TECHNICAL SUPPORT DOCUMENT FOR PROCESS EMISSIONS FROM ELECTRONICS MANUFACTURE (e.g., MICRO-ELECTRO-MECHANICAL SYSTEMS, LIQUID CRYSTAL DISPLAYS, PHOTOVOLTAICS, AND SEMICONDUCTORS):

PROPOSED RULE FOR MANDATORY REPORTING OF GREENHOUSE GASES

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Office of Air and Radiation

U.S. Environmental Protection Agency

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1 Source Description

The electronics industry uses multiple long-lived fluorinated greenhouse gases (fluorinated GHGs), as well as nitrous oxide (N_2O) during manufacturing of electronic devices, including, but not limited to, liquid crystal displays (LCDs), micro-electro-mechanical systems (MEMS), photovoltaic cells (PV), and semiconductors (including light-emitting diodes (LEDs)[1]). Fluorinated GHGs are used mainly for plasma etching of silicon materials, cleaning deposition tool chambers, and wafer cleaning, but may be used in other types of electronics manufacturing processes. Besides dielectric film etching and chamber cleaning, much smaller quantities of fluorinated GHGs are used to etch polysilicon films and refractory metal films like tungsten. Additionally, some electronics manufacturing equipment may employ fluorinated GHG liquids as heat transfer fluids (HTFs). The most common fluorinated GHGs in use are trifluoromethane (HFC-23 or CHF_3), perfluoromethane (CF_4), perfluoroethane (C_2F_6), nitrogen trifluoride (NF_3), and sulfur hexafluoride (SF_6), although other compounds such as perfluoropropane (C_3F_8) and perfluorocyclobutane ($c\text{-}C_4F_8$) are also used (EPA, 2008a). Table 1-1 presents examples of fluorinated GHGs known to be used during manufacture of different types of electronics. N_2O, another GHG used in the manufacture of electronics, is used in depositing certain films and other manufacturing processes.

Table 1-1. Selected Fluorinated Greenhouse Gases Used by the Electronics Industry

Product Type	Fluorinated GHGs Used During Manufacture
Semiconductor	CF_4, C_2F_6, C_3F_8, $c\text{-}C_4F_8$, $c\text{-}C_4F_8O$, C_4F_6, C_5F_8, CHF_3, CH_2F_2, NF_3, SF_6, and HTFs.[a]
MEMS[b]	CF_4, $c\text{-}C_4F_8$, and SF_6
LCD	CF_4, CHF_3, $c\text{-}C_4F_8$, NF_3, and SF_6
PV	CF_4, C_2F_6, CHF_3, C_3F_8, NF_3, SF_6

[a] For commonly used heat transfer fluids please refer to the U.S. EPA report entitled "Uses and Emissions of Liquid PFC Heat Transfer Fluids" available at: http://www.epa.gov/semiconductor-pfc/documents/pfc_heat_tranfer_fluid_emission.pdf.
[b] IPCC guidelines do not specify the fluorinated GHGs used by the MEMS industry. Literature reviews revealed that among others, CF_4, SF_6, and the Bosch process (e.g., Bosch process consists of alternating steps of SF_6 and C_4F_8) are used to manufacture MEMS.
Source: IPCC, 2006; Lyshevshi, S., 2001; Gaitan, M. & Takacs, M., 2008.

The electronics manufacture source category consists of the five production processes described below.

- The etching process uses plasma-generated fluorine atoms and other reactive fluorine-containing fragments, which chemically react with exposed thin-films (e.g., dielectric, metals) or substrate (e.g., silicon), to selectively remove the desired portions of the material. The material removed, as well as undissociated fluorinated gases, flow into waste streams and, unless abatement systems are employed, into the atmosphere.

- Chambers used for depositing dielectric films are cleaned periodically using plasma-generated fluorine atoms and other reactive fluorine-containing fragments and other gases, such as N_2O. During the cleaning cycle the gas is converted to fluorine atoms in plasma, which etches away residual material from chamber walls, electrodes, and chamber hardware. Undissociated fluorinated gases and other products pass from the chamber to waste streams and, unless abatement systems are employed, are emitted into the atmosphere.

- During wafer processing, any residual photoresist material can be removed through an ashing process, which consists of placing partially processed wafers in an oxygen plasma to which CF_4 may be added. The edges of wafers (the bevel) may also require cleaning to remove yield-reducing residual material. Bevel cleaning may also use a plasma process with fluorinated GHG chemistry. In both of these wafer cleaning processes, unused fluorinated GHGs are emitted unless abated.

- Deposition is a fundamental step in the fabrication of a variety of electronic devices. During deposition, layers of dielectric, barrier, or electrically conductive films are deposited or grown on a wafer or other substrate. Chemical vapor deposition (CVD) enables the deposition of dielectric or metal films. During the CVD process, gases that contain atoms of the material to be deposited react on the wafer surface to form a thin film of solid material. Films deposited by CVD may be silicon oxide, single-layer crystal epitaxial silicon, amorphous silicon, silicon nitride,

[1] LEDs are a semiconductor light source. When a LED is switched on electrons are able to recombine with holes within the device, releasing energy in the form of light whose color is governed by the nature of the semiconductor. Many LEDs are manufactured on a wafer (usually different than silicon) using methods that are similar to the manufacture of integrated circuits.

dielectric anti-reflective coatings, low-k dielectric, aluminum, titanium, titanium nitride, polysilicon, tungsten, refractory metals or silicides. N_2O may be the oxidizer of choice during deposition of silicon oxide films.

- Additionally, fluorinated GHG liquids are frequently used as HTFs at semiconductor facilities to cool process equipment, to control temperature during device testing, to clean substrate surfaces and other parts, and for soldering, and their high vapor pressures can lead to evaporative losses during use (EPA, 2008b; IPCC, 2006). Other electronics manufacturing facilities may also employ HTFs for similar uses. HTFs commonly used in electronics manufacturing include those sold under the trade names "Galden®" and "Fluorinert™."

1.1 Total U.S. Emissions

Emissions of fluorinated GHGs from 216 electronics manufacturing facilities were estimated to be 6.0 Tg CO_2e in 2006. Below is a breakdown of emissions by electronics product type.

- Semiconductor: Emissions of fluorinated GHGs, including emissions from the use of HTFs, from 175 facilities were estimated to be 5.74 Tg CO_2e in 2006 (EPA, 2008a; Burton, C.S., & Beizaie, R., 2001; ITRS, 2008; SEMI, 2008; VLSI Research, Inc., 2008).[2] Of the total semiconductor emissions 5.19 Tg CO_2e are from etching/chamber cleaning at full-scale facilities and 0.55 Tg CO_2e are from HTF usage from all facilities.[3] Only etching/cleaning emissions from full-scale facilities are accounted for in the *U.S. Inventory of GHG Emissions and Sinks* (EPA, 2008a). Partners of the *PFC Reduction/Climate Partnership for Semiconductors* comprise approximately 80 percent of U.S. semiconductor production capacity. These Partners have committed to reduce their emissions (exclusive of HTF emissions) to 10 percent below their 1995 levels by 2010, and their emissions have been on a general decline toward attainment of this goal since 1999.

- MEMS: Emissions of fluorinated GHGs from 12 facilities were estimated to be 0.15 Tg CO_2e in 2006 (SEMI, 2008.[4]

- LCD: Emissions of fluorinated GHGs from 9 facilities were estimated to be 0.02 Tg CO_2e in 2006 (DisplaySearch, 2007).[5]

- PV: Emissions of fluorinated GHGs from 20 PV facilities were estimated to be 0.07 Tg CO_2e in 2006 (Burton, 2006; Roedern, B.V. & Ullal, H.S., 2008; Earth Policy Institute, 2007).[6]

1.2 GHGs to be Reported

EPA is requiring the electronics industry to report emissions and consumption from the following processes and activities:

- Fluorinated GHGs emitted from plasma etching.
- Fluorinated GHGs emitted from chamber cleaning.
- Fluorinated GHGs emitted from wafer cleaning.
- N_2O emitted from chemical vapor deposition or other electronics manufacturing processes.
- Fluorinated GHGs emitted from use of HTFs.

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[2] Total semiconductor facilities include both full-scale, pilot, and R&D facilities.

[3] All full scale facilities are assumed to have the same utilization.

[4] The estimated total number of MEMS facilities in the U.S. is an underestimate. The estimate was based on the World Fab Watch database, which provides an incomplete listing of total U.S. MEMS facilities (SEMI, 2007).

[5] Estimated total LCD facilities include LCOS, a-Si TFT-LCDs, OLEDs (assuming active matrix), HTPS, TFT, Single Crystal AMLCD, LTPS facilities. Where, TFT = Thin Film Transistor; LCOS = Liquid Crystal on Silicon; a-Si = amorphous silicon; OLED = Organic Light Emitting Diode; HTPS = High Temperature Polysilicon; and AMLCD = Active Matrix Liquid Crystal Display.

[6] Estimated total PV facilities includes only silicon based PV facilities (both crystalline and amorphous silicon based PV facilities are included).

- Consumption of all fluorinated GHGs and N_2O, including gases used for manufacturing processes other than those listed above.
- CO_2, CH_4, and N_2O combustion emissions from stationary combustion units by following the requirements of 40 CFR part 98, subpart C (General Stationary Fuel Combustion Sources).[7]

2 Options for and Selection of Reporting Threshold

2.1 Options Considered for Reporting Thresholds

EPA evaluated a range of emissions threshold options for electronics manufacturing facilities.[8] This range included emissions thresholds of 1,000, 10,000, 25,000, and 100,000 metric tons CO_2e per year for each type of electronics device manufacturing facility. Table 2-1 shows these emissions-based threshold options and the number of electronics manufacturing facilities that are expected to be captured by the respective emissions thresholds. EPA selected 25,000 metric tons CO_2e per year threshold, which covers 44 percent of electronics manufacturing facilities and 94 percent of the industry's national emissions, thereby maximizing emissions reporting while excluding small facilities that do not contribute significantly to the overall GHG emissions.

Table 2-1. Emissions-Based Threshold for Electronics Manufacture (1,000, 10,000, 25,000 and 100,000 Mt CO_2e)

Emission Threshold Level (Metric tons CO_2e/yr)	Total National Emissions ($MtCO_2$e)	Total National Facilities	Emissions Covered		Facilities Covered	
			Metric tons CO_2e/yr	Percent	Facilities	Percent
1,000	5,984,463	216	5,962,091	99.6%	165	76%
10,000	5,984,463	216	5,813,200	97%	114	53%
25,000	5,984,463	216	5,622,570	94%	94	44%
100,000	5,984,463	216	4,737,622	79%	55	26%

Table 2-2 shows the estimated emissions that would be covered and number of facilities that would report for each type of electronics manufacturing facility; semiconductors, MEMS, LCD, and PV, under the 25,000 metric tons CO_2e emissions-based threshold. The emissions-based threshold is estimated to include approximately 50 percent of facilities that manufacture semiconductors and approximately 17 percent and 5 percent of the facilities manufacturing MEMS and PV, respectively. At the same time, the threshold is expected to cover 96 percent of fluorinated GHG emissions from facilities that manufacture semiconductors, 66 percent of fluorinated GHG emissions from facilities manufacturing MEMS, and 47 percent of fluorinated GHG emissions from facilities manufacturing PVs.

[7] On-site combustion emissions from electronics manufacturing facilities are not addressed within this document; please see the Technical Support Document for Stationary Combustion (EPA-HQ-OAR-2008-0508-046) for more information.

[8] For more details on the subpart I threshold analysis, please see the Subpart I Detailed Threshold Analysis available in the docket, EPA-HQ-OAR-2009-0927.

Facilities that manufacture LCDs are not expected to meet the 25,000 Mt CO_2e threshold; however, the information available and used in the analysis at this time is limited and incomplete. Facilities that manufacture LCDs are nonetheless covered by the rule because they use similar fluorinated GHG and N_2O manufacturing processes as semiconductor manufacturing, and because emissions are expected to increase due to high growth in the LCD manufacturing.

