and the need to meet safety-code and related design and environmental requirements.

To maintain the integrity of the overall semiconductor manufacturing process as well as the devices it makes, the industry references a well-established timeline to illustrate the required stages associated with development and qualification processes, the timelines required, and the checkpoints to cross. The timeline needed to develop, qualify and implement alternatives falls into four broad categories:

- **Three to four years.** If an existing non-PFAS alternative is available, does not require infrastructure alterations, and demonstrates adequate performance for a specific application, then it typically takes three to four years to conduct the trial testing and implement the alternative into high-volume manufacturing.
- **Three to more than 10 years.** In some applications, an existing non-PFAS alternative may be viable, but requires tooling and/or process changes before its successful introduction into high-volume manufacturing. In these cases, it may take between three and 10-plus years to introduce changes to semiconductor manufacturing and related equipment and/or processes, perform qualification testing, and implement the non-PFAS alternative into high-volume manufacturing.
- **Five to more than 25 years and successful invention required.** For some applications, it may not be possible to demonstrate that an available non-PFAS alternative can fulfill the application-specific performance requirements. In those cases, it may be necessary to invent and synthesize 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 endeavor, with no guarantee of success.

- **No alternative achievable.** In some cases, a non-PFAS alternative may not be capable of providing the required chemical function. If it is not possible to invent a non-PFAS alternative chemical, and if PFAS use is prohibited by regulatory authorities, then it may be necessary to abandon or significantly redesign the semiconductor equipment currently needed for manufacturing integrated circuit devices.

3.3 Existing Non-PFAS Alternative HTFs

The Semiconductor PFAS Consortium reviewed a number of potential, nonfluorinated HTFs, but none simultaneously met the requirements for dry-etch or testing applications. The nonfluorinated HTFs considered for use in semiconductor manufacturing operations included:

- Synthetic hydrocarbon oils (which have kinematic viscosity values much higher than the F-HTFs currently in use) leads to an inability to maintain tight temperature tolerances. Residuals of these HTFs can cause contamination in the fab, leading to process yield impacts. Additionally, flashpoints are much lower than fluorinated HTFs and could drive extensive – and possibly prohibitive – changes to equipment chiller designs.
- Silicone-based HTFs, which are inert and have unique properties such as extreme stability against thermal oxidation, low freezing points (–95°C), wide operating temperatures (–100°C to 260°C), good dielectric strength, favorable environmental properties and low toxicity (Czaplicka, et al. 2021). While silicone-based fluids have many advantageous properties for use as an alternative heat transfer solution, they are nonviable for semiconductor manufacturing processes like dry etch because they can cause catastrophic contamination issues.
  When silicone based HTFs vaporize or have residuals that deposit on surfaces, they are known to contaminate very sensitive semiconductor manufacturing processes (R&D Editors 2012). Similarly, other industries have reported the need to scrap parts that have become contaminated with silicone oil residues (Luey and Coleman 2002). Accidental transfers of HTFs – in the order of a few drops of fluid – are normally expected during certain maintenance activities like the exchange of replaceable parts connected to the chiller loop. If silicone oils were to replace the current F-HTFs in dry-etch applications, the transfer of even a few drops could result in the need for extensive cleaning, complete chamber rebuilds or the replacement of contaminated parts.
- EG/DI mixtures, which are common in HTF applications, including semiconductor applications. Where F-HTFs are currently in use, it is because EG/DI combinations cannot meet boiling-point and pour-point requirements to support operational temperature ranges. In addition, EG/DI mixtures can exhibit a reduction in resistivity during use that increases over time, making etch and deposition process control more difficult.
  Similar to synthetic hydrocarbon oils, the residuals of EG/DI HTFs can cause contamination in fab environments, leading to decreases in process yields.

Tables 2 and 3 include side-by-side comparisons of the properties of these compounds. Cells colored green indicate that the compound is suitable for use as an HTF. These tables illustrate how the performance characteristics of F-HTFs compare against three available non-PFAS HTFs, and are based on a combination of available data and professional judgment. Note that F-HTFs, synthetic hydrocarbon oils and silicone oils represent a class of fluids, and the tables include representative values applicable for direct comparison. The selection of heat transfer fluids for semiconductor manufacturing is a complicated process and depends significantly on the parameters required of the process, various components within the process equipment, and the heat transfer materials themselves. Tables 2 and 3 present representative, semiconductor, fluorinated and nonfluorinated heat transfer materials to demonstrate the complexity of selecting a heat transfer material based on meeting a range of requirements.

