



Review

Environmental and health risks of chlorine trifluoride (ClF₃), an alternative to potent greenhouse gases in the semiconductor industry

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ABSTRACT

The first accident involving chlorine trifluoride (ClF₃) in the history of semiconductor fabrication processes occurred on 28 July 2006 at Hsinchu (Taiwan), resulting in a large release of the highly reactive material and causing the chemical burn to several workers. ClF₃ is used primarily as an *in situ* cleaning gas in the manufacture of semiconductor silicon-wafer devices in replacement of perfluorocompounds (PFCs) because they have the high potential to contribute significantly to the global warming. This article aimed at reviewing ClF₃ in the physicochemical properties, the industrial uses, and the environmental implications on the basis of its toxicity, reactivity, health hazards and exposure limits. The health hazards of probable decomposition/hydrolysis products from ClF₃ were also evaluated based on their basic physicochemical properties and occupational exposure limits. The occupational exposure assessment was further discussed to understand potentially hazardous risks caused by hydrogen fluoride and fluorides from the decomposition/hydrolysis products of ClF₃.

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1. Introduction

The halogen fluorides are inorganic compounds that are comprised of binary of bromine, chlorine, and iodine with fluorine.

Of the eight known compounds, only four compounds, including chlorine trifluoride (ClF₃), bromine trifluoride (BrF₃), bromine pentafluoride (BrF₅) and iodine pentafluoride (IF₅), have been of commercial importance due to their powerful oxidizing potentials [1]. Furthermore, ClF₃ is the most reactive compound among the halogen fluorides, suggesting that it can be used as effective cleaning gas for some chemical vapor deposition (CVD) processes in the semiconductor industries [2–6].

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Table 1
Some atmospheric status and global warming properties for perfluorocompounds (PFCs).^a

PFCs	Atmospheric conc. (ppt)	Radiative efficiency (W m ⁻² ppb ⁻¹)	Atmospheric lifetime (year)	Global warming potential (100-year time horizon)
Trifluoromethane (CHF ₃)	18	0.19	270	14,800
Tetrafluoromethane (CF ₄)	74	0.10	50,000	7390
Hexafluoroethane (C ₂ F ₆)	2.9	0.26	10,000	12,200
Octafluoropropane (C ₃ F ₈)	~0.5 ^b	0.26	2600	8830
Nitrogen trifluoride (NF ₃) ^b	<0.10 ^c	0.21	740	17,200
Sulfur hexafluoride (SF ₆)	5.6	0.52	3200	22,800

^a The data were compiled from the Ref. [7].

^b The data were compiled from the Ref. [8].

^c The data were compiled from the Ref. [9].

It is well known that the semiconductor industry depends conventionally on perfluorocompounds (PFCs) or hydrofluorocarbon (HFCs) for CVD chamber cleaning. However, these human-made fluorine-containing compounds such as trifluoromethane (HFC-23), and perfluorocompounds (PFCs), including tetrafluoromethane (CF₄), hexafluoroethane (C₂F₆), octafluoropropane (C₃F₈), nitrogen trifluoride (NF₃) and sulfur hexafluoride (SF₆) are so effective absorbers of infrared (IR) radiation that even small amounts can lead to the global warming. Based on the 1995 scientific assessment of the Intergovernmental Panel on Climate Change (IPCC), these synthetically potent and persistent greenhouse gases (GHGs) were included in the Kyoto Protocol under the United Nations' Framework Convention on Climate Change (UNFCCC). Table 1 listed some atmospheric status and global warming properties for these non-CO₂ GHGs [7–9]. In Taiwan, the rapid growth of the semiconductor and thin film transistor liquid crystal display (TFT-LCD) manufacturing industries has resulted in the consumption of the large quantities of PFCs since the early 2000s. According to the surveys by the author, the annual consumption amounts of common PFCs for CF₄, SF₆ and NF₃ in Taiwan are about 240, 640 and 1,500 metric tons, respectively. It should be remarked that their atmospheric concentrations have increased over the past decades with a parallel trend [7], suggesting that the sources could be related to the production and industrial uses of PFCs and HFCs. Due to the goals of reducing these gases by the Kyoto Protocol, several specialty gases have been used as replacements for PFCs and HFCs. In this regard, ClF₃ has been introduced to the wafer fabrication processes for plasmaless cleaning of deposition chambers since the early 1990s. The primary advantage of ClF₃ over other gaseous PFCs (e.g., NF₃, SF₆, or CF₄) is that its high reactivity allows the maintenance operation to be accomplished at relative low temperatures without requiring plasma or high temperature heating to disassociate it for use during the cleaning process. Notably, this CVD cleaning has demonstrated the feature to prolong chamber component life and tool dismantling requirements without posing to the toxic gas leakage in the closed system. Because of its high etching rate, higher effectiveness, relatively easy storage (compared to fluorine) and no global warming potential, ClF₃ has been widely used as a fluorine source in the Asian semiconductor industry [5,10].