As part of this analysis, EPA also evaluated facilities that manufacture LEDs in the US. There are only a few facilities that manufacture LEDs in the US; however, the data that was used at this time is dated, limited, and incomplete. With a strong demand for energy efficient lighting, LED manufacturing is poised for high growth in the coming years. According to recent industry trade association reports, LED manufacturing is expected to grow significantly. "LED and solid state lighting (SSL) are two markets in the spotlight that attract a lot of attention and new investments. Driven mostly by the surge of LED-backlight demand for LCD TV panels and the huge potential market in general lighting, demand for LED is set to explode in the coming years. In view of supply tightness and market potential, new facility and capacity addition plans have suddenly emerged all over the world in the past year." (Tsang, Clark, 2010). Therefore production processes used to manufacture LEDs are covered under the electronics manufacturing source category as one specific type of semiconductor device.

Table 2-2. Rule Applicability under the Proposed Emissions-Based Thresholds

Emissions Source	Threshold	Total National Facilities	Total Emissions of Source (metric tons CO_2e)	Emissions Covered		Facilities Covered	
				metric tons CO_2e/yr	Percent	Facilities	Percent
Semiconductors	25,000 Mt CO_2e.	175	5,741,676	5,492,066	96%	91	52%
MEMS	25,000 Mt CO_2e	12	146,115	96,164	66%	2	17%
LCD	25,000 Mt CO_2e	9	23,632	0	0%	0	0%
PV	25,000 Mt CO_2e.	20	73,039	34,340	47%	1	5%

2.2 Emissions-Based Threshold Calculations

Emissions-based threshold estimations for each electronics manufacturing sector were derived in the following ways:

Semiconductors emissions-based threshold estimations were derived using outputs from the EPA PFC Emissions Vintaging Model (PEVM), as well as EPA PFC Reduction/Climate Partnership for Semiconductors partner and non-partner shares of U.S. emissions. Additionally, the semiconductor emissions threshold estimations determined accounted for heat transfer fluid emissions by assuming that these emissions were equivalent to 11 percent of total clean and etch emissions at a facility.

MEMS emissions-based threshold estimations were derived using an emission factor developed by EPA. EPA estimated an emission factor because no IPCC Tier 1 default emission factor exists. Assuming that MEMS are manufactured using the Bosch etching process, the utilization of SF_6 in the production of MEMS was assumed to be the same as the utilization of SF_6 in the etching of semiconductors due to the similarity between both of the manufacturing processes.[9] However, because SF_6 is used in only about 20 percent of semiconductor processes, the majority of which are etching processes, and

[9] Although the Bosch etching process uses both SF_6 and C_4F_8, C_4F_8 was not included because it has a high utilization rate (i.e., a high fraction of C_4F_8 is dissociated during the etching or cleaning process).

it is assumed in this analysis that SF_6 is used in all MEMS processes, the 2006 IPCC Tier 1 SF_6 semiconductor emission factor (per area of substrate) was multiplied by five to estimate the MEMS emission factor per area of substrate. Additionally, the MEMS emission factor was scaled up by an additional factor of 1.2 to account for increased SF_6 usage in MEMS manufacturing as compared to semiconductor manufacturing .

LCD and PV emissions-based threshold estimations were derived using 2006 IPCC Tier 1 emission factors.

Emissions reductions from the use of abatement systems were not accounted for in the any of the threshold analyses.

2.3 Reporter Threshold Applicability Determinations

Presented below are the methods reporters are required to use to determine whether their electronics manufacturing facility(ies) meets or exceeds the threshold of 25,000 metric tons CO_2e.

Facilities that Manufacture Semiconductor and LCD: To determine whether a facility that manufactures semiconductors (including LEDs) or LCDs meets the threshold, the facility would use the IPCC Tier 1 approach and IPCC Tier 1 emission factors. To account for heat transfer fluid use at semiconductor facilities, a facility would add an additional 10 percent of their clean and etch emissions to their total facility emissions.[10]

Facilities that Manufacture MEMS: To determine whether a facility that manufactures MEMS meets the threshold, the facility would use the IPCC Tier 1 approach and the EPA estimated emission factor for MEMS.

Facilities that Manufacture PV: To determine whether a facility that manufactures PV meets the threshold, the facility would multiply annual fluorinated GHG purchases or consumption by the gas-appropriate 100-year GWPs (as defined in Table A-1 to subpart A of part 98). This method for PV facilities is expected to provide a more representative estimate of emissions than the IPCC Tier 1 approach and emission factors. IPCC Tier 1 factors for PV are highly uncertain because they were developed based on analogy to the IPCC Tier 1 factors for LCD due to limited PV data availability.

Calculations to determine threshold applicability are presented below. Note that the equations below are to be used only for determining whether an electronics manufacturing facility falls above or below the threshold of 25,000 metric tons CO_2e.

For calculating emissions of each fluorinated GHG i, for facilities that manufacture semiconductors or MEMS:

$$E_i = S * EF_i * GWP_i * 0.001 \qquad \text{(Eq. 1)}$$

Where:

E_i = Annual production process emissions of input gas i (metric tons CO_2e).

S = 100% of annual manufacturing capacity of a facility (m^2). (see Eq. 5)

EF_i = Emission factor for input gas i (kg/m^2) (see Appendix A).

GWP_i = Gas-appropriate GWP (see Table A-1 to subpart A, Global Warming Potentials).

0.001 = Conversion factor from kg to metric tons.

i = Input gas.

For calculating emissions of each fluorinated GHG i, for facilities that manufacture LCDs:

[10] For simplicity, semiconductor facilities would estimate HTF emissions as 10% of total clean and etch emissions, as opposed to 11% which was used in our threshold analyses as presented above.

$$E_i = S * EF_i * GWP_i * 0.000001 \qquad \text{(Eq. 2)}$$

Where:

E_i = Annual production process emissions of input gas i (metric tons CO_2e).

S = 100% of annual manufacturing capacity of a facility (m^2). (see Eq. 5)

EF_i = Emission factor for input gas i (g/m^2) (see Appendix A).

GWP_i = Gas-appropriate GWP (see Table A-1 to subpart A, Global Warming Potentials).

0.000001 = Conversion factor from g to metric tons.

i = Input gas.

For calculating emissions of each fluorinated GHG i, for facilities that manufacture PVs:

$$E_i = C_i * GWP_i * 0.001 \qquad \text{(Eq. 3)}$$

Where:

E_i = Annual production process emissions of input gas i (metric tons CO_2e).

C_i = Annual fluorinated GHG (gas i) purchases or consumption (kg).

GWP_i = Gas-appropriate GWP (see Table A-1 to subpart A, Global Warming Potentials).

0.001 = Conversion factor from kg to metric tons.

i = Input gas.

To sum emissions of all input gases i for all facilities:

$$E_T = \delta * \sum_i E_i \qquad \text{(Eq. 4)}$$

Where:

E_T = Annual production process emissions of all fluorinated GHGs (metric tons CO_2e).

δ = Factor accounting for heat transfer fluid emissions, estimated as 10 percent of total annual production process emissions at a semiconductor facility. Set equal to 1.1 when calculating total annual production process emissions from semiconductor manufacturing. Set equal to 1 calculating total annual production process emissions from MEMS, LCD, or PV manufacturing.

E_i = Annual production process emissions of input gas i (metric tons CO_2e), as calculated Eqs. 1, 2, or 3.

i = Input gas.

For calculating a facility's annual manufacturing capacity:

To determine 100 percent of annual manufacturing capacity, facilities would sum the maximum designed substrate starts of a facility over each month of a year as presented in Equation 5 below. Maximum designed substrate starts is defined as the maximum quantity of substrates, expressed as surface area, that could be started each month during a reporting year if the facility were fully equipped as defined in the facility design specifications and if the equipment were fully utilized. It denotes 100 percent of annual manufacturing capacity of a facility.

$$S = \sum_{x}^{12} W_x \qquad \text{(Eq. 5)}$$

Where:

S = 100 percent of annual manufacturing capacity of a facility (m^2).

W_x = Maximum designed substrate starts of a facility in month x (m^2 per month).

x = Month.

None of the methods for determining threshold applicability account for controlled emissions by abatement systems. EPA is not permitting accounting for emissions reductions from abatement systems because while electronics manufacturers may employ emissions abatement systems (e.g., thermal oxidizers) to lower their emissions and use the manufacturer published destruction or removal efficiency (DRE) for the system, abatement systems may fail to achieve their rated DREs for two reasons. First, the equipment may not be properly operated and maintained. Second, the DRE itself may have been incorrectly measured due to a failure to account for the effects of dilution (e.g., CF_4 can be off by as much as a factor of 20 to 50 and C_2F_6 can be off by a factor of up to 10 because of failure to properly account for dilution [Burton, 2007].) In either event, the actual emissions from facilities employing abatement systems may exceed estimates based on the rated DREs of the systems and may therefore exceed the $MtCO_2e$ threshold without the knowledge of the facility operators. Hence, accounting for reductions in emissions from the use of abatement systems when determining if a facility exceeds the proposed 25,000 metric ton CO_2e threshold limit is not permitted because the DRE used in such a calculation cannot be verified.

3 Options for Emissions Calculation and Monitoring Methods

EPA evaluated a range of options for estimating process emissions from productions processes used in electronics manufacturing. Each one of these options is briefly described below.

3.1 Options for Estimating Fluorinated GHG Emissions from Etching and Cleaning

To estimate and report fluorinated GHGs from etching and cleaning, EPA evaluated the 2006 IPCC Tier 1, Tier 2a, Tier 2b, and Tier 3 methods, as well as hybrids, refinements of, and modifications to those methods.[11] Lastly, EPA evaluated the use of continuous monitoring emissions systems (CEMS).

Many of the options described below, including the IPCC Tier 2b, Modified Tier 2b, Refined Method, Tier 2c, Tier 2d, and the IPCC Tier 3 methods use the typology presented in Figure 3-1 below. At the top of the typology figure are process types, which are broad groups of manufacturing steps used at a facility associated with substrate (e.g., wafer) processing during device manufacture for which fluorinated GHG emissions and fluorinated GHG usages are calculated and reported. The process types are plasma etching, chamber cleaning, and wafer cleaning. Process types for various methods include etching and chamber cleaning, and for some methods, wafer cleaning.

The second level in the figure consists of process sub-types. Process sub-types are sets of similar manufacturing steps, more closely related within a broad process type. (Note, for clarity, EPA is referring to what was previously termed process categories in the April 2010 proposed rule (75 FR 18652) as process sub-types). Figure 3-1 only identifies process sub-types for the chamber cleaning process type, however in an option described below (mainly the Refined Method) process sub-types could be established for any process type. For example, under the plasma etching process type either film-based (e.g., oxide etch, nitride etch) or feature-based (e.g., gate etch, deep trench etch) process sub-types could be established; under the wafer cleaning process type, the sub-types of ashing and bevel cleaning could be established. At the lowest level of the typology tree in Figure 3-1 are production process recipes ("recipes"). The recipe typology is discussed further in section 3.1.7.1 below.

[11] It is important to note that the IPCC methods were developed to estimate national averages of emissions for specific sources (e.g. national emissions from semiconductor manufacturing) and not for facility-specific emissions.

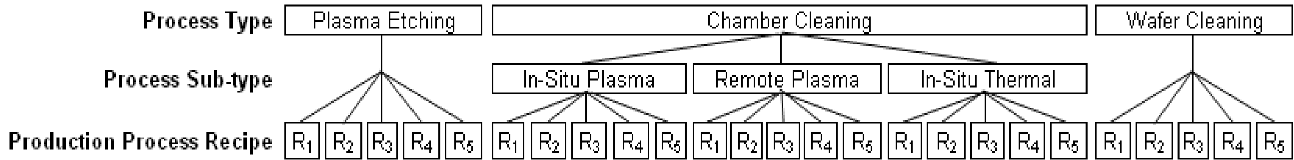

Figure 3-1. Typology for Calculating Fluorinated GHG Emissions from Electronics Manufacturing

For some of the methods for estimating emissions from etching and cleaning discussed below, a distinction is made for facilities that manufacture semiconductors (see Tier 2c, Tier 2d, and Hybrid Approaches). Semiconductor manufacturing facilities would select the appropriate etch and clean emission estimation methods based upon facility size expressed in terms of annual manufacturing capacity.