Table 2: Comparing F-HTFs semiconductor materials with example alternative non-PFAS HTFs in the context of representative dry-etch performance parameters.

Property	Representative Dry-Etch Performance Parameters	F-HTFs	Synthetic Hydrocarbon Oils	Silicone Oils	EG/DI (50:50)
Balancing Boiling Point[1] [°C] with Pour Point[2] [°C]	≥135°C	135°C	181°C	260°C	107°C
(A range of temperatures that can be as high as 135°C or as low as –80°C)	≤–80°C	–100°C	–81°C	–100°C	–35°C
Kinematic Viscosity	Acceptable Viscosity at the Required Lowest Operating Temperature	Acceptable	Not Acceptable	Not Acceptable	Not Acceptable
Dielectric Constant	≤2	1.92	2.1	2.28	>37
Volume Resistance [Ω·cm]	$>1.0 \times 10^6$	$>1 \times 10^8$	1.0×10^{14}	1.0×10^{15}	3.0×10^6
Risk of Contamination and Impacts to Process Yields from Use	Non-contaminating	Non-contaminating	Semiconductor Manufacturing Contaminant	Catastrophic Contaminant to Etch Process Yields and in Semiconductor Manufacturing	Semiconductor Manufacturing Contaminant
Stability	Physiochemically and Electrically Stable	Stable	Stable	Stable	Decrease in Resistance Noted over Time
Flammability Based on Flash Point (FP) and NFPA 704 Rating	0 to 1 rating	0 FP Undetectable	2 FP = 58°C	2 FP = 47°C	1 FP = 142°C
References		(Galden 2014); (3M 2022); (3M 2019); (Applied Thermal Fluids 2023)	(Dow J-HTF 2023)	(Dow Dowsil 2023); (Dow Syltherm 2023)	(The Engineering Toolbox 2008); (Pratt 2015)

[1] Generally, the boiling point of an HTF must be approximately 15°C higher than the highest operational set point.
[2] Generally, the pour point of a fluid must be approximately 20°C lower than the lowest operational set point.

Red	The material is not suitable for use and would require new manufacturing equipment or chiller inventions, an extensive redesign of processes, or impacts the surrounding manufacturing space.
Yellow	The material may not be suitable for use in dry-etch processes and/or may require significant design changes before accommodating the characteristic.
Green	The material is suitable for use in most dry-etch processes.

Table 3: Comparing F-HTFs and example alternative non-PFAS HTFs in the context of semiconductor representative test application performance parameters.

Property	Representative Test Application Performance Parameters	F-HTFs	Synthetic Hydrocarbon Oils	Silicone Oils	EG/DI (50:50)
Balancing Boiling Point[1] [°C] with Pour Point[2] [°C]	≥135°C	135°C	181°C	260°C	107°C
(A range of temperatures that can be as high as 135°C or as low as –80°C)	≤–80°C	–100°C	–81°C	–100°C	–35°C
Kinematic Viscosity	Acceptable Viscosity at the Required Lowest Operating Temperature	Acceptable	Acceptable	Not Acceptable	Not Acceptable
Dielectric Constant at 1 kHz	<6	1.92	2.1	2.28	>37
Flammability Based on FP and NFPA 704 Rating	0 to 1 rating	0 FP Undetectable	2 FP = 58°C	2 FP = 47°C	1 FP = 142°C
References		(Galden 2014); (3M 2022); (3M 2019); (Applied Thermal Fluids 2023)	(Dow J-HTF 2023)	(Dow Dowsil 2023); (Dow Syltherm 2023)	(The Engineering Toolbox 2008); (Pratt 2015)

[1] Generally, the boiling point of an HTF must be approximately 15°C higher than the highest operational set point.
[2] Generally, the pour point of a fluid must be approximately 20°C lower than the lowest operational set point.

Red	The material is not suitable for use and would require new manufacturing equipment or chiller inventions, an extensive redesign of processes, or impacts the surrounding manufacturing space.
Yellow	The material may not be suitable for use in test applications and/or may require significant design changes before accommodating the characteristic.
Green	The material is suitable for use in test applications.

3.4 Existing Non-PFAS Alternative Refrigerants

Process equipment chillers currently use fluorinated refrigerants in their compressor systems to act as a heat sink and as heat transfer agents between the manufacturing process and facility chiller system. This section discusses the potential impacts of replacing these fluorinated refrigerants with two non-PFAS alternatives: carbon dioxide (CO_2) and ammonia (NH_3) (as a refrigerant-only replacement).