ClF₃ is a colorless, nonflammable, toxic and heavy gas with high reactivity and powerful oxidizing potential that make it especially applicable to the industrial processes. Currently, it is used primarily and increasingly as a cleaning gas of CVD chambers to phase out PFCs and HFCs, which are high global warming potential being eliminated under the Kyoto Protocol. On the other hand, ClF₃ is considered to be highly toxic based primarily on its corrosive effects on surfaces of contact. The damage caused by ClF₃ is derived from its diverse hydrolysis products [11], including mostly hydrogen fluoride (HF), chlorine (Cl₂), chlorine dioxide (ClO₂) and various oxyhalogen compounds. Thus it is extremely irritating to the respiratory tract and eyes. Among these highly reactive and toxic species, Cl₂, ClO₂ and HF are of the most concern because

of their occupational exposure limits such as the American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV). The exhausts containing ClF₃ and its probable decomposition products can be expected to pose the hazards to human health and the environment due to the exposure to the fluorides (as F⁻) excreted in the metabolic system and formed in the water environment.

On 28 July 2006, a large release of ClF₃ occurred in a Taiwan's semiconductor workshop, where this reactive gas was discharged from the loading area, causing the eye contact and inhalation by about ten people, of whom one injured [12]. Obviously, the hazards (e.g., toxic release) in semiconductor fabrication processes differ from those in the chemical process industries [13]. From the literature surveyed, only few researches have addressed the environmental chemistry of ClF₃ and its atmospheric implications in terms of high fluorosis risks due to its significant increase in the commercial uses, especially in the semiconductor industry [5]. Furthermore, scarcely addressed or reviewed in the literature was the published information on the hazards to occupational health and environmental risks of exposing to its probable decomposition products. The manuscript is based on the previous works that addressed the analysis of the environmental and health risk of SF₆ and NF₃ and their identified decomposition products [14,15]. This paper aimed at presenting reviews on the physicochemical properties and industrial applications of ClF₃, and its toxicity, health hazards, exposure limits and environmental implications. Because all ClF₃ decomposition products will be converted into fluorides in the discharged effluents and vented gases, the exposure to fluoride, being potential for causing fluorosis or chronic fluorine intoxication, and possible changes in environmental quality were also addressed in this paper.

2. Physicochemical properties of ClF₃

2.1. Physical properties

From the viewpoints of industrial applications, ClF₃ is the most important halogen fluorides because the compound is a powerful oxidizing agent like fluorine. In addition, ClF₃, which is a colorless heavy gas or a pale yellow liquid (boiling point about 285 K), offers an advantage over fluorine in that the former can be stored as liquid in container, suggesting that it can be shipped in steel cylinders under its own vapor pressure.

The information on the vapor pressure (*P*, kPa) of ClF₃ with temperature (*T*, K) was obtained from the literature [16,17], and given as follows:

$$\log_{10} P = 6.49201 - \frac{1096.917}{T - 40.41} \quad (226.16 \text{ K} < T < 303.16 \text{ K}) \quad (1)$$

$$\log_{10} P = 6.38984 - \frac{1048.94}{T - 45.5987} \quad (300 \text{ K} < T < 317 \text{ K}) \quad (2)$$

This property has been used to relate to the vapor hazard index (VHI) for volatile chemicals [18]. It is a measure of the vapor amount by which a saturated atmosphere would exceed its threshold limit value (TLV), which is devised by the American Conference of Governmental Industrial Hygienists (ACGIH). The data on the specific gravity, liquid density and the latent heat of vaporization of ClF_3 indicated the following characteristics: heavier than air as a gas, heavier than water as a liquid, and more easily vaporized than other important halogen fluorides such as bromine trifluoride and iodine pentafluoride [1].