The largest semiconductor manufacturing facilities are defined as those with a capacity of greater than 10,500 m^2 of substrate (e.g., silicon), as calculated using Equation 5 above. The largest semiconductor manufacturing facilities account for nearly two-thirds of uncontrolled emissions from semiconductor manufacturing while accounting for less than 20 percent of all semiconductor facilities expected to report under subpart I. Applying this distinction, EPA expects that 29 of the estimated 175 semiconductor facilities will be classified as "large" facilities. These results were based on the analysis illustrated in Figure 3-2 below.[12]

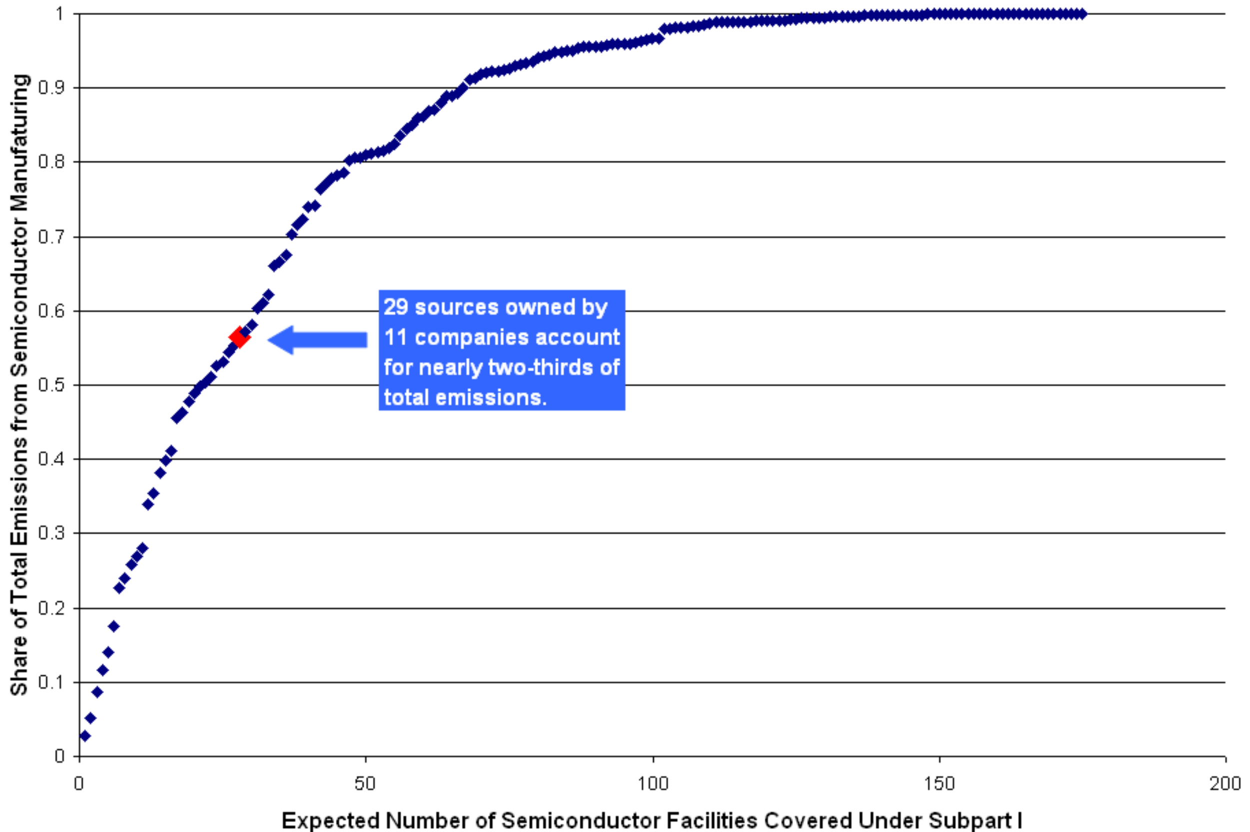

Figure 3-2. Expected Facility Contributions to Total Emissions from Semiconductor Manufacturing

3.1.1 2006 IPCC Tier 1 Method

For the Tier 1 approach, the surface area of substrate (e.g., silicon, LCD or PV-cell) produced during electronics manufacture is multiplied by default gas-specific emission factors. The advantages of the Tier 1 approach lie in its

[12] See footnote 8.

simplicity. However, this method does not account for the differences among process types (i.e., etching versus cleaning), individual processes, recipes, or tools, which leads to uncertainties in the default emission factors of up to 200 percent at the 95 percent confidence interval (IPCC, 2006).[13] Moreover, facilities routinely monitor gas consumption in the ordinary course of business, making it technically feasible to employ a method with the complexity of at least the 2006 IPCC Tier 2a approach without additional data collection efforts.

3.1.2 2006 IPCC Tier 2a Method

For the Tier 2a approach, chemical-specific gas consumption is multiplied by default emission factors for utilization, and by-product formation. The Tier 2a approach is relatively simple, given that gas consumption data is collected in the ordinary course of business. However, due to variation in gas utilization between etching and cleaning processes, the emissions estimated using the Tier 2a approach have greater uncertainty than emissions estimated using the Tier 2b approach.

3.1.3 2006 IPCC Tier 2b Method

For the Tier 2b approach, chemical-specific gas consumption by process type (etch or chamber clean) is multiplied by default emission factors for utilization and by-product formation.[14] This approach requires facilities to determine gas consumption by process type (etch and clean). Equation 6 below is used to estimate fluorinated GHG emissions for process type (j) for input gas (i), and Equation 7 below is used to estimate byproduct gas (k) that results from input gas (i) utilization during process type (j).[15]

$$E_{ij} = C_{ij} * (1 - U_{ij}) * (1 - a_{ij} * d_{ij}) * 0.001 \qquad \text{(Eq. 6)}$$

Where:

E_{ij}	=	Annual emissions of input gas i from process type j (metric tons).
C_{ij}	=	Amount of input gas i consumed for process type j (kg). (see Eq. 8)
U_{ij}	=	Process utilization for input gas i for process type j (decimal fraction).
a_{ij}	=	Fraction of input gas i used in process type j with abatement systems (decimal fraction).
d_{ij}	=	Fraction of input gas i destroyed or removed in abatement systems connected to process tools where process type j is used (decimal fraction). (see Eq. 13)
0.001	=	Conversion factor from kg to metric tons.
i	=	Input gas.
j	=	Process type.

$$BE_{ijk} = B_{ijk} * C_{ij} * (1 - a_{ij} * d_{jk}) * 0.001 \qquad \text{(Eq. 7)}$$

Where:

BE_{ijk}	=	Annual emissions of by-product k formed from input gas i from process type j (metric tons).
B_{ijk}	=	Amount of gas k created as a by-product per kg of input gas i consumed for process type j (kg).
C_{ij}	=	Amount of input gas i consumed for process type j (kg). (see Eq. 8)

[13] This uncertainty refers only to semiconductors and LCDs. Tier 1 emission factor uncertainty for PV was not estimated in the IPCC Guidelines (IPCC, 2006). Additionally, emissions from MEMS are not addressed in the 2006 IPCC Guidelines.

[14] For all methods based on default emission factors specified in the final rule (e.g., the Tier 2b, Tier 2c, and Tier 2d methods), a facility must use the default factors provided by EPA; the only exception is if a facility uses a fluorinated GHG for a particular process type or sub-type for which default emission factors are not provided. Where defaults are not provided, the facility must either use utilization and by-product formation rates of 0 or, in that particular instance, use directly measured recipe-specific emission factors following the methods outlined in section 3.1.7.1.

[15] Note the *2006 IPCC Guidance for National Greenhouse Gas Inventories* equations for estimating emissions and by-product emissions in the electronics industry (Equations 6.7 through 6.11) include a term for the heel of gas cylinders/containers. However, the heel term has been excluded in Equations 6 and 7 because it is already accounted for when overall gas consumption is estimated (shown in Equations 8 and 9).

a_{ij} = Fraction of input gas i used in process type j with abatement systems.
d_{jk} = Fraction of input gas i destroyed in abatement systems connected to process tools where process type j is used (decimal fraction). (see Eq. 13)
0.001 = Conversion factor from kg to metric tons.
i = Input gas.
j = Process type.
k = By-product gas.

Although the uncertainty relative to Tier 2a is reduced, the Tier 2b approach also does not account for variation among individual recipes, processes or tools and, therefore, the estimated emissions will have greater uncertainty compared to Tier 3 emissions estimates. The Tier 2b method, as shown in the uncertainty analysis performed by EPA, may understate actual emissions. (see Appendix C)

3.1.4 Modified Tier 2b Method

The Modified IPCC Tier 2b approach is based on the 2006 IPCC Tier 2b method (as described above). However, the Modified Tier 2b approach takes into account gas- and facility- specific heel factors, as opposed to utilizing a default value for heel factor as suggested in the IPCC Guidelines. Emission estimations using the Modified IPCC Tier 2b approach are assumed to be less uncertain than estimations determined using the 2006 IPCC Tier 2b method. This is because when using a default heel factor, gas consumption is likely to be less representative of actual gas consumption, and hence emissions, in comparison to using gas- and facility- specific heel factors. (see section 3.2 for more discussion on the use of default versus gas- and facility- specific heel factors)

3.1.5 Tier 2c Method (Defaults for 5 Process Types/Subtypes)

The Tier 2c Method expands on the Modified Tier 2b method for facilities that manufacture semiconductors. In the Tier 2c method, emissions would be estimated for five process type/subtypes: plasma etching, chamber cleaning (including in-situ plasma, remote plasma, and in-situ thermal), and wafer cleaning. For the Tier 2c Method, gas consumption apportioned to process types or sub-types is multiplied by default emission factors for utilization and by-product formation, (dependent on the size of wafer manufactured at a facility)[16], using Equations 6 and 7, respectively.[17] EPA considered the Tier 2c method for facilities that manufacture semiconductor facilities and that have annual manufacturing capacities of 10,500 m^2 or less (ass calculated using Equation 5).[18] Because the Tier 2c method is more granular than the IPCC and Modified Tier 2b methods,[19] EPA anticipates that its use will result in more accurate emission estimates.

3.1.6 The Refined Method (Defaults Factors for 9 Process Types/Subtypes)

The Refined Method, which was evaluated as part of the April 2010 proposal, expands on the two process types (etch and clean) of the IPCC Tier 2b method by requiring that emissions be estimated from the etch, chamber clean and wafer clean process types by summing emissions from various process sub-types For the Refined Method, gas consumption apportioned by process sub-type is multiplied by default emission factors for utilization and by-product formation[20], using Equations 6 and 7, respectively.[21]

While process sub-types can be defined in many ways, the Refined Method utilizes nine process sub-types which include four sub-types for etching, three sub-types for chamber cleaning, and two sub-types for wafer cleaning. The etching categories include oxide etch, nitride etch, silicon etch, and metal etch; the chamber cleaning categories include in situ

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[16] See Appendix A for the default factors, and Appendix B for background on how the default factors were developed.

[17] When using Equations 6 and 7 for the Tier 2c method “j” indexes process sub-types or process types.

[18] The Tier 2c method was finalized as part of the final rule, and all semiconductor facilities with annual manufacturing capacities of 10,500 m^2 substrate of less are required to calculate and report process emissions using this method. See the preamble for a discussion why EPA selected this method.

[19] For the Tier 2c method emissions must be estimated for three chamber cleaning process sub-types as opposed to just the broad chamber cleaning process type used in the Tier 2b methods.

[20] EPA did not finalize default emission factors for the etch subtypes presented in the Refined Method.

[21] When using Equations 6 and 7 for the Refined Method “j” indexes process sub-types as opposed to process types.

plasma cleaning, remote plasma cleaning, and in situ thermal cleaning; and the wafer cleaning categories include bevel cleaning and ashing.