The required operational temperature range for dry-etch and semiconductor test applications requires minimum operational temperatures of –60°C, which both CO_2 and NH_3 cannot support. The CO_2 triple point is documented as 216.58 Kelvin (–56.57°C) (National Institute of Standards and Technology 2023), which means that the operational temperature range has a lower limit of about –50°C. As a liquid approaches the temperature and pressure where three phases can coexist (the triple point), it becomes more difficult to control the operational temperature. As such, CO_2 use with dry-etch and test systems that require operational temperature ranges below –50°C would not be feasible, nor would the use of NH_3 as a refrigerant in process equipment chillers supporting etch and test systems.

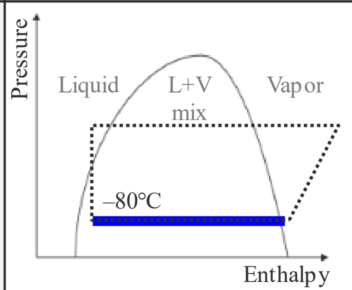
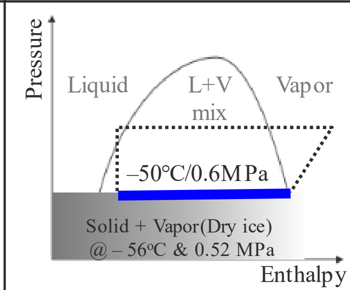
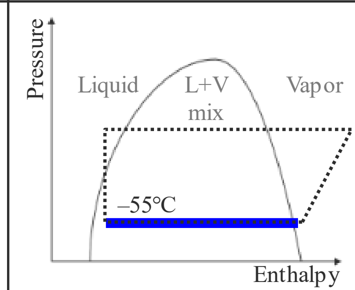
Chillers using CO_2 and NH_3 are not as energy-efficient, noting that cooling capacity (1 kW for CO_2 and 4 kW for NH_3) is at the lower end of its effective temperature range. When compared to the cooling capacity of fluorinated refrigerants like R14, process equipment chillers using CO_2 and NH_3 as a refrigerant are significantly less efficient. Achieving a similar level of cooling would require the installation of more chilling capacity, which in turn would require significantly more space.

The use of NH_3 as a refrigerant is associated with an American National Standards Institute/American Society of Heating, Refrigerating and Air-Conditioning Engineers Standard 34 safety classification rating of B2L, where B indicates a refrigerant for which there is evidence of toxicity at concentrations below 400 ppm per volume, and 2L indicates a refrigerant that is mildly flammable. This classification is associated with building and fire-code requirements that often necessitate the installation of NH_3-refrigerant chillers in a separate building with NH_3 monitoring and other controls, such as pressure relief valves and associated abatement.

Requirements to separate chiller equipment from manufacturing areas are likely to drive other concerns related to process temperature control and energy efficiency, as this implies a need for longer piping installations between process equipment and process equipment chillers, which would be more susceptible to warming and temperature fluctuations than current equipment and chiller installations located close to one another.

Table 4 is a side-by-side comparison of fluorinated refrigerants with CO_2 and NH_3. The adoption of CO_2 or NH_3 as refrigerants within process equipment chillers supporting semiconductor manufacturing equipment is limited by the lowest temperatures that these alternatives can support, as well as reduced efficiencies and requirements associated with safety classifications.

Table 4: Comparing refrigeration characteristics of R14, CO2 and NH3.

Refrigerant	Fluorinated Refrigerant (example:R14)	CO_2	NH_3
Pressure-Enthalpy (P-H) Diagram *Note: Each diagram does not scale*			
Cooling method	Vapor compression refrigeration cycle	Vapor compression refrigeration cycle	Vapor compression refrigeration cycle
Lowest operational temperature	–80°C	–50°C	–55°C
Cooling capacity @ –50°C	10 kilowatts (kW)	1 kW	4 kW
Refrigeration efficiency	Good	Poor The minimum temperature is too close to the target of -60°C. There is a risk of phase change to solid (dry ice) with a small fluctuation of pressure control.	Poor Cooling capacity decreases significantly below -30°C due to relatively high boiling point under atmospheric pressure.
Safety Classification *per ANSI/ASHRAE Standard 34*	A1	A1	B2L Requires built-in abatement and installation must be outside of building.

Red	The material is not suitable for use in semiconductor manufacturing applications and would require new manufacturing equipment or chiller inventions, an extensive redesign of processes, or impacts the surrounding manufacturing space.
Yellow	The material may not be suitable for use and/or may require significant design changes before accommodating the characteristic.
Green	The material is suitable for use in semiconductor manufacturing applications.