On the other hand, ClF_3 is thermally stable, but it is liable to dissociate at elevated temperatures according to the following reaction:



The degree of dissociation is given as 1.7, 4.9, 11.9 and 50.0% at 523, 573, 623 and 733 K, respectively [19]. At temperature above 873 K, the dissociation is almost complete. Further, ClF_3 is nonflammable in air, but may form a flammable mixture with other flammable gases (e.g., dichlorosilane) as a result of accidental mixing in the CVD chamber [20]. It was found that the lower flammability limit (LFL) of a $\text{ClF}_3/\text{SiH}_2\text{Cl}_2/\text{N}_2$ mixture is 0.3 vol% for both ClF_3 and dichlorosilane (SiH_2Cl_2), which is lower than the LFL (i.e., 4.1%) of SiH_2Cl_2 in air [13]. It is very important because dichlorosilane (SiH_2Cl_2) is a flammable gas, which is used in the tungsten-silicon CVD process [20]. During the cleaning progress, the flammable gas (i.e., SiH_2Cl_2) should be first purged before introducing ClF_3 into the chamber. The explosion accident could be thus prevented by diluting all exhaust gases to ensure the concentration well below the LFL.

2.2. Chemical properties

Like fluorine, ClF_3 was used as a powerful oxidizing and fluorinating agent in a variety of industrial applications such as deep oil-well drilling, nuclear fuel processing and CVD chamber etching (cleaning) [1]. Under the proper conditions, it reacts vigorously with most organic compounds, nonmetals and all metals, indicating that the reactivity is the basis for its commercial uses in the semiconductor manufacturing industry. For example, tungsten and silicon materials react with ClF_3 at low-moderate temperature to form the volatile tungsten (VI) fluoride (WF_6) and tetrafluorosilane (SiF_4), respectively [5].

The most outstanding chemical property of ClF_3 is its highly corrosive nature due to its violent reaction with water. Depending on the $\text{ClF}_3/\text{H}_2\text{O}$ ratio [11,21,22], their hydrolysis reaction products include hydrogen fluoride (HF) along with oxygen (O_2), chlorine (Cl_2), chlorine monofluoride (ClF), chlorine hypofluoride (ClOF), chloryl fluoride (ClO_2F), perchloryl fluoride (ClO_3F), chlorine dioxide (ClO_2), and oxygen difluoride (OF_2), depending on the reaction conditions and the concentration of the reactants (especially moisture).

3. Commercial uses of ClF_3 in the semiconductor industry

In the manufacture of semiconductor devices using thin films such as integrated circuit (IC), thin film transistor (TFT) or solar cells, various film materials (products), including silicon dioxide (SiO_2), silicon nitride (Si_3N_4), polysilicon, tungsten (W), or tungsten silicide (WSi_2), are deposited on silicon wafers using chemical vapor deposition (CVD) processes such as low-pressure CVD (LPCVD) and plasma-enhanced CVD (PECVD). The common deposition gases used to form these film materials are silane (SiH_4), dichlorosilane (SiH_2Cl_2), and tungsten hexafluoride (WF_6). In general, the CVD system includes the following components: reaction (process) chamber, gas supply (control) cabinet, heat source for substrates,

exhaust handling system (vacuum pump and gas treatment units), and time and sequence control system. With respect to the core CVD equipment, the following components are found in the process chamber: process tube, wafer board, and heating elements. During the wafer film deposition process, the film material is inevitably deposited on the CVD chamber and will further accumulate within the inside walls of the exhaust system, causing wafer contamination and device malfunction. As a result, the CVD tools must be periodically cleaned to eliminate the deposits and to improve the system reliability.