For the Refined Method EPA considered additional potential process sub-types for etching and chamber cleaning to replace or complement the process sub-types defined above. For etching, in addition to the four thin-film based sub-types defined above, EPA considered the use of the feature-based sub-types contact etch, self-alignment contact etch, gate etch, deep trench etch, isolation trench etch, through silicon vias and regular vias. Each of these represents a specific feature achieved through etching (instead of subcategories based on the type of thin film etched). For chamber clean, alternative sub-types may distinguish between the types of films being removed from the chamber during cleaning. These might include distinguishing between chambers coated with tungsten and silicon-based films, or distinguishing between thin-film deposition equipment manufacturers.

There are no published emission factors for the refined process categories as defined in the Refined Method, therefore to obtain emission factors (i.e., utilization and by-product formation rates) for each process category, EPA undertook a process to collect data from industry, and evaluated its robustness and usefulness for creating emission factors through an averaging scheme, either simple or weighted depending on information received. This process is further discussed in the TECHNICAL SUPPORT DOCUMENT (UPDATED) FOR PROCESS EMISSIONS FROM ELECTRONICS MANUFACTURE (e.g., SEMICONDUCTORS, LIQUID CRYSTAL DISPLAYS, PHOTOVOLTAICS, AND MICRO-ELECTRO-MECHANICAL SYSTEMS): PROPOSED RULE FOR MANDATORY REPORTING OF GREENHOUSE GASES (March 22, 2010) and the Subpart I Notice of Data Availability (75 FR 26904).[22] EPA obtained a sufficient amount of information to establish default emissions factors for multiple chamber clean process sub-types, but there was an insufficient amount of information to support establishing default emission factors for multiple etch process sub-types. Therefore the Refined Method was not adopted for the final rule.[23]

EPA considered the Refined Method for semiconductor facilities only, as semiconductor manufacturing is understood to be more variable and complex than other electronics manufacturing. The goal in establishing process sub-types under each process type is to account for variability in emission factors across processes to reduce uncertainty in emission estimates, while limiting the total number of process sub-types for which gas usage must be tracked. EPA expects that estimating emissions based on process sub-types for etch with robust default factors would result in more accurate facility-level emission estimates as compared to estimating emissions using a single broad etch process type as presented in the IPCC and Modified Tier 2b methods.

3.1.7 Tier 2d Method (Defaults for 4 Process Types/Subtypes, Recipe-specific emission factors for 1 Process Type)

For the Tier 2d method,[24] which uses the same process types/sub-types as the Tier 2c method, gas consumption is apportioned to the chamber cleaning process sub-types (including in-situ plasma, remote plasma, and in-situ thermal) and the wafer cleaning process type and is multiplied by various default emission factors for utilization and by-product formation, (dependent on the size of wafer manufactured at a facility, see Appendix A), using Equations 6 and 7, respectively.[25] However, for the plasma etching process type, emissions are estimated by apportioning gas consumption to etch recipes, each with directly measured recipe-specific emissions factors for utilization and by-product formation. Based on an uncertainty analysis conducted by EPA, the Tier 2d method appears to be more precise than the Tier 2c method (see Appendix C). EPA evaluated the Tier 2d method for the largest semiconductor manufacturing facilities because, as discussed above, the largest facilities are expected to account for nearly 2/3 of all potential emissions, while accounting for less than 20 percent of all covered semiconductor facilities.[26]

The Tier 2d method is focused on recipe-specific emission factors for etching processes because of the apparent gaps in the available emission factor knowledge base for etching processes used in the industry. While more than half of the gas consumed in semiconductor manufacturing is for chamber cleaning, most of the variability in gas consumption, and hence

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[22] Both documents are available in the docket at EPA-HQ-OAR-2009-0927.

[23] Please see the preamble for more discussion on the reasons why the Refined Method was not finalized.

[24] The Tier 2d method was finalized as part of the final rule, and all large semiconductor facilities (semiconductor facilities with annual manufacturing capacities greater than 10,500 m^2 substrate) are required to calculate and report process emissions using this method. See the preamble for a discussion why EPA selected this method.

[25] When using Equations 6 and 7 for the Tier 2d method “j” indexes recipes, process sub-types, or process types.

[26] See the preamble for further discussion of EPA’s considerations for the Tier 2d method and steps taken to reduce burden.

emissions, across many facilities is found for recipes used for etching. Semiconductor etch recipes utilize approximately six or more fluorinated GHGs, either alone or in combination and in various mixtures. Process recipes may vary between facilities because they are considered a function of company competitiveness and innovation.

3.1.7.1 Development of Recipe-Specific Emission Factors

Recipe-specific emission factors would be developed for each individual recipe, or for a set of similar recipes. An individual recipe refers a specific combination of gases, under specific conditions of reactor temperature, pressure, flow, radio frequency (RF) power and duration, used repeatedly to fabricate a specific feature on a specific film or substrate. Recipe-specific emissions factors developed for measurements already made for an individual recipe may be applied to a set of similar recipes, where similar, with respect to recipes means those recipes that are composed of the same set of chemicals and have the same flow stabilization times and where the documented differences, considered separately, in reactor pressure, individual gas flow rates, and applied radio frequency (RF) power are less than or equal to plus or minus 10 percent. For purposes of comparing and documenting recipes that are similar, facilities may use either the best known method provided by an equipment manufacturer or the process of record, for which emission factors for either have been measured. (Technical support for the definition of similar recipes can be found in Appendix D)

This definition of similar recipe applies to in-situ and RPS chamber cleaning as well as etching. It applies to in-situ chamber cleaning by virtue of the representative in situ chamber cleaning studies reviewed in Appendix D, which show that for changes in individual recipe variables of 10 percent or less results in corresponding changes in emissions of less than 10 percent. The recipes considered in Appendix D used NF_3, C_2F_6 and C_3F_8. The definition remains valid for contemporary RPS chamber cleaning recipes. As shown by Chen et. Al (2003), NF_3 utilization, which together with duration of cleaning time governs emissions during NF_3-based RPS chamber cleaning, is relatively insensitive to changes in flow rate (over the wide range 2 to 6 lpm) and pressure (over the relatively wide range of 3 to 10 torr). Over these ranges, Chen et. al (2003) report NF_3 utilization efficiencies at 99 percent or above.

In a given reporting year, a facility must develop new recipe-specific emission factors only for recipes that are not similar to any recipe used in a previous reporting year. Three examples of how a facility may develop (or obtain) recipe-specific emission factors are presented below:

1. Make direct measurements on-site at the facility.
2. Obtain measurement information, and hence emission factors, from tests performed by a third-party, such as a tool supplier. (Any measurements made by a third-party are required to have been made for recipes that are similar recipes (as defined above) to those used at the facility.
3. Use factors from another facility that uses similar recipes. (For example, there are instances where a company operating multiple facilities will use the same or similar recipes in more than one facility; in this instance, measured recipe-specific emission factors for a recipe used at one facility may also be used for estimating emissions from the use of a similar recipe at another facility.)

All recipe-specific emission factors must be measured using the International SEMATECH Technology Transfer (#06124825A-ENG) (December 2006). A facility may use recipe-specific emission factors that were developed prior to January 1, 2007, provided they were measured using the International SEMATECH Technology Transfer (#01104197A-XFR) (December 2001).

3.1.8 2006 IPCC Tier 3 Method

The Tier 3 method uses the same equations as the IPCC Tier 2b, Refined Method, Tier 2c and Tier 2d approaches (Equations 6 and 7)[27], but requires facility-specific data on (1) gas consumption, (2) gas utilization, (3) by-product formation, rather than applying any default values. The 2006 IPCC Guidelines state that for the Tier 3 method, plant-specific values should be used for each individual process or for each small sets of processes. There may be various ways processes or sets of processes could be defined, for instance by process platforms, processes or recipes. The Tier 3 method in the context of this rule uses gas consumption to be apportioned to recipes, multiplied by requires facility-specific, recipe-specific emission factors for utilization and by-production formation, developed for each individual recipe or set of similar

[27] When using Equations 6 and 7 for the IPCC Tier 3 approach "j" indexes recipes as opposed to process types.

recipes as discussed above in section 3.1.7.1. The use of the Tier 3 method is estimated to result in the least uncertain estimates amongst the methods presented by IPCC (IPCC 2006).

3.1.9 Hybrid Approach A

Hybrid Approach A, which was evaluated as part of the April 2009 proposal, requires the largest semiconductor facilities (facilities with production capacities of greater than 10,500 m^2 silicon) to estimate their etching and cleaning emissions using an approach based on the IPCC Tier 3 method; all other facilities (including other semiconductor manufacturing and other electronics manufacturing facilities) would be required to use the IPCC Tier 2b method.

3.1.10 Hybrid Approach B

Hybrid Approach B, which was evaluated as part of the April 2009 proposal, requires Tier 3 reporting for all semiconductor facilities, but only for the top three gases emitted at each facility. For all other gases, the Tier 2b approach is required. The top three gases emitted, based on data in the Inventory of U.S. GHG Emissions and Sinks, are C_2F_6, CF_4, and SF_6 (EPA, 2008a). These top three gases accounted for approximately 80 percent of total fluorinated GHG emissions from semiconductor manufacturing during etching and chamber cleaning in 2006.

3.1.11 Continuous Emissions Monitoring Systems (CEMS)

CEMS requires facilities to install and operate CEMS to measure process emissions. A typical electronics manufacturing facility may have many individual process tools that influence emissions. Process tool exhaust is managed within the facility using stainless steel plumbing and ductwork. Due to the complexity of the manufacturing layout, CEMS would either need to be attached to every tool or to a final exhaust point (e.g., scrubber stacks). One possible option is to use Fourier Transform Infrared Spectrometers (FTIRs) in scrubber stacks to measure facility emissions. FTIR spectroscopy is presently used to conduct short-term fluorinated GHG emission measurements on single tools. Another option would be to either continuously or intermittently bring a gas sample to one or more centrally located FTIRs, in which case any dilution issues that may arise when measuring fluorinated GHGs in stacks may be avoided.

3.2 Options for Estimating Facility Gas Consumption

Several of the estimation methods described above require gas consumption to be used to estimate emissions. Equations 8 and 9 below are used to estimate gas consumption for any input gas i used at an electronics manufacturing facility.

$$C_i = (I_{Bi} - I_{Ei} + A_i - D_i) \quad \text{(Eq. 8)}$$

Where:

C_i	=	Annual consumption of input gas i (kg).
I_{Bi}	=	Inventory of input gas i stored in containers at the beginning of the reporting year, including heels (kg).[28]
I_{Ei}	=	Inventory of input gas i stored in cylinders or other containers at the end of the reporting year, including heels (kg).[29]
A_i	=	Acquisitions of input gas i during the reporting year through purchases or other transactions, including heels in containers returned to the electronics manufacturing facility (kg).
D_i	=	Disbursements of input gas i through sales or other transactions during the year, including heels in containers returned by the electronics manufacturing facility to the chemical supplier (kg). (see Eq. 9)
i	=	Input gas.

[28] For containers in service at the beginning of a reporting year, account for the quantity in these containers as if they were full.

[29] For containers in service at the end of a reporting year, account for the quantity in these containers as if they were full.

$$D_i = \sum_{l=1}^{M} \left(h_{il} * N_{il} * F_{il} \right) + X_i \quad \text{(Eq. 9)}$$

Where:

D_i	=	Disbursements of input gas i through sales or other transactions during the reporting year, including heels in containers returned by the electronics manufacturing facility to the gas distributor (kg).
h_{il}	=	Facility-wide gas-specific heel factor for input gas i and container size and type l (expressed as a decimal fraction), as determined in §98.94(b).[30]
N_{il}	=	Number of containers of size and type l returned to the gas distributor containing the standard heel of input gas i.
F_{il}	=	Full capacity of containers of size and type l containing input gas i (kg).
X_i	=	Disbursements under exceptional circumstances of input gas i through sales or other transactions during the reporting year, including those measured in exceptional circumstances (kg).
i	=	Input gas.
l	=	Size and type of gas container.
M	=	The total number of different sized container types. If only one size and container type is used for an input gas i, M=1.

For the heel factor[31] (h_{il}) used in Equation 9, EPA evaluated two options including the IPCC default heel factor and gas-and facility-specific heel factors. Both of these options are described below.