3.5 Potential Areas for R&D

Most applications that use F-HTFs and fluorinated refrigerants as heat transfer fluids in process equipment chillers have the ability to simultaneously meet the required operational temperature ranges, be stable in the manufacturing process, be safe for use, have a low risk of contaminating the manufacturing process, be energy efficient, and meet space requirements.

Any effort to develop new non-PFAS heat transfer fluids and/or process chiller equipment should focus on:

- The development of new fluids that may have an increased potential to serve as drop-in substitutes, including the ability to support operation within extremely low and high operational temperatures, with similar energy and space requirements and favorable environmental and toxicological profiles.
- The identification and mitigation of impacts resulting from the substitution of F-HTFs and fluorinated refrigerants with non-PFAS alternatives in equipment, with a focus on:
    - Compatibility with construction materials.
    - Energy and space efficiency.
    - The ability to modify the design of process equipment and process equipment chillers in order to meet building and fire-code requirements.

- R&D of methods to measure and mitigate impacts that non-PFAS fluids may have on plasma, bias potentials and etch rates, as well as the proper operation of equipment like electrostatic chucks and wafer anodes that currently require HTFs to be nonconductive and remain stable over time.

4.0 Workplace Health and Safety Considerations

Overall, potential exposures to heat transfer fluids are well controlled, as they are used in closed-loop systems that contain vapors and gases. Low-level exposures may occur during certain maintenance activities such as filling and draining, or chiller system maintenance activities. The information provided in this section focuses on workplace health and safety considerations of fluorinated and refrigerants; however, nonfluorinated alternatives have their own safety and health considerations and may be corrosive, toxic and/or flammable.

The toxicological potential of F-HTFs is very low. Industry supplier information obtained on low-molecular-weight PFPE fluids has shown no relevant acute toxic potential (LD/LC50 values above the thresholds for classification). They are nonirritating to skin and eyes and have no indication of skin sensitization. Results from a four-week oral toxicity study showed that the “no observed adverse effect” level was at the limit dose of 1,000 mg/kg of body weight per day, with essentially no adverse effect of treatment. Moreover, no mutagenicity or genotoxicity was evident.

HFE fluids have a similarly low toxicity. HFE compounds are not classified as an acute toxicity hazard under the Globally Harmonized System. HFEs are nonmutagenic and are dermally and ocularly nonirritating. They have relatively high exposure guidelines compared to the typical occupational exposures from their use as HTFs, resulting in a wide margin of safety. For example, the American Industrial Hygiene Association has set an eight-hour worker exposure guideline of 750 ppm for HFE-7100 (C4F9OCH3, 163702-08-7) based on the results of a 90-day inhalation study (Tuma and Knoll 2003); (Owens 2011).

5.0 Environmental Releases and Controls

This section focuses on environmental releases and controls of fluorinated heat transfer fluids; however, nonfluorinated alternatives have their own environmental release pathways and may be aquatically toxic, nonbiodegradable, bioaccumulative and/or contribute to global warming (Dow J-HTF 2023); (Dow Syltherm 2023); (Dow Dowsil 2023); (The Engineering Toolbox 2008); (Pratt 2015).

As designed, fluorinated heat transfer fluids used in chiller and test equipment are contained; only trained technicians can access and maintain them. Their containment is the primary environmental control that minimizes releases to the environment. Before the initiation of chiller loop and/or distribution system maintenance or service activities, the F-HTF contents of the chiller and associated equipment are first drained into collection containers that are managed either for direct reuse, or for reclamation at the F-HTF supplier location. If liquid HTF becomes waste, the fluid is typically managed by incineration at appropriately certified waste management facilities.

Similarly, for fluorinated refrigerants, the refrigeration loop is evacuated, and the refrigerant is captured before performing maintenance or service. In some jurisdictions, regulations require performing this recovery (European Union 2014). Captured refrigerants are commonly reclaimed and recycled (Daikin 2023); (U.S. EPA 2023).

Some heat transfer fluids are released to the air as a fugitive loss from HTF and refrigerant loops during maintenance or service tasks, such as the changeout of parts that require replacement, as well as during filling and draining or evacuation. Additionally, fugitive releases may occur from failures of components such as couplers, seals or gaskets. Through the years, chiller and heat exchanger and fluid supply lines have transitioned from threaded fittings to compression fittings in an effort to mitigate fugitive losses. System designs have also changed to alleviate tolerances within equipment on items like recirculation pumps and level sensors where fugitive losses occurred.