Traditionally, the dry method is performed to clean CVD systems by plasma etching using halogen-containing compound as the etching gas. Based on the generation of plasma by a radio frequency power (RF) technique in a gas at low pressure, the main principle of cleaning is to react with and remove the residual deposits adhering to the chamber system using the free radicals thus ionized. Because of their unique chemical properties (stable compounds) and low impact on labor health (low toxicity), the common used cleaning gases are HFCs such as HFC-23, and PFCs, including CF_4 , C_2F_6 , C_3F_8 , NF_3 and SF_6 . Although the plasma (*in situ*) cleaning method can be operated without disassembling the process chamber, it encounters some problems regarding environmental and occupational issues as follows [23]:

- These cleaning gases have significant values of global warming potential (GWP) and long lifetimes in the atmosphere.
- Besides NF_3 , this chamber cleaning process is low-yield reactions due to the difficult decomposition. Thus, most of these gases are released into the exhaust gas treatment system and then vented to the atmosphere.
- It is not suitable to clean the thermal CVD systems because a plasma generation system is necessary in the CVD equipment.
- It may cause serious damage to the CVD components due to the induction effects by plasma.
- It cannot clean the residual deposits on the backside of the RF electrode and on the inside walls of the exhaust venting pipes.

Therefore, the semiconductor industry in Asian countries (especially in Japan) conducted the research to find suitable alternative chemicals using the highly reactive fluorine-containing gases for *in situ* chamber cleaning of CVD systems since the 1980s [5,10]. Since 1993, the application of ClF_3 for plasmaless dry cleaning of LPCVD and PECVD reactors has been used successfully in most Japanese companies. It should be remarked incidentally that ClF_3 effectively reacts with non-volatile solid materials such as silicon and tungsten, thus forming volatile fluorinated and chlorinated reaction products that are further pumped to an exhaust abatement system prior to the vent to the atmosphere. In brief, ClF_3 has the following advantages [24]:

- Sufficient capacity to etch a wide range of deposits or coatings.
- Increase of CVD tool productivity because of high etching rate and *in situ* chamber cleaning.
- Low temperature process to clean all the parts used in the CVD systems.
- No release of high GWP gases compared to the typical used PFCs such as CF_4 , C_2F_6 and NF_3 .

4. Toxicity, health hazards and exposure limits of ClF_3

As mentioned above, ClF_3 is a highly reactive and corrosive substance due to its violent hydrolysis and powerful oxidizing potential. Therefore, the toxicity of ClF_3 is based primarily on its corrosive effects on surface of contact, suggesting that precautions and preventive measures should be taken to avoid inhalation of

its vapors, or to contact with skin or eye. The harmful damage caused by ClF_3 can be attributed to a variety of hazardous hydrolysis products, which may form in varying proportions in the humid atmosphere [11]. Of these decomposition products, Cl_2 , HF and ClO_2 are of concern mainly due to their high toxicity to most living organisms. With respect to its effects of short exposure, ClF_3 is corrosive to eyes, the skin and the respiratory tract. It is highly irritating to the respiratory tract, including the mouth, nose, throat, and lower airways. Coughing, sneezing and burning sensation are early symptoms by inhalation exposure of ClF_3 . Prolonged exposure to the corrosive action of ClF_3 may result in painful red burns, attack bone selectively, stimulate pain nerves and cause a potentially lethal poisoning from lung (pulmonary) edema. As demonstrated by Dost et al. [11], the inhalation toxicity of ClF_3 on animals has been found that 800 ppm ClF_3 is lethal to rats in exposures of 15 min or more. In earlier similar experiments, Darmer et al. [25] studied the acute toxicity of exposures of animals to the fluorinated oxidizers and HF, showing that ClF_3 was found to be far less toxic than oxygen difluoride (OF_2), only around half as toxic as chlorine pentafluoride (ClF_5), and about three to eight times as toxic as HF based on the LC_{50} values (60-min exposure toxicity data). The LC_{50} values for ClF_3 showed to be 299, 178 and 230 ppm for rats, mice and monkeys, respectively [25]. Regarding its chronic toxicity, ClF_3 had no carcinogenic, reproductive, teratogenic, or mutagenic characteristics.