3.2.1 IPCC Default Heel Factor

The IPCC default value for the fraction of gas remaining in the shipping container (i.e. the "heel") is 10 percent (IPCC, 2006). This value is intended to be applicable to all gas containers, regardless of the gas type or container size or shape. However, heels may vary among gases and container sizes and shapes. Differences in gas usage practices may also exist between facilities which would not be accounted for when using the IPCC default heel factor. Therefore, the use of the IPCC default heel factor may result in misestimating gas consumption and emissions.

3.2.2 Gas-and Facility-Specific Heel Factors

Facility-specific heel factors for each gas and container type and size are based on the residual weight or pressure of the gas container, or trigger point for change out, that a facility uses to change out that container for each container type for each gas used. By using these trigger points, along with the initial mass of the container, gas-and facility-specific heel factors can be calculated.[32]

To account for exceptional circumstances[33] when gas containers are not changed precisely when they reach the targeted trigger points, EPA evaluated the option of requiring reporters to weigh or determine the pressure of the gas container as opposed to using the facility-wide gas-specific heel factor as part of determining the net amount of gas used at a facility. To account for changes in gas consumption practices, EPA considered two situations in which facility-wide gas-specific heel

[30] If a facility uses less than 50 kg of a fluorinated GHG or N_2O in one reporting year, the facility may assume that any h_{il} for that fluorinated GHG or N_2O is equal to zero.

[31] Heel is defined as the amount of gas that remains in a gas cylinder or container after it is discharged or off-loaded.

[32] The initial mass of a container may be determined through gas supplier documents; however the reporter remains responsible for the accuracy of these records.

[33] EPA is requiring an exceptional circumstance be defined as one in which a cylinder/container is changed at a residual mass or pressure that differs by more than 20 percent from the "trigger point for change out." When using mass based trigger points for change, it should be determined if exceptional circumstances have occurred based on the net weight of gas in containers, excluding the tare weight of the container.

factors would have to be recalculated; both when the trigger point for change out used to establish a heel factor for a gas and container type differs by more than one percent or five percent from the previously used trigger point for change out.

The use of a gas-and facility-specific heel factor is expected to produce more accurate estimates of gas consumption in comparison to the use of the IPCC default value of 10 percent. This is because the amount of gas that remains in a gas container after it is discharged or off-loaded is not the same for every gas and container type, and the default value does not account for exceptional circumstances or variations in gas consumption practices within or between facilities. Therefore applying a broad default value to every gas container will lead to estimations that may not be representative of actual facility gas consumption, and hence facility emissions.

3.3 Option for Apportioning Gas Consumption

When estimating emissions using methods such as the Modified IPCC Tier 2b or the Tier 2c or Tier 2d methods, and a fluorinated GHG is used in more than one process type or sub-type (e.g., C_2F_6 used for both etch and clean processes), facility-wide gas consumption must be apportioned to the appropriate process types, process sub-types, or recipes through the use of Equation 10. The product of that apportioned gas usage and the corresponding emission factor (either default or recipe-specific) will equate to a facility's uncontrolled emissions for a specific process type, process sub-type, or recipe . These emissions can be summed within and over all process types and categories at a facility to determine total facility-wide uncontrolled emissions.

$$C_{ij} = f_{ij} * C_i \quad \text{(Eq. 10)}$$

Where:

C_{ij} = Annual amount of input gas i consumed for recipe, process subtype, or process type j (kg).

f_{ij} = Recipe-specific, process sub-type-specific, or process type-specific gas apportioning factor (decimal fraction).[34]

C_i = Annual consumption of input gas i (kg). (see Eq. 8)

i = Input gas.

j = Recipe, process sub-type or process type.

Apportioning factors (f_{ij}) used in Equation 10, would be developed using facility-specific engineering models based on a quantifiable metric selected by a facility (such as wafer passes or wafer starts).[35] This model, utilizing measurable process information, may be based on the most appropriate quantifiable metric for each facility. Such a model utilizes facility process information to determine apportioning factors using the ratio of the amount of input gas i used per recipe (process category, process type) multiplied by the number of times that recipe is used on a tool and the number of tools that recipe is used on over the total amount of gas i used.

Given that facilities may select how to construct, and on which quantifiable metric to base facility-specific engineering models for gas apportioning, EPA considered various documentation and verification steps for facilities to take.

Documentation

As part of recordkeeping requirements, in site GHG Monitoring Plans (required in §98.3(g)(5)), specific information about their facility-specific engineering model, including definitions of variables, derivations of equations and formulas, and example calculations to ensure apportioning factors are repeatable[36] would be documented and updated annually. This

[34] See Section 3.3 discussion on apportioning.

[35] Wafer passes is a count of the number of times a wafer substrate is processed in a specific process recipe, sub-type, or type. The total number of wafer passes over a reporting year is the number of wafer passes per tool multiplied by the number of operational process tools in use during the reporting year. Wafer starts means the number of fresh wafers that are introduced into the fabrication sequence each month. It includes test wafers, which means wafers that are exposed to all of the conditions of process characterization, including but not limited to actual etch conditions or actual film deposition conditions.

[36] Repeatable means that the variables used in the formulas for the facility's engineering model for gas apportioning factors are based on observable and measurable quantities that govern gas consumption rather than engineering judgment about those quantities or gas consumption.

information would be updated each year for each facility to account for changes to tools or process at a facility between reporting years.

Verification

To verify engineering models used to apportion gas consumption, EPA requires facilities to demonstrate that the results from the model are repeatable and to compare the difference between modeled gas usage and actual gas usage. Facilities would verify a facility-specific engineering model through the following:

1. Analyzing at least a 30-day period of operation during which the capacity utilization of the facility equals or exceeds 60 percent of its design capacity.[37]
2. Comparing the actual gas consumed of input gas i to the modeled gas consumed of input gas i for one fluorinated GHG used for the plasma etching process type and one fluorinated GHG used for the chamber cleaning process type. The fluorinated GHGs selected for comparison would be the ones used in the largest quantities, on a mass basis, for each of the identified process types.
3. Ensuring that the comparison performed for the gas used in the largest quantity for the plasma etching process type does not result in a difference between the actual and modeled gas consumption that exceeds five percent relative to actual gas consumption, reported to one significant figure using standard rounding conventions.

3.3.1 Example of Facility-Specific Engineering Model Based on Wafer Pass

One example of a quantifiable metric on which a facility may base an engineering model to apportion gas consumption is wafer pass. During semiconductor device manufacturing, counts of wafer passes for each manufacturing step, over the course of a year, carry information about fab productivity and fluorinated GHG usage. The design and profitable operation of a modern fab entails detailed considerations of the functional performance of the equipment and its cost-of-ownership. Cost of ownership is governed in large part by its productivity—the number of wafers processed per hour, the time to maintain and time to failure.

Fab managers use information about counts of wafer passes to reduce variable costs by identifying practices that increase fab throughput and that reduce material costs. Wafer pass counts in modern fabs are typically available through the manufacturing execution software (MES) that comes with process equipment. MES is capable of tracking the activities associated with each piece of manufacturing equipment. In older fabs that may not employ MES, wafer pass counts are available through process flow information for each product manufactured.

While wafer-pass-count information is available, it is not routinely gathered. Instead, it's gathered at the request of fab and product line managers for purposes of managing work-in-process load, reducing fab cycle time, reducing product cycle time, identifying and removing process bottlenecks, etc.

For estimating gas usage, wafer pass counts could be collected either electronically or physically. For those fabs with MES, wafer pass counts could be collected electronically, either continuously or intermittently. In those fabs without MES, wafer pass counts would be collected intermittently at periods chosen to be representative of manufacturing over the reporting period.

The example following is a demonstration of the use of wafer pass in apportioning NF_3 consumption at a hypothetical facility for the following three process sub-types defined by the Refined Method: oxide etch, silicon etch, and remote plasma clean. For simplicity and demonstration purposes, it is assumed that at the hypothetical facility NF_3 is the gas used in the largest quantity, on a mass basis, for the plasma etching process type and the chamber cleaning process type.

An illustrative case for a semiconductor facility that can be considered where wafer passes are the quantifiable metric of gas usage activity used, in a facility-specific engineering model, is a facility that uses NF_3 for chamber cleaning with remote plasma systems and for etching polysilicon and oxide films. With knowledge of the NF_3-specfic heel and the number of NF_3 containers used, the facility knows the amount of NF_3 consumed. To estimate emissions the facility must now apportion NF_3 usage between the chamber cleaning, polysilicon etching, and oxide etching process sub-types. To do this it might use the total number of wafer passes through each and every NF_3-cleaning system together with the time and *nominal* (not measured actual) gas flow rate for each and every NF_3-cleaning system and the corresponding figures for polysilicon

[37] If a facility operates below 60 percent of its design capacity during the reporting year, the period during which the facility experiences its highest 30-day average utilization would be used for model verification.

etch processes and oxide etch processes to arrive at the proportion of NF_3 used for cleaning chambers and etching polysilicon and oxide films. Once developed, these apportioning factors could be used to estimate NF_3 gas usage for the cleaning and etching process sub-types proposed in our method. This example is illustrated further in Table 3-1 below.

Table 3-1. Illustrative Calculation for NF_3 Example at One Facility

Gas Type – Annual Usage, kg.	Process Sub-type	Apportioning Factor	Process sub-type gas usage, kg.
NF_3 – 56,286 kg	RPS Chamber Cleaning	82%	46,202
	Polysilicon Etch	17%	9,561
	Oxide Etch	1%	523

Note: Annual gas usage presented is the modeled usage not the nominal usage.

For the example presented in Table 3-1, the annual nominal gas usage is 56,009 kg of NF_3, with 520 kg of NF_3 used for oxide etch, 9,514 kg of NF_3 use for polysilicon etch, and 45,974 kg of NF_3 used for RPS chamber clean. Using this information, as well as the modeled amount of gas consumed for each of the three process sub-types considered, an example verification is presented in below in Table 3-2.

Table 3-2. Illustrative Verification for Hypothetical Facility-Specific Gas Apportioning Model

Process Sub-Type	Nominal Usage	Modeled Usage
Chamber Clean Process Type		
RPS	45,974	46,202
	Comparison	0.5%
Etch Process Type		
Oxide etch process	520	523
Silicon etch process	9,514	9,561
Total	10,034	10,084
	Verification Comparison	0.5%

While the manufacturing process for other electronics manufacturers are less complex as compared to semiconductor manufacturing as most gases are used for a single process type, facilities that manufacture LCDs, MEMS and PV may also use engineering models based on quantifiable metrics of manufacturing activity for apportioning gas consumption by process type. The approach of using a facility-specific model may also be applied to apportion consumption of N_2O.

3.4 Options for Estimating Nitrous Oxide (N_2O) Emissions

EPA evaluated two methods to estimate emissions of N_2O during CVD or other N_2O-using manufacturing processes, such as chamber cleaning, both of which would utilize Equation 11. The first option is the use of two facility-specific N_2O utilization factors for each CVD and other N_2O-using manufacturing processes. These factors would be developed by directly measuring N_2O utilization at a facility using the 2006 ISMI Guidelines or the 2001 ISMI Guidelines, provided the measurements were made prior to January 1, 2007.[38] Gas consumption used in Equation 11 would be determined using the estimation and apportioning methods discussed above in sections 3.2 and 3.3.

$$E(N_2O)_j = C_{N_2O,j} * (1 - U_{N_2O,j}) * (1 - a_{N_2O,j} * d_{N_2O,j}) * 0.001 \quad \text{(Eq.11)}$$

Where:

$E(N_2O)_j$ = Annual emissions of N_2O for N_2O-using process j (metric tons).
$C_{N2O,j}$ = Amount of N_2O consumed for N_2O-using process j and apportioned to N_2O processes (kg).
$U_{N2O,j}$ = Process utilization factor for N_2O-using process j.

[38] If a third party has measured facility-specific N_2O utilization factors, the conditions under which the measurements were made must be representative of the facility's N_2O-emitting processes.