The industry has a propensity to reuse equipment throughout the manufacturing process, and there is the potential for a 15-year-old (or older) piece of equipment to still be in operation and meeting process requirements. Semiconductor chiller and heat-exchanger manufacturers implemented features that allow for the purging and reclaiming of F-HTF in lines connecting equipment during chamber maintenance. The reclamation process entails pushing F-HTF from the chiller or heat-exchanger supply line through the tool and back down to the F-HTF reservoir, where it is then sealed off through valving during chamber or line maintenance. For this reclamation process to work, the chiller or heat exchanger needs to have adequate room within the reservoir to capture the F-HTF. Since not all equipment in operation has this design change, the practice of capturing the F-HTF when lines are broken still exists and can contribute to fugitive losses. Liquid F-HTFs used in semiconductor manufacturing and testing applications have relatively high vapor pressures, and refrigerants are typically gaseous; therefore, fluorinated heat transfer fluid that escapes containment is typically released to the air.

The fate in the atmosphere depends on the specific F-HTF or refrigerant. Depending on their chemical structures, fully or partially fluorinated heat transfer fluids have 100-year global warming potentials ranging from less than 1 to over 10,000, and are considered greenhouse gases. Perfluorinated liquid F-HTFs (perfluoroalkanes, perfluoroamines, perfluoroethers) are resistant to any degradation in the lower atmosphere and finally degrade after long transport times to the upper atmosphere (mesosphere). At those altitudes, F-HTFs are exposed to low-enough wavelength radiation to break all carbon-carbon bonds to produce only hydrofluoric acid, which mineralizes to form inorganic fluoride salts, and CO_2 as degradation products (Ravishankara, et al. 1993); (Young, et al. 2006). Partial F-HTFs will degrade in the lower atmosphere (troposphere) through a series of chemical reactions initiated by the hydroxyl radical (Goto, et al. 2002); (Jubb, et al. 2014); (Wallington, et al. 1997); (Barry, et al. 1997); (Zhang, et al. 1992); (Taketani, et al. 2005); (Christensen, et al. 1998). The final degradation products will again contain CO_2 and inorganic fluoride salts, but in many cases can also include trifluoroacetic acid.

6.0 Conclusions

The semiconductor manufacturing process employs heat transfer fluids in both cooling and heating applications to provide precise temperature control for specific manufacturing operations. Refrigerants help transfer heat from process equipment to a facility's central cooling system. Manufacturers also use heat transfer fluids to test devices at anticipated end-use operating temperatures of finished electronic products.

While the temperature set points for device manufacturing may vary, precise temperature control of these set points is required. Conversely, during testing devices may be exposed to a wide temperature range, while still requiring precise control.

The physical and chemical properties of the carbon-fluorine bond give F-HTF and fluorinated refrigerants multiple performance characteristics that are essential for manufacturing and testing advanced semiconductor chips. The two types of fluorinated heat transfer fluids in use in semiconductor manufacturing – liquid F-HTFs and fluorinated refrigerants – have the ability to provide several performance characteristics at once, including a high boiling point, a low pour point, low kinematic viscosity at working temperatures, and electrical nonconductivity as measured by low dielectric constants and high-volume resistance.

No non-PFAS alternatives are currently viable for the drop-in replacement of current fluorinated heat transfer fluids used within dry-etch and semiconductor device test applications, and the effort to develop new heat transfer fluids and/or technologies that would enable substitution would take 10 to 12 or more years to ensure the viability of use within semiconductor manufacturing processes, as well as the appropriate functioning of semiconductor devices.

The heat transfer fluids used in semiconductor manufacturing are of low toxicity and operate within closed-loop systems that are designed to contain vapors and gases. Any waste generated is managed either for direct reuse, reclaimed by the supplier, or managed by incineration.

7.0 References

3M. 2019. "3M™ Fluorinert™ Electronic Liquid FC-3283." *3M.* September. https://multimedia.3m.com/mws/media/64886O/3m-fluorinert-electronic-liquid-fc3283-en.pdf .

—. 2022. "Heat Transfer Applications using 3M™ Novec™ Engineered Fluids." *3M.* https://multimedia.3m.com/mws/media/1091997O/3m-novec-engineered-fluids-for-heat-transfer-line-card.pdf .

Applied Thermal Fluids. 2023. *Galden HT-135 Perfluorinated PFPE Heat Transfer Fluid.* Accessed 2023. https://www.appliedthermalfluids.com/product/galden-ht-135-heat-transfer-fluid-5kg-bottle/.