Due to its highly chemical reactivity, it is expected that ClF_3 should have significant health effects on human and has been recognized as physiologically toxic. Inhalation is the primary exposure pathway for ClF_3 . Thus, its occupational exposure limit (OEL) or workplace exposure limit (WEL) has been set to be at 0.1 ppm (ceiling) by the countries such as USA and Taiwan, meaning that the concentration limit should not be exceeded even instantaneously. Also, the chemical substance that is given a TLV-C is predominantly fast-acting and requires a ceiling in response to this character. On the other hand, limits for occupational exposure are complemented by limits for emergency exposure. The common used emergency exposure limits, defined by various organizations (especially in USA), include the following:

4.1. Immediately dangerous to life and health (IDLH)

According the description in 29 CFR 1910.120, the U.S. National Institute for Occupational Safety and Health (NIOSH) of the Occupational Safety and Health Administration (OSHA) defines an IDLH value in their hazardous waste operations and emergency response regulation as “An atmospheric concentration of any toxic, corrosive or asphyxiant substance that poses an immediate threat to life or would cause irreversible or delayed adverse health effects or would interfere with an individual’s ability to escape from a dangerous atmosphere.” After examining the physicochemical property, toxicity, production volume, likelihood of release, and accident history, the US Environmental Protection Agency (EPA) selected the IDLH values as the level of concern (LOC) for determining threshold quantities involving the Risk Management Program (RMP) [26].

4.2. Acute exposure guideline levels (AEGLs)

In 1980s, the US EPA commissioned the National Research Council to develop a community exposure guidance levels (i.e., AEGLs) for short-term exposures to airborne concentrations of acutely toxic, high priority chemicals [27]. Therefore, AEGLs represent threshold exposure limits for the general public and are applicable to emergency exposure periods ranging from 10 min to 8 h. The three AEGLs have been defined as follows:

- AEGL-1: It is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic nonsensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.
- AEGL-2: It is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.
- AEGL-3: It is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

4.3. Emergency response planning guideline (ERPG)

An ERPG, published by the American Industrial Hygiene Association (AIHA), is the maximum airborne concentration below which, it is believed nearly all individuals could be exposed for up to 1 h without experiencing or developing certain defined effects. Further, three ERPGs are established based on the defined effects:

- ERPG-1: Effects other than mild transient adverse health effects or perception of a clearly defined objectionable odor.
- ERPG-2: Irreversible or other serious health effects or symptoms that could impair an individual’s ability to take protective action.
- ERPG-3: Life threatening health effects.

For ClF_3 , its emergency exposure limits are listed as follows:

NIOSH IDLH	20 ppm
AIHA ERPGs	ERPG-1 = 0.1 ppm
	ERPG-2 = 1 ppm
	ERPG-3 = 10 ppm
EPA AEGLs (60 min)	AEGL-1 = 0.12 ppm
	AEGL-2 = 2.0 ppm
	AEGL-3 = 21 ppm

It should be noted, however, that eye and upper respiratory tract irritation and lung damage are the critical effects on which the TLV of ClF_3 is based, implying that it may occur under the respiratory overexposure through inhalation routes.

5. Health hazards of ClF_3 decomposition/hydrolysis products

As summarized above, the main hazards of ClF_3 include: (1) it is a vigorous fluorinating agent and also unstable when it is exposed to easily fluorinated materials; (2) it reacts with water to produce HF and various oxyhalogen compounds, which are also unstable and toxic; (3) its hydrolysis products are liable to generate acids, which can be very corrosive and toxic.

5.1. Chemical and physical information on ClF_3 decomposition/hydrolysis products

ClF_3 is a highly reactive (oxidizing), toxic, and corrosive liquefied gas at typical storage temperature. This means that its fate is most likely to sink in the aqueous or moist environment under normal conditions. In the vapor phase, ClF_3 may thermally decompose and/or hydrolyze to ClF , Cl_2 , F_2 , ClOF , ClO_2F , ClO_3F , ClO_2 , HCl , and HF, depending on the relative ratio of water to ClF_3 . It should be noted, however, that its decomposition products, probably produced by electrical and thermal decomposition of ClF_3 in the presences of other molecules (e.g., H_2O), are all toxic and even corrosive. Of these products, HF, Cl_2 and ClO_2 are probably of significant concern because they have a major impact on the respiratory system.