$a_{N2O,j}$	=	Fraction of N_2O used in N_2O-using process j with abatement systems.
$d_{N2O,j}$	=	Fraction of N_2O for N_2O-using process j destroyed by abatement devices connected process j.
0.001	=	Conversion factor for kg to metric tons.
j	=	Type of N_2O-using process.

Alternatively, default N_2O utilization factors for CVD and other N_2O-using manufacturing processes would be applied in Equation 11. The default N_2O utilization factor for CVD used is 20 percent (emission factor of 0.8), which is the midpoint of the utilization range of 0 percent to 40 percent. EPA determined the upper bound of this range through information collected in an industry survey presented in a comment received in response to the April 2009 rule proposal. This industry survey concluded that on average the utilization of N_2O for all processes at a fab is ~40 percent. In the industry survey, the measured utilization factors were largely from newer 300 mm manufacturing equipment. EPA did not consider the 40 percent as representative because N_2O utilization of older manufacturing equipment, such as 150 mm and 250 mm tools is not fully represented. In addition, the information provided did not fully identify the specific processes from which the average N_2O utilization factor was calculated. EPA understands that the majority of N_2O is used in CVD processes; therefore 40 percent was considered the upper bound of the range for the CVD default N_2O utilization factor. To be conservative and to avoid the potential for underestimation of emissions the lower bound of ~0 percent was considered.

For other manufacturing processes, such as chamber cleaning, the default N_2O utilization factor applied would be 0 percent (emission factor of 1.0), which is equivalent to assuming that all N_2O used in manufacturing processes, other than CVD, is emitted. EPA took this approach because of a lack of information about N_2O utilization for other N_2O-using process.

3.5 Options for Estimating Heat Transfer Fluids (HTFs) Emissions

3.5.1 IPCC Tier 1 Approach

The Tier 1 approach for HTF emissions is based on the utilization capacity of a semiconductor facility multiplied by a default emission factor. Although, the Tier 1 approach has the advantages of simplicity, it relies on a default emissions factor to estimate HTF emissions and has relatively high uncertainty compared to the Tier 2 approach (IPCC, 2006).

3.5.2 IPCC Tier 2 Approach

The IPCC Tier 2 approach, which is a mass-balance approach, uses company-specific data and accounts for differences among electronics manufacturing facilities' HTFs (which vary in their global warming potentials), leak rates, and service practices, and has an uncertainty on the order of ±20 percent at the 95 percent confidence interval (IPCC, 2006). Equation 12 below shows the company-specific mass-balance equation for estimating HTF emissions. Facilities are required to provide the total nameplate capacity (HTF charge) of equipment that contains fluorinated heat transfer fluids "newly installed" during the reporting period.

$$EH_i = density_i * (I_{iB} + P_i - N_i + R_i - I_{iE} - D_i) * 0.001 \qquad \text{(Eq. 12)}$$

Where:

EH_i	=	Emissions of fluorinated GHG heat transfer fluid i (metric tons/year).
$density_i$	=	Density of fluorinated heat transfer fluid i (kg/l).
Ii_B	=	Inventory of fluorinated heat transfer fluid i in containers other than equipment at the beginning of the reporting year (in stock or storage) (l).
P_i	=	Acquisitions of fluorinated heat transfer fluid i during the reporting year (l). Includes amounts purchased from chemical suppliers, amounts purchased from equipment suppliers with or inside of equipment, and amounts returned to the facility after off-site recycling.
N_i	=	Total nameplate capacity (full and proper charge) of equipment that uses fluorinated heat transfer fluid i and that is newly installed during the reporting year (l).
R_i	=	Total nameplate capacity (full and proper charge) of equipment that uses fluorinated heat transfer fluid i and that is removed from service during the current reporting year (l).

I_{iE}	=	Inventory of fluorinated heat transfer fluid i (in containers other than equipment) at the end of the reporting year (in stock or storage) (l).
D_i	=	Disbursements of fluorinated heat transfer fluid i during the reporting year (l). Includes amounts returned to chemical suppliers, sold with or inside of equipment, and sent off site for verifiable recycling or destruction.
0.001	=	Conversion factor from kg to metric tons.
i	=	Heat transfer fluid.

3.6 Options for Reporting Controlled Emissions from Abatement Systems

While the 2006 IPCC Guidelines offer gas-specific default DREs, these values were optimized for specific processes and tools, and are not expected to be representative for all tools and gas flow rates. The IPCC default DRE values are also not applicable to abatement systems which cannot abate CF_4 at DREs greater than 85 percent (IPCC, 2006). Because of the aforementioned reasons and to ensure the accuracy of controlled emissions[39] estimations, EPA evaluated the following two options for the reporting of controlled emissions: the use of an EPA developed DRE default value and the direct, proper measurement of DRE values using *EPA's Protocol for Measuring Destruction or Removal Efficiency of Fluorinated Greenhouse Gas Abatement Equipment in Electronics Manufacturing (EPA 430-R-10-003)* (EPA DRE Protocol) (EPA, 2010). As part of both of these options, EPA evaluated requiring certification of proper installation, maintenance, and operation of abatement systems, as well as monitoring the uptime of abatement systems.

3.6.1 Proper Installation, Operation, and Maintenance

There are many abatement system manufacturers, all of whom manufacture many models of systems that are marketed as fluorinated GHG-destruction capable (Beu, L. 2005). While some of these systems may be capable of destroying some fluorinated GHGs, they may not be effective in abating CF_4 (Beu, L., 2005), which in some processes can constitute 10 percent – 20 percent (by volume) of fluorinated GHG exhaust composition (EPA, 2008d). This variability may be partially attributable to installation as well as operating and maintenance practices (Beu, L. 2005), although variations in how destruction is measured may also contribute to this variability (Beu, L., 2005). Additionally it is well known across the industry that abatement system performance varies greatly depending on a variety of abatement device and process parameters such as temperature, flow and exhaust composition (Beu, L., 2005, EPA 2008c, 2008d)).

Therefore, ensuring that abatement systems are properly installed, operated, and maintained according to manufacturers' specifications is important to reduce the likelihood of inaccurate estimations of DREs. It should be noted that this is also in line with 2006 IPCC applicability requirements for reporting controlled emissions due to abatement system use (IPCC,2006).

3.6.2 Monitoring Abatement System Uptime

Applying a DRE value that is not discounted for the time an abatement system at a facility is being operated within the range of parameters as specified in the operations manual provided by the system manufacturer (or is on "operational mode"), would result in an underestimation of total facility emissions. Uptime refers to the ratio of the total time during which the abatement system is in an operational mode with fluorinated GHGs or N_2O flowing through production process tool(s) connected to that abatement system, to the total time during which fluorinated GHGs or N_2O are flowing through production process tool(s) connected to that abatement system. An exception to this is time during which exhaust flows are passed through a redundant abatement system[40] that is in the same abatement system class[41] as the primary abatement system. Such time may be included in the uptime of the primary system.

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[39] Controlled emissions are defined as the quantity of emissions that are released to the atmosphere after application of an emission control device (e.g., abatement system).

[40] A redundant abatement system is defined as a system that is specifically designed, installed and operated for the purpose of destroying fluorinated GHGs and N_2O gases. A redundant abatement system is used as a backup to the main fluorinated GHGs and N_2O abatement system during those times when the main system is not functioning or operating in accordance with design and operating specifications.

[41] Class means a category of abatement systems grouped by manufacturer model number(s) and by the gas that the system abates, including N_2O and carbon tetrafluoride (CF_4) direct emissions and by-product formation, and all other fluorinated GHG direct emissions and by-product formation. Classes may also include any other abatement systems for which the reporting facility wishes to report

Equation 13 below can be used to calculate the fraction of input gas destroyed or removed in abatement systems connected to process tools where a recipe, process sub-type, or process type is used. This number is used to calculate the annual emissions from input gas and by-product in the above Equations 6 and 7, respectively. Equation 14 below is used to calculate the uptime.

$$d_{i,j} = \frac{\sum_p C_{ijp} * d_{ijp} * u_p}{\sum_p C_{ijp}} \quad \text{(Eq. 13)}$$

d_{ij} = Fraction of input gas i destroyed or removed in abatement systems connected to process tools where recipe, process sub-type, or process type j is used (decimal fraction).

C_{ijp} = Amount of input gas i consumed for recipe, process sub-type, or process type j fed into abatement system p (kg).

d_{ijp} = Destruction or removal efficiency for input gas i in abatement system p connected to process tools where recipe, process sub-type, or process type j is used (decimal fraction).

u_p = Uptime of abatement system (decimal fraction). (see Eq. 14)

i = Input gas.

j = Recipe, process sub-type, or process type.

p = Abatement system.

$$u_p = \frac{t_p}{T_p} \quad \text{(Eq. 14)}$$

u_p = The uptime of abatement system p (decimal fraction).

t_p = The total time in which abatement system p is in an operational mode when fluorinated GHGs or N_2O are flowing through production process tool(s) connected to abatement system p (hours).

T_p = Total time in which fluorinated GHGs or N_2O are flowing through production process tool(s) connected to abatement system p (hours).

p = Abatement system.

EPA considered two options for values for d_{ijp} expressed in Equation 13 above, the use of an EPA developed DRE factor, or properly measured DREs. Both of these options are discussed in the following sections.

3.6.3 EPA Default DRE Value

As discussed previously, the 2006 IPCC gas-specific default DRE values were optimized for specific processes and tools. However DREs are expected to vary across abatement systems and gas flow rates. For this reason, EPA estimates that the use of the IPCC default DRE value will result in controlled emissions estimates that are not representative of actual facility operations. Manufacturer supplied DREs may also result in emissions estimates that are not representative of actual facility operations because the DRE itself may have been incorrectly measured due to a failure to account for the effects of dilution (e.g., CF_4 can be off by as much as a factor of 20 to 50 and C_2F_6 can be off by a factor of up to 10 [Burton, 2007].) This understanding is supported by industry assessments as presented in Beu, 2005. Therefore, EPA developed a default DRE to be used to report controlled emissions provided that the abatement system for which the default value is representing is properly installed, operated, and maintained and is specifically designed for fluorinated GHG and N_2O abatement.

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controlled emissions provided that class is identified.

EPA developed the DRE default value using data from the EPA DRE measurement program, in which measurements have been made at three separate facilities.[42] All of the data collected through the measurement program properly took into account the effects of dilution. Using the DRE data set from these measurement studies, the following data selection criteria were applied to determine values to include in the development of the default DRE.

- ***Data must be from abatement devices that were properly installed, operated, and maintained, as well as designed to abate fluorinated GHGs and N_2O.*** [43] This is consistent with the requirements for all abatement systems for which emissions are reported. In cases where this criterion was not met, the DRE values measured were often indistinguishable from zero.
- ***Data must be in the form of a discrete value.*** Under the EPA DRE measurement program, some DRE measurements taken exceeded 99 percent. In these instance the measured data was expressed as a non-discrete value, (i.e. ≥ 99 percent (e.g. for CHF_3, NF_3, SF_6)), which could not be applied to a method to determine a default DRE value.

After evaluating the data based on these criteria, a set with a population of 11 measured DREs was used to develop the EPA default DRE value. These 11 DREs in the set were for CF_4, and were measured on two thermal abatement systems each attached to two etch tools, which, in turn, had four chambers. This data set, which can be referenced in Table 3-3 contains results from two measurement conditions: (a) DRE measurement when the process tool plasma is off, when just CF_4 and diluent gas from each chamber enters the abatement system, and (b) measurement of DRE during wafer processing, when CF_4 together with other waste effluents leave the tool during actual wafer processing enters the abatement system. Measured DREs are shown for each etch tool. These are regarded as independent measurements of the DRE for abating CF_4 for each abatement system.

Table 3-3. Data Set Used to Develop EPA Default DRE Value

Experiment ID	Comment about experiment	Measured CF_4 DRE	Source of data[a]
FK15 #1	No plasma	87.5	Table IV
FK15 #2	No plasma	63.1	Table IV
FK15 #3	No plasma	79.4	Table IV
FK15 #4	No plasma	77.4	Table IV
FE05#1	No plasma	84.5	Table IV
FE05#2	No plasma	82.2	Table IV
FE05#3	No plasma	91.7	Table IV
FE05#4	No plasma	96.0	Table IV
Additional data from wafer tests, all chambers			
FK15	Trench etch, #1 & #3 only	83	Table VIII
FK15	Via etch, #1 & #3 only	85	Table VIII
FE05	FE etch #3 & #4 only	90	Table IX

[a] Source: EPA, 2009.