ASHRAE. 2019. "Designation and Safety Classification of Refrigerants." *ASHRAE.* December 12. https://www.ashrae.org/file%20library/technical%20resources/standards%20and%20guidelines/standards%20addenda/34_2019_f_20191213.pdf.

Avantco. 2023. *Avantco A-49R-HC 54" Solid Door Reach-In Refrigerator.* Accessed 2023. https://www.avantcorefrigeration.com/product/178A49RHC/.

Barry, John, Garrett Locke, Donncha Scollard, Howard Sidebottom, Jack Treacy, Cathy Clerbaux, Reginald Colin, and James Franklin. 1997. "1,1,1,3,3-Pentafluorobutane (HFC-365mfc): Atmospheric degradation and contribution to radiative forcing." *Chemical Kinetics* 607-617.

Christensen, L. K., SehestedJ., O. J. Nielsen, T. J. Wallington, A. Guschin, T. Molina, and M. J. Molina. 1998. "Atmospheric Chemistry of HFE-7200 (C4F9OC2H5): Reaction with OH Radicals and Fate of C4F9OCH2CH2O(•) and C4F9OCHO(•)CH3 Radicals." *The Journal of Physical Chemistry A* 4839-4845.

Clot, Eric, Odile Eisenstein, Naserella Jasim, Stuart Macgregor, John E McGrady, and Robin N Perutz. 2011. "C-F and C-H bond activation of fluorobenzenes and fluoropyridines at transition metal centers: how fluorine tips the scales." *Accounts of Chemical Research* 333-348.

Cousins, Ian T, Gretta Goldenman, Dorte Herzke, Rainer Lohmann, Mark Miller, Carla A Ng, Sharyle Patton, et al. 2019. "The concept of essential use for determining when uses of PFASs can be phased out." *Environmental Science: Processes & Impacts* 21 (11): 1803-1815.

Czaplicka, Natalia, Anna Grzegórska, Jan Wajs, Joanna Sobczak, and Andrzej Rogala. 2021. "Promising Nanoparticle-Based Heat Transfer Fluids—Environmental and Techno-Economic Analysis Compared to Conventional Fluids." *International Journal of Molecular Sciences* 9201.

Daikin. 2023. *Refrigerant Recovery – What is it and How Does It Work?* Accessed 2023. https://www.daikin.com.sg/blog-post/refrigerant-recovery.

Dow Dowsil. 2023. "Technical Data Sheet DOWSIL™ ICL-1000 Fluid." *DOW*. https://www.dow.com/documents/en-us/productdatasheet/11/11-42/11-4298-01-dowsil-icl-1000-fluid.pdf.

Dow J-HTF. 2023. *DOWTHERM™ J Heat Transfer Fluid.* https://www.dow.com/en-us/pdp.dowtherm-j-heat-transfer-fluid.25619z.html#overview.

Dow Syltherm. 2023. "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.

European Union. 2014. "Regulation (EU) No 517/2014 of the European Parliament and of the Council on fluorinated greenhouse gases and repealing Regulation (EC) No 842/2006." *Official Journal of the European Union*, April 16: 195-230.

Galden. 2014. "Galden® HT PFPE Heat Transfer Fluids." *Galden.* https://content.solvay.com/galden-HT-PFPE-heat-transfer-fluids-v2.2.

Goto, M, Y Inoue, M Kawasaki, A G Guschin, L T Molina, J M Molina, T J Wallington, and M D Hurley. 2002. "Atmospheric chemistry of HFE-7500 [n-C3F7(OC2H5)CF(CF3)2]: Reaction with OH radicals and Cl atoms and atmospheric fate of n-C3F7(OCHO)CF(CF3)2 and n-C3F7CF(OCH2CH2O)CF(CF3)2 radicals." *Environmental Science and Technology* 2395-2402.

Jubb, Aaron M, Tomasz Gierczak, Munkhbayar Baasandorj, Robert L Waterland, and James B Burkholder. 2014. "Methyl-perfluoroheptene-ethers (CH3OC7F13): Measured OH radical reaction rate coefficients for several isomer and enantiomers and their atmospheric lifetimes and global warming potentials." *Environmental Science & Technology* 4954-4962.

Krafft, M.P., and J.G. Riess. 2015. "Selected physicochemical aspects of poly and perfluoroalkylated substances relevant to performances, environment and sustainability—part one." *Chemosphere* 4-19.

Luey, K, and D. J. Coleman. 2002. *The Removal of Silicone Contaminants from Spacecraft Hardware.* Los Angeles Air Force Base: The Aerospace Corporation.