Table 2
Health hazards of ClF_3 and its probable decomposition/hydrolysis products.

Compound	Health hazard rating ^a	TLV basis-critical effect(s) ^b	TLV-TWA
Chlorine trifluoride (ClF_3)	4	Eye and upper respiratory tract irritation; lung damage	0.1 ppm (Ceiling)
Chlorine (Cl_2)	4	Upper respiratory tract and eye irritation	0.5 ppm (TWA)
Chlorine dioxide (ClO_2)	4	Lower respiratory tract irritation; bronchitis	0.1 ppm (TWA)
Fluorine (F_2)	4	Upper respiratory tract, eye and skin irritation	1 ppm (TWA)
Hydrogen chloride (HCl)	3	Upper respiratory tract irritation	2 ppm (Ceiling)
Hydrogen fluoride (HF)	4	Upper/lower respiratory tract, skin and eye irritation; fluorosis	0.5 ppm (TWA)
Oxygen difluoride (OF_2)	4	Headache; pulmonary edema; upper respiratory tract irritation	0.05 ppm (Ceiling)
Perchloryl fluoride (ClO_3F)	4	Upper/lower respiratory tract irritation; methemoglobinemia; fluorosis	3 ppm (TWA)

^a Rating: 4 = severe hazard, 3 = serious hazard.

^b The data are from the reference [31].

Therefore, HF, HCl and Cl_2 have been categorized as hazardous air pollutants in the US Clean Air Act Amendments (CAAA) of 1990. It should be noted that some decomposition products such as WF_6 and SiF_4 may be produced from the reaction of ClF_3 with materials deposited on wafer chambers.

5.2. Health hazards

In general, the decomposition/hydrolysis products of ClF_3 are soluble in the aqueous system. Like ClF_3 , some of them are easily hydrolyzed to form HF, ClO_2 and ClO_x^- anions [22]. For example, perchloryl fluoride (ClO_3F), one of the hydrolysis products of ClF_3 , is thermally stable and chemically inert [28,29], but will hydrolyze aqueous solutions to give HF and ClO_4^- . Therefore, all of the ClF_3 decomposition products are gases and have very high solubility and/or reactivity in water and humid air at room temperature. In a word, they are likely to remain in water and atmospheric air as fluorides, which may exist in the forms of hydrogen fluoride, fluoride ion, and hydrofluoric acid. Table 2 summarized health hazards of ClF_3 and its probable decomposition products [30,31]. These toxic decomposition products are similar in health hazards because of the chemical properties in the highly acidic nature and the reactivity in the physiological effects. These gaseous decomposed chemicals irritate the respiratory system and skin and/or eye contact. Thus, the inhalation of relatively low concentration of these gases and vapors will cause an unpleasantness, and pungent sensation, followed by a feeling of suffocation, cough, and a sensation of constriction in the chest. However, the toxicity of these decomposition products varies extensively. Some of these products from the reaction of ClF_3 with water are flammable and even more toxic than ClF_3 (Table 2). Oxygen difluoride (OF_2), a toxic product probably produced under an open flame or spark, is a strong irritant to the entire respiratory tract and causes acute lung injury (pulmonary edema) due to its hydrolysis in contact with water, producing HF or fluorides. The lethal effect of chlorine dioxide (ClO_2), another terminal product of ClF_3 hydrolysis, is similar to that of ClF_3 on a chlorine equivalent basis [11].