The summary statistics of the data set is presented in Table 3-3 is presented in

Table 3-4. Also presented in

[42] For more information about the three studies, please see the following reports: *Developing a Reliable Fluorinated Greenhouse Gas (F-GHG) Destruction or Removal Efficiency (DRE) Measurement Method for Electronics Manufacturing: A Cooperative Evaluation with IBM* (EPA 430-R-10-004); *Developing a Reliable Fluorinated Greenhouse Gas (F-GHG) Destruction or Removal Efficiency (DRE) Measurement Method for Electronics Manufacturing: A Cooperative Evaluation with NEC Electronics, Inc.* (EPA 430-R-10-005); and *Developing a Reliable Fluorinated Greenhouse Gas (F-GHG) Destruction or Removal Efficiency (DRE) Measurement Method for Electronics Manufacturing: A Cooperative Evaluation with Qimonda* (EPA 430-R-08-017).

[43] While the EPA DRE measurement program only looked at abatement systems performance for fluorinated GHGs, it was assumed, for this use, that abatement systems that were designed to treat fluorinated GHGs were also designed to treat N_2O.

Table 3-4 is the default DRE determined under the assumption that the measured DREs are distributed normally, and under the condition that 95 percent of the population will be above the value of 59% (i.e. the lower one-sided tolerance interval). For simplicity the value was rounded to one significant figure, equating to a default DRE of 60 percent.

Table 3-4. Summary Statistics and Default DRE (Lower One-Sided Tolerance Interval)

	Mean of Measured Values	Stdev of Measured Values	Lower One-Sided Tolerance Interval
No Plasma Measured DRE	82.73	10.054	-
All Measured DRE	83.62	8.70	59

3.6.4 Proper Measurement of Abatement System DRE

For purposes of this rule, proper measurement of DRE values are those measured in accordance EPA's DRE Protocol. The EPA DRE Protocol provides a practical and reliable method for measuring DREs of POU abatement devices while also providing flexibility to users. In addition, the use of the EPA DRE Protocol will ensure dilution is properly accounted for when determining DREs. (Please refer to the EPA DRE Protocol for a more detailed discussion on the justification for the development and application of the Protocol).

A representative random sampling approach can be used to reduce burden associated with directly and properly measuring DREs of each abatement system at a facility. Therefore, EPA evaluated the use of a random sampling abatement system testing program (RSASTP) that would span all classes of abatement systems for which controlled emissions are reported. (Class means a category of abatement systems grouped by manufacturer model number(s) and by the gas that the system abates, including N_2O and carbon tetrafluoride (CF_4) direct emissions and by-product formation, and all other fluorinated GHG direct emissions and by-product formation. Classes may also include any other abatement systems for which the reporting facility wishes to report controlled emissions provided that class is identified.[44])

EPA qualitatively evaluated a range of options, from 10 percent to 100 percent, for what would constitute an appropriate annual representative sample of abatement systems to be tested in a reporting year. EPA selected 20 percent as it would balance the annual measurement burden for reporters and anticipate reliable maintenance periods and useful lifetimes of abatement systems. The RSASTP, with the selected 20 percent sample size, is described below.

An annual representative sample would consist of three or 20 percent of installed abatement devices, whichever is greater, for each model type each year. In the case that 20 percent of total abatement systems at a facility does not equal a whole number, the number of devices to be tested should be rounded up.[45] Each reporting period the DRE for a different three or 20 percent set of devices would be measured. For systems for which a DRE has not been measured in a reporting period, a simple average of the measured DREs for systems of that specific class of abatement system is used. If redundant abatement systems are tested during periods of maintenance or repair, then the most recently measured or class average DRE for that system may be used.

Using the RSASTP, as outlined in the paragraph above, would ensure the eventual measurement of each device but over the course of several years. The importance of measuring the DRE for each abatement device lies in the fact that the robustness of installed abatement systems varies by gas and operating principle. Therefore, while some abatement devices may receive regular maintenance and perform optimally, others may, because of the specific nature of the exhaust they treat, not be functioning properly. As well, it is well known across the industry that abatement system performance varies greatly depending on a variety of abatement device and process parameters such as temperature, flow and exhaust composition. (Beu, 2005) Facilities often develop and ultimately use new processes potentially every year, and the parameters of these processes vary, hence the use of the RSASTP will capture these changes over time.

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[44] CF_4 is a very stable chemical and especially difficult to effectively abate. It may be used as an input gas and generated as a byproduct of other fluorinated GHG process reactions.

[45] For example, 16 abatement devices, 20 percent of which equals 3.2; therefore, four abatement devices would be measured each year, which exceeds three.

4 QA/QC Requirements

QA/QC methods for reporting fluorinated GHG and N_2O emissions include:

- Following the 2006 ISMI Guidelines for QA/QC procedures when measuring and calculating facility-specific, recipe specific fluorinated GHGs and N_2O utilization and by-product formation rates.
- Where facility-specific, recipe-specific fluorinated GHG and N_2O utilization and by-product formation rates were measured prior to January 1, 2007, verify that the QA/QC procedures in International SEMATECH #01104197A-XFR (2001 ISMI Guidelines) were followed when the factors were measured and calculated.
- Following the QA/QC procedures in the EPA DRE Protocol when calculating abatement system DREs.
- Demonstrating that as part of normal facility operations the inventory of gas stored in containers at the beginning of a reporting year is the same as the inventory of gas stored in containers at the end of the previous reporting year.

QA/QC methods for reporting emissions from HTFs use and annual gas consumption for each fluorinated GHG and N_2O used include:

- Reviewing inputs to the gas consumption equation and HTF mass balance equation (Eqs. 8 and 12), to ensure inputs and outputs are all accounted for.
- Ensuring no negative inputs are entered in the gas consumption equation and HTF mass balance equation (Eqs. 8 and 12) and negative emissions are not calculated.
- Ensuring that the beginning of year inventory is identical to the end of year inventory from previous year.
- Ensuring that the total quantity of gas in containers in service at the end of the reporting year is accounted for as if the in-service containers were full. Ensuring also that the same quantity is accounted for in the inventory of gas stored in containers at the beginning of the subsequent reporting year.

General QA/QC methods include:

- Ensuring all flowmeters, weigh scales, pressure gauges, and thermometers used to measure quantities that are used to meet requirements of subpart I have an accuracy and precision of one percent of full scale or better.

5 Procedures for Estimating Missing Data

It is expected that collecting gas consumption data and quantifiable metrics for apportioning gas consumption will always be feasible for facilities, with the exception of the time period facilities are permitted to use Best Available Monitoring Methods (BAMM).[46] When estimating HTF emissions, the use of the mass-balance approach requires correct records for all inputs. Therefore facilities that use HTFs and have missing data for one or more of the inputs for the mass-balance equation (see Eq. 12) can estimate HTF emissions using the arithmetic average of the emission rates for the reporting year immediately preceding the period of missing data and the months immediately following the period of missing data. Alternatively, missing information may be estimated from the heat transfer fluid supplier's records. All methods and values used for all missing data values must be documented.

6 Reporting and Recordkeeping Procedures

The following data, which is additional to the information generally required to be reported and/or retained as records for all facilities covered under the MRR (see §98.3(c) and §98.3(g) (74 FR 56379, October 2009), would be useful for confirming emissions calculations and/or calculating emission factors that could be compared across facilities for quality control purposes:

- For each facility report:

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[46] See the Electronics Manufacturing section of the preamble to the Final Rule for a discussion on the use of Best Available Monitoring Methods under subpart I.

- Annual manufacturing capacity of a facility.
- For facilities that manufacture semiconductors, the diameter of wafers manufactured at the facility.
- Annual emissions of:
  - Each fluorinated GHG emitted from each process type for which the facility is required to calculate emissions.
  - Each fluorinated GHG emitted from each individual recipe (including those in a set of similar recipes), or process sub-type.
  - N_2O emitted from each chemical vapor deposition processes and from other N_2O-using manufacturing processes.
  - Each HTF emitted.
- The method used to calculate fluorinated GHG emissions.
- Annual production in terms of substrate surface area (e.g., silicon, PV-cell, glass).
- When factors for fluorinated GHG process utilization and by-product formation rates and/or N_2O utilization factors other than the default values provided in the appendices are used, the following:
  - The recipe-specific utilization and by-product formation rates for each individual recipe (or set of similar recipes) and/or facility-specific N_2O utilization factors.
  - For recipe-specific utilization and by-product formation rates, the film or substrate that was etched/cleaned and the feature type that was etched, as applicable.
  - Certification that the recipes included in a set of similar recipes are similar.
  - Certification that the measurements for all reported recipe-specific utilization and by-product formation rates and/or facility specific N_2O utilization factors were made using the 2006 ISMI Guidelines, or the 2001 ISMI Guidelines if measurements were made prior to January 1, 2007.
  - Source of the recipe-specific utilization and by-product formation rates and/or facility-specific-N_2O utilization factors.
  - Certification that the conditions under which the measurements were made for facility-specific N_2O utilization factors are representative of the facility's N_2O-emitting production processes.
- Annual gas consumption for each fluorinated GHG and N_2O, including where the facility used less than 50 kg of a particular fluorinated GHG or N_2O used at the facility. For all fluorinated GHGs and N_2O used at the facility for which emissions have not been calculated, the chemical name of the fluorinated GHG used, the annual consumption of the gas, and a brief description of its use.
- All inputs used to calculate gas consumption of each fluorinated GHG and N_2O used.
- Disbursements of each fluorinated GHG and N_2O during the reporting year.
- All inputs used to calculate disbursements for each fluorinated GHG and N_2O used, including all facility-wide gas-specific heel factors used for each fluorinated GHG and N_2O. If the facility used less than 50 kg of a particular fluorinated GHG during the reporting year, facility-wide gas-specific heel factors do not need to be reported for those gases.
- Annual amount of each fluorinated GHG consumed for each recipe, process sub-type, or process type, as appropriate, and the annual amount of N_2O consumed for each chemical vapor deposition and other electronics manufacturing production process.
- All apportioning factors used to apportion fluorinated GHG and N_2O consumption.
- For the facility-specific apportioning model used to apportion fluorinated GHG and N_2O consumption the following:
  - Identification of the quantifiable metric used in the facility-specific engineering model to apportion gas consumption.
  - The start and end dates selected to monitor for verification of the model.

        - Certification that the gases selected for comparisons correspond to the largest quantities consumed on a mass basis, at the facility in the reporting year for the plasma etching process type and the chamber cleaning process type.
        - The result of the calculations comparing the actual and modeled gas consumptions.
    - Fraction each fluorinated GHG or N_2O fed into a recipe, process sub-type, or process type that is fed into tools connected to abatement systems.
    - Fraction of each fluorinated GHG or N_2O destroyed or removed in abatement systems connected to process tools where a recipe, process sub-type, or process type is used, as well as all inputs and calculations used to determine the inputs to calculate this fraction.
    - Inventory and description of all abatement devices through which fluorinated GHGs or N_2O flow at the facility, including the number of devices of each manufacturer, model numbers, manufacturer claimed fluorinated GHG and N_2O DREs, if any, and records of DRE measurements over their in-use lives. The inventory of abatement systems must describe the tools with model numbers and the recipe(s), process sub-type, or process type for which these systems treat exhaust.
    - For each abatement system through which fluorinated GHGs or N_2O flow at the facility, for which controlled emissions are reported, the following:
        - Certification that the abatement device has been installed, maintained, and operated in accordance with manufacturers' specifications.
        - All inputs and results of calculations made accounting for the uptime of abatement systems used during the reporting year.
        - The default DRE value or properly measured DREs for each abatement system used in that reporting year.
        - Where the default DRE value is used to report controlled emissions, certification that the abatement systems for which emissions are being reported were specifically designed for fluorinated GHG and N_2O abatement. Documentation stating that the system was designed for fluorinated GHG and N_2O abatement should be provided to show this.
        - Where properly measured DREs or class averages of DREs are used, the following must be reported:
            - A description of the class, including the abatement system manufacturer and model number, and the fluorinated GHG and N_2O in the process effluent stream.
            - The total number of systems in that class for the reporting year.
            - The total number of systems for which DREs were properly measured in that class for the reporting year.
            - A description of the calculation used to determine the class average, including all inputs of the calculation.
            - A description of method of randomly selecting class members for testing.
    - For HTF emissions, inputs used in the mass-balance equation for each fluorinated GHG used.
    - Where missing data procedures were used to estimate inputs into the HTF mass-balance equation, the number of times missing data procedures were followed in the reporting year, the method used to estimate the missing data, and the estimates of those data.
    - A brief description of each "best available monitoring method" used, the parameter measured or estimated using the method, and the time period during which the "best available monitoring method" was used.