Marchionni, G., G. Ajiroldi, and G. Pezzin. 1996. "Structure-property Relationships in Perfluoropolyethers: A Family of Polymeric Oils." *Comprehensive Polymer Science* 347-388.

National Institute of Standards and Technology. 2023. *NIST Chemistry WebBook, SRD 69: Carbon Dioxide.* https://webbook.nist.gov/cgi/inchi?ID=C124389&Mask=4 .

Nieman, Marko. 2016. *Liquid to liquid ambient cooling systems for semiconductor tools.* September. https://sst.semiconductor-digest.com/2016/09/liquid-to-liquid-ambient-cooling-systems-for-semiconductor-tools/.

Owens, J. 2011. "Hydrofluoroethers." In *Handbook for Critical Cleaning 2nd Edition*, by Barbara Kanegsburg and Edward Kanegsburg, 115-130. Boca Raton: CRC Press.

Pratt, Scott. 2015. "Proper fluid selection and maintenance for heat transfer applications." *ThermoFisher Scientific.* https://assets.thermofisher.com/TFS-Assets/LPD/Product-Information/Proper-Fluid-Selection-TechNote-TNTCFLUIDS-EN.pdf .

R&D Editors. 2012. *Please help us determine the source of the silicon contamination.* May 24. https://www.rdworldonline.com/please-help-us-determine-the-source-of-the-silicone-contamination/.

Ravishankara, A.R., S. Solomon, A.A. Turnipseed, and R.F. Warren. 1993. "Atmospheric lifetimes of long-lived halogenated species." *Science* 194-199.

Smart, B.E. 2001. "Fluorine substituent effects (on bioactivity)." *Journal of Fluorine Chemistry* 3-11.

Taketani, Fumikazu, Tomoki Nakayama, Kenshi Takahashi, Yutaka Matsumi, Michael D. Hurley, Timothy J. Wallington, Anne Toft, and M.P. Sulbaek Andersen. 2005. "Atmospheric chemistry of CH3CHF2 (HFC-152a): Kinetics, mechanisms, and products of Cl atom- and OH radical-Initiated oxidation in the presence and absence of NOx." *Journal of Physical Chemistry A* 9061-9069.

The Engineering Toolbox. 2008. *Liquids- Dielectric Constants.* https://www.engineeringtoolbox.com/liquid-dielectric-constants-d_1263.html .

Tuma, P., and L. Tousignant. 2002. *Reducing Emissions of PFC Heat Transfer Fluids.* 3M.

Tuma, P., and S. Knoll. 2003. "A comparison of fluorinated and DI/glycol heat transfer fluids." *Solid State Technology.*

Tuma, Phil E. 2001. "Using Segregated HFEs as Heat Transfer Fluids Avoiding problems in system design." *Chemical Processing.*

U.S. EPA. 2023. *Stationary Refrigeration Refrigerant Reclamation Requirements.* Accessed 2023. https://www.epa.gov/section608/stationary-refrigeration-refrigerant-reclamation-requirements#:~:text=Where%20to%20Return%20Used%20Refrigerant,directly%20to%20an%20EPA%20reclaimer.

—. 2006. "Uses and Emissions of Liquid PFC Heat Transfer Fluids from the Electronics Sector." *EPA Documents.* February. https://www.epa.gov/sites/default/files/2016-02/documents/pfc_heat_tranfer_fluid_emission.pdf.

U.S. SEMI. 2023. *SEMI E72 - Specification and Guide for Equipment Footprint, Height, and Weight.* https://store-us.semi.org/products/e07200-semi-e72-specification-and-guide-for-equipment-footprint-height-and-weight.

Wallington, T, W Schneider, J Sehested, M Bilde, J Platz, O Nielsen, L K Christensen, L Molina, and P W Woolridge. 1997. "Atmospheric chemistry of HFE-7100 (C4F9OCH3): Reaction with OH radicals, UV spectra and kinetic data for C4F9OCH2· and C4F9OCH2O2· radicals and the atmospheric fate of C4F9OCH2OŸ radicals." *Journal of Physical Chemistry A* 8264-8274.

Welbilt. 2023. *6000XL® Reach-In Refrigerators.* Accessed 2023. https://direct.welbiltgreen.com/product/fam_ejfmef/6000XL-Reach-Ins.

Young, Cora J, Michael D Hurley, Timothy J Wallington, and Scott A Mabury. 2006. "Atmospheric lifetime and global warming potential of a perfluoropolyether." *Environmental Science and Technology* 2242-2246.