5.3. Exhaust and abatement system for meeting occupational exposure limit

Due to its applications in the semiconductor manufacturing industries, ClF_3 is expected to pose a high health risk for human. The accidental cases resulting from its spill or leakage were reported [12,13]. Furthermore, the extreme reactivity of ClF_3 may produce many hazardous products. Thus, on the basis of the American Conference of Governmental Industrial Hygienists (ACGIH, USA)-threshold limit value (TLV), the occupational exposure limits of some decomposition/hydrolysis products (including Cl_2 , ClO_2 , F_2 , HF, HCl, OF_2 and ClO_3F) have been established, as listed in Table 2. Although the occupational exposure limit (OEL) is not commonly used as a relative index of toxicity for chemicals, the information is

the most common and useful guideline for determining their safe levels in order to adopt adequate protection system and handling procedures. Based on the TLV values in Table 2, oxygen difluoride (OF_2) is of the most concern because of its high toxicity. Accordingly, its current occupational concentration standard for human exposure in air should not exceed 50 parts per billion (ppb) during any part of the working exposure (i.e., ceiling).

It is remarked that fabrication of highly integrated circuits or wafer is presently accomplished with mostly halogen compounds containing etching and cleaning gases being used and thus produced. These corrosive and toxic gases emitted from the process chamber and even diffused into the clean room pose high health risks for wafer fabrication workers. In practice, point-of-use (POU) abatement system [32], which may include wet scrubbing, oxidation, cold bed, hot bed, reactor, and recycle or reclaim system, is often used to minimize the overall environmental, health and safety impacts of various semiconductor processes, including deposition and etch [32]. POU devices are designed to remove the toxic contaminants before they enter the centralized exhaust system for the purpose of increasing production uptime and protecting fabrication equipments and personnel health/safety. To safely and efficiently treat all exhaust gases from deposition/cleaning processes and prevent these toxic gases from contaminating the clean room and exhaust system, a POU abatement system or customer-designed ventilation system should be designed and installed with excellent exhaust management and wet scrubbing technologies because the unreacted ClF_3 and deposition gases along with their decomposition reaction products present occupational safety and hygiene concerns [33]. In the POU wet scrubbing system by design with packed bed, venturi, or spray tower, the halogenated gases to be scrubbed will react the chemicals in the scrubbing solution (e.g., chlorine will react with a calcium hydroxide or sodium hydroxide solution) to form stable solids (i.e., CaCl_2 or CaF_2) or salts [5].

6. Environmental implications of ClF_3

6.1. Environmental risk of fluoride exposure

On first insight and the description discussed above, ClF_3 and its decomposition products are gases and have very high solubility and/or reactivity in water and humid air at room temperature; therefore, they are likely to remain in water and atmospheric air as fluorides, which may exist in the forms of hydrogen fluoride, fluoride ion, and hydrofluoric acid. It is well known that hydrogen halides are relatively toxic gases. The most concerned of these gases is hydrogen fluoride (HF) or fluoride (as F^-) because it is an extreme irritant to any part of the human body that they contact, causing ulcers in affected area of the upper respiratory tract as well as pulmonary edema and even fatality at high levels [34]. Therefore, acute exposures to HF or fluoride ions (F^-) cause local damage to reddening and burning of the skin and mucous membranes in the

Table 3
Occupational exposure limits of ClF₃ and common PFCs used in the semiconductor industry.

ClF ₃ and PFCs	TLV ^a	PEL ^b	MAK ^c	PCS ^d	TLV basis ^a
Chlorine trifluoride (ClF ₃)	0.1 ppm (Ceiling)	0.1 ppm (Ceiling)	0.1 ppm	0.1 ppm (Ceiling)	Eye and upper respiratory tract irritation; lung damage
Nitrogen trifluoride (NF ₃)	10 ppm	10 ppm	– ^e	10 ppm	Methemoglobinemia; liver and kidney damage
Sulfur hexafluoride (SF ₆)	1000 ppm	1000 ppm	1000 ppm	1000 ppm	Asphyxia

^a Threshold limit value (ACGIH, USA).

^b Permissible exposure limit (OSHA, USA).

^c Maximum allowable concentration (DFG, German).

^d Permissible Concentration Standard, Council of Labor Affairs (Taiwan).