Zhang, Zhengyu, R. Saini, M. Kurlyo, and R. Huie. 1992. "Rate constants for the reactions of hydroxyl radical with CHF2CF3CF2CHF2 and CF3CHFCHFCF2CF3." *Chemical Physics Letters* 230-234.

Appendix A: Terminology

This appendix defines some of the terms used throughout this white paper.

Boiling point

The temperature at which a pure substance transitions from a liquid to a gaseous phase. At this point, the vapor pressure of the liquid is equal to the applied pressure on the liquid.

Compatibility

The balance of chemical and physical properties between an HTF and the construction materials used in HTF loops and refrigeration systems in process equipment chillers. To remain contained and useful in closed-loop systems, the HTF must be compatible with the system's tubing, seals, valves, pumps and other components.

Contamination

The presence of an unwanted source of particulates or another airborne vapor or gas that can negatively affect the manufacturing process. In particular, particle contamination and airborne molecular contamination in fabs and process chambers in fabs can have a detrimental effect on manufacturing yields and semiconductor device reliability.

Cooling capacity

The amount of cooling (usually expressed in terms of kilowatts or tons of cooling) delivered by a system divided by the amount of air passing through the system (in kilograms per second or cubic feet per minute).

Density

The mass per unit of volume of a liquid or gas.

Dielectric constant

The measure of a substance or material's ability to store electrical energy. It is an expression of the extent to which a material holds or concentrates electric flux.

Dielectric strength

The maximum voltage that a material can withstand under ideal conditions, up to which no electrical breakdown occurs in that material.

Die yield

The percent of microchips that function correctly in a wafer.

Dry-etch and thin-films deposition

Dry-etch processes (also known as plasma etch or plasma-enabled etch) and plasma chamber clean processes use a partially ionized gaseous medium to remove solid materials from targeted areas of the semiconductor surface or process equipment chamber walls.

The thin-films deposition process vaporizes materials to react on a semiconductor surface to create thin metal or dielectric layers. These films, or layers, change the electrical properties of the wafer surface and form the basis of the main features in a computer chip. Physical vapor deposition, chemical vapor deposition and electroplating are the main types of thin-film deposition used in semiconductor manufacturing.

F-HTF

A fluorinated liquid heat transfer fluid used within an HTF loop to transfer heat between semiconductor manufacturing process equipment and an associated process equipment chiller.

Flammability

The ease with which a substance can be ignited, causing a fire, combustion or even an explosion.

Heat transfer fluid

Broadly, a liquid or gas used to move heat between high- and low-temperature sources or sinks to provide temperature control. In the context of this white paper, a heat transfer fluid is a term that is inclusive of liquid HTF and gaseous refrigerants, as both fluids serve the purpose of moving heat.

HTF

A component of the broader heat transfer fluid category, HTF indicates a liquid heat transfer fluid used within an HTF loop that transfers heat between semiconductor manufacturing (process) equipment and an associated process equipment chiller. This is a generic term that describes HTFs of all types, including fluorinated and nonfluorinated fluids.

Kinematic viscosity

The measure of a fluid's resistance caused by the intermolecular friction exerted when layers of fluid are forced to slide by one another. The kinematic viscosity of a fluid is the ratio of its absolute viscosity to its density and is temperature-dependent, as fluids generally become exponentially more viscous with decreasing temperatures.

Operational temperature range

The range of temperatures within which a semiconductor process operates in order to meet a performance specification for its particular function. Examples include completing an etch according to required device design characteristics, or a testing application to appropriately stress or determine the functionality of a semiconductor device.

Pour point

Also called Fluid Point. The temperature below which a liquid loses its flow characteristics.

Process module

A vessel internal to semiconductor manufacturing equipment, within which wafer processing takes place.

Refrigerant

A gaseous heat transfer fluid that works within a hermetically closed system containing a compressor and that has the ability to undergo repeated phase transitions from a liquid to a gas and from a gas to a liquid.

Specific heat

A measure of the amount of heat required to raise the temperature of 1 g of an HTF by 1°C.

Thermal conductivity

The measure of a heat transfer fluid's ability to conduct (absorb and release) heat.

Volumetric expansion coefficient

The factor by which a fluid expands in response to an increase in temperature.

Volume resistance

The measure of a material's resistance to the flow of electrical current.

Water solubility

The amount of water that can be dissolved in a heat transfer fluid, as a heat transfer fluid's inherent ability to absorb additional water can affect other performance characteristics.