^e Not available.

eyes, nose and respiratory tract [30]. On the other hand, they will lead to changes in the skeletal system and in the teeth after chronic exposures, causing fluorosis, which is characterized by bone abnormalities (i.e., osteoporosis, or decalcification of the bones) and mottled, soft teeth. Generally, the most significant pathway to exposure to all sources of fluoride is via ingestion [35], including fluoridated public drinking water, soft drinks and fruit juices (beverages), infant formula, cow's milk, foodstuffs, fluoride supplement tablets, and incidental ingestions of soil (by children) and toothpaste containing fluoride. Although atmospheric air was considered as only a small fraction of total fluoride exposure sources, the fluoride concentration in the workplace environment could be elevated from accidental leaks and/or spills from the industrial processes using ClF₃ as processing gases.

6.2. Environmental implications of reducing potent greenhouse gases emissions

Perfluorocompounds (PFCs) gases such as CF₄, C₂F₆, C₃F₈, NF₃ and SF₆ are used extensively in the semiconductor manufacturing processes, as an *in situ* process gas for cleaning CVD chambers. Due to their unique properties about the radiative efficiency, atmospheric lifetime and 100-year time horizon GWP [7], PFCs except NF₃ have been considered as one of the six target GHGs under the Kyoto Protocol of the United Nations' Framework Convention on Climate Change (UNFCCC) in 1997. According to the commission by the World Semiconductor Council (WSC), the semiconductor industry associations of EU, Japan, Korea, USA, and Taiwan, committed in 1999 to reduce the emissions of PFCs to 10% below their respective baseline levels by 2010. One of the best strategies for reducing the emissions is to search for environmentally friendly alternatives for PFCs in CVD chamber cleaning applications. As mentioned above, ClF₃ provides a dry, nonplasma alternative for chamber cleaning and has been used successfully in Asian countries since the mid-1990s. Also, this alternative proves to be especially effective for etching single-crystalline silicon and silicon nitride film chamber cleans in highly integrated devices, thus eliminating the emissions of potent greenhouse gases from these chambers.

Due to its high reactivity, ClF₃ has significant health risks on human and has been recognized as physiologically toxic. Thus, its occupational exposure limit (OEL), as described above, has been set at 0.1 ppm (ceiling), listed in Table 3. By contrast with ClF₃, most of the PFCs have extremely attractive properties, particularly non-flammability, non-corrosiveness, very low-toxicity and non-ozone depleting. As listed in Table 3, it is significant that the OEL of SF₆ set at 1000 ppm is the same to the exposure guidance level of hydrofluorocarbons (HFCs) by the American Industrial Hygiene Association (AIHA)-Workplace Environmental Exposure Level (WEEL), including HFC-32, HFC-125, HFC-134a, HFC-143a, HFC-152a, HFC-227ea and HFC-236fa [36]. It should be noted, however, that NF₃ has been demonstrated to induce the production of methemoglobin, which will reduce the level of oxygen transferred to the body tissues [37]. As a result, its OEL has been set at 10 ppm based on 8-h time-weighted average (TWA).

7. Conclusions

Chlorine trifluoride (ClF₃) is a widely used specialty gas in replacement of perfluorocompounds (PFCs) gases such as CF₄, C₂F₆, C₃F₈, NF₃ and SF₆, which are currently committed by the World Semiconductor Council (WSC) for reducing their emissions. Though ClF₃ addressed in this paper has no global warming potential, the inorganic gas poses some environmental and health hazards on the basis of the updated data on the powerful reactivity and high toxicity. Furthermore, it should be cautious of using ClF₃ since the accidental cases have been reported from acute poisoning. Under the conditions such as electrical discharge, hydrolysis, and combustion, the toxic decomposition products from ClF₃ may include ClF, Cl₂, F₂, ClOF, ClO₂F, ClO₃F, ClO₂, HCl, and HF. With respect to the protection of the environmental quality and of human health, the emissions of inorganic vapors containing ClF₃ and its toxic decomposition species in the wafer fabrication processes still need to be further exhausted and abated to reduce the non-occupational and occupational exposure risks. As reviewed in the paper, the atmospheric implications of reducing potent greenhouse gases emissions are significant. However, to meet a demand for a variety of industrial uses, ClF₃ would have more significant impacts on the environmental quality and human health in the future because of its rampant production and fluorides thus produced as by-products.

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