- Retain records of:
    - All data used and copies of calculations made as a part of estimating gas consumption and emissions.

- Documentation for the values used for fluorinated GHG and N_2O utilization and by-product formation rates. Where facility-specific, recipe-specific gas utilization and by-product formation rates were used, the following records must also be retained:
  - Complete documentation and final report for measurements for recipe-specific utilization and by-product formation rates demonstrating that the values were measured using the 2006 ISMI Guidelines, provided the measurements were made prior to January 1, 2007.
  - Documentation that recipe-specific utilization and by-product formation rates developed for the facility are measured for recipes that are similar to those used at the facility. Included in the documentation, recorded to two significant figures, should be reactor pressure, flow rates, chemical composition, applied RF power, direct current (DC) bias, temperature, flow stabilization time, and duration.
  - Documentation that the facility's N_2O measurements are representative of the N_2O-emitting processes at the facility.
  - The date and results of the initial and any subsequent tests to determine utilization and by-product formation rates.
- Documentation for the facility-specific engineering model used to apportion fluorinated GHG and N_2O consumption. This documentation must be part of the site GHG Monitoring Plan. At a minimum, the following must be retained:
  - A clear, detailed description of the facility-specific model, including how it was developed; the quantifiable metric used in the model; all sources of information, equations, and formulas, each with clear definitions of terms and variables; and a clear record of any changes made to the model while it was used to apportion fluorinated GHG and N_2O consumption across individual recipes (including those that are similar recipes), process sub-types, and/or process types.
  - Sample calculations used for developing a recipe-specific, process sub-type-specific, or process type-specific gas apportioning factor for the fluorinated GHG used at a facility in the largest quantity, on a mass basis, during the reporting year for each individual recipe (including those that are similar recipe), process sub-type, or process type.
- For each abatement device through which fluorinated GHGs or N_2O flows at the facility, for which the facility is reporting controlled emissions, the following:
  - Documentation to certify that the abatement device is installed, maintained, and operated in accordance with manufacturers' specifications.
  - Abatement system calibration and maintenance records.
  - Where the default DRE value is used, documentation from the abatement system supplier describing the equipment's designed purpose and emission control capabilities for fluorinated GHG and N_2O.
  - Where properly measured DRE is used to report emissions, dated certification by the technician who made the measurement that the DRE was calculated according to methods in the EPA's DRE Protocol, complete documentation of the results of any initial and subsequent tests, and final reports as specified in the EPA DRE Protocol.
- Purchase records for gas purchased.
- Invoices for gas purchases and sales.
- Documents and records used to monitor and calculate abatement system uptime.

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Appendix A - Default Emission Factors for Threshold Applicability Determination and Etch and Clean Emission Estimation Methods

Table A-1. Default Emission Factors for Threshold Applicability Determination

Product Type	Emission Factors EF_i					
	CF_4	C_2F_6	CHF_3	C_3F_8	NF_3	SF_6
Semiconductors (kg/m^2)	0.90	1.00	0.04	0.05	0.04	0.20
LCD (g/m^2)	0.50	NA	NA	NA	0.90	4.00
MEMS (kg/m^2)	NA	NA	NA	NA	NA	1.02

Notes: NA denotes not applicable based on currently available information.
Source: IPCC, 2006

Table A-2. Default Emission Factors (1-U_{ij}) for Gas Utilization (U_{ij}) and By-Product Formation Rates (B_{ijk}) for MEMS, LCD, and PV Manufacturing

	Process Gas	Greenhouse Gases with TAR GWP									Greenhouse Gases without TAR GWP			Non-GHGs Producing FC By-products‡	
		CF_4	C_2F_6	CHF_3	CH_2F_2	C_3F_8	c-C_4F_8	NF_3 Remote	NF_3	SF_6	C_4F_6	C_5F_8	C_4F_8O	F_2	COF_2
MEMS MANUFACTURING[a]	Etch 1-Ui	0.7*	0.4*	0.4*	0.06*	NA	0.2*	NA	0.2	0.2	0.1	0.2	NA	NA	NA
	CVD 1-Ui	0.9	0.6	NA	NA	0.4	0.1	0.02	0.2	NA	NA	0.1	0.1	NA	NA
	Etch BCF_4	NA	0.4*	0.07*	0.08*	NA	0.2	NA	NA	NA	0.3*	0.2	NA	NA	NA
	Etch BC_2F_6	NA	NA	NA	NA	NA	0.2	NA	NA	NA	0.2*	0.2	NA	NA	NA
	CVD BCF_4	NA	0.1	NA	NA	0.1	0.1	0.02†	0.1†	NA	NA	0.1	0.1	0.02†	0.02†
	CVD BC_2F_6	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	CVD BC_3F_8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.04	NA	NA
LCD MANUFACTURING	Etch 1-Ui	0.6	NA	0.2	NA	NA	0.1	NA	NA	0.3	NA	NA	NA	NA	NA
	CVD 1-Ui	NA	NA	NA	NA	NA	NA	0.03	0.3	0.9	NA	NA	NA	NA	NA
	Etch BCF_4	NA	NA	0.07	NA	NA	0.009	NA	NA	NA	NA	NA	NA	NA	NA
	Etch $BCHF_3$	NA	NA	NA	NA	NA	0.02	NA	NA	NA	NA	NA	NA	NA	NA
	Etch BC_2F_6	NA	NA	0.05	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	CVD BCF_4	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	CVD BC_2F_6	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	CVD BC_3F_8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
PV MANUFACTURING	Etch 1-Ui	0.7	0.4	0.4	NA	NA	0.2	NA	NA	0.4	NA	NA	NA	NA	NA
	CVD 1-Ui	NA	0.6	NA	NA	0.1	0.1	NA	0.3	0.4	NA	NA	NA	NA	NA
	Etch BCF_4	NA	0.2	NA	NA	NA	0.1	NA	NA	NA	NA	NA	NA	NA	NA
	Etch BC_2F_6	NA	NA	NA	NA	NA	0.1	NA	NA	NA	NA	NA	NA	NA	NA
	CVD BCF_4	NA	0.2	NA	NA	0.2	0.1	NA	NA	NA	NA	NA	NA	NA	NA
	CVD BC_2F_6	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	CVD BC_3F_8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

Notes: NA denotes not applicable based on currently available information

‡ The default emission factors for F_2 and COF_2 may be applied to cleaning low-k CVD reactors with ClF_3.

* Estimate includes multi-gas etch processes

[a] MEMS manufacturing EFs are consistent with the 2006 IPCC Tier 2b EFs for the manufacture of semiconductors.

† Estimate reflects presence of low-k, carbide and multi-gas etch processes that may contain a C-containing FC additive

Source: IPCC, 2006

Table A-3. Default Emission Factors ($1-U_{ij}$) for Gas Utilization (U_{ij}) and By-Product Formation Rates (B_{ijk}) for Semiconductor Manufacturing for 150 mm and 200 mm Wafer Sizes

Process Type/Sub-type	Process Gas i										
	CF_4	C_2F_6	CHF_3	CH_2F_2	C_3F_8	c-C_4F_8	NF_3	SF_6	C_4F_6	C_5F_8	C_4F_8O
Plasma Etching											
$1-U_i$	0.69	0.56	0.38	0.093	NA	0.25	0.038	0.20	0.14	NA	NA
B_{CF_4}	NA	0.23	0.026	0.021	NA	0.19	0.0040	NA	0.13	NA	NA
$B_{C_2F_6}$	NA	NA	NA	NA	NA	0.08	NA	NA	0.12	NA	NA
$B_{C_3F_8}$	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Chamber Cleaning											
In situ plasma cleaning											
$1-U_i$	0.92	0.55	NA	NA	0.40	0.10	0.18	NA	NA	NA	0.14
B_{CF_4}	NA	0.19	NA	NA	0.20	0.11	0.011	NA	NA	NA	0.13
$B_{C_2F_6}$	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.030
$B_{C_3F_8}$	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Remote plasma cleaning											
$1-U_i$	NA	NA	NA	NA	NA	NA	0.018	NA	NA	NA	NA
B_{CF_4}	NA	NA	NA	NA	NA	NA	0.0047	NA	NA	NA	NA
$B_{C_2F_6}$	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
$B_{C_3F_8}$	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
In situ thermal cleaning											
$1-U_i$	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
B_{CF_4}	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
$B_{C_2F_6}$	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
$B_{C_3F_8}$	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Wafer Cleaning											
$1-U_i$	0.77	NA	NA	0.24	NA	NA	0.23	0.20	NA	NA	NA
B_{CF_4}	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

Process Type/Sub-type	Process Gas i										
	CF_4	C_2F_6	CHF_3	CH_2F_2	C_3F_8	$c\text{-}C_4F_8$	NF_3	SF_6	C_4F_6	C_5F_8	C_4F_8O
BC_2F_6	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
BC_3F_8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

Notes: NA denotes not applicable based on currently available information.

Table A-4. Default Emission Factors ($1-U_{ij}$) for Gas Utilization (U_{ij}) and By-Product Formation Rates (B_{ijk}) for Semiconductor Manufacturing for 300 mm Wafer Size

Process Type/Sub-type	Process Gas i										
	CF_4	C_2F_6	CHF_3	CH_2F_2	C_3F_8	$c\text{-}C_4F_8$	NF_3	SF_6	C_4F_6	C_5F_8	C_4F_8O
Plasma Etching											
$1-U_i$	0.80	0.80	0.48	0.14	NA	0.29	0.32	0.37	0.09	NA	NA
BCF_4	NA	NA	0.0018	0.0011	NA	0.079	NA	NA	0.27	NA	NA
BC_2F_6	NA	NA	0.0011	NA	NA	0.12	NA	NA	0.29	NA	NA
BC_3F_8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Chamber Cleaning											
In situ plasma cleaning											
$1-U_i$	NA	NA	NA	NA	NA	NA	0.23	NA	NA	NA	NA
BCF_4	NA	NA	NA	NA	NA	NA	0.0046	NA	NA	NA	NA
BC_2F_6	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
BC_3F_8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Remote Plasma Cleaning											
$1-U_i$	NA	NA	NA	NA	0.063	NA	0.018	NA	NA	NA	NA
BCF_4	NA	NA	NA	NA	NA	NA	0.040	NA	NA	NA	NA
BC_2F_6	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
BC_3F_8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
In Situ Thermal Cleaning											
$1-U_i$	NA	NA	NA	NA	NA	NA	0.28	NA	NA	NA	NA

Process Type/Sub-type	Process Gas i										
	CF_4	C_2F_6	CHF_3	CH_2F_2	C_3F_8	$c\text{-}C_4F_8$	NF_3	SF_6	C_4F_6	C_5F_8	C_4F_8O
B_{CF_4}	NA	NA	NA	NA	NA	NA	0.010	NA	NA	NA	NA
$B_{C_2F_6}$	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
$B_{C_3F_8}$	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Wafer Cleaning											
$1-U_i$	0.77	NA	NA	0.24	NA	NA	0.23	0.20	NA	NA	NA
B_{CF_4}	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
$B_{C_2F_6}$	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
$B_{C_3F_8}$	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

Notes: NA denotes not applicable based on currently available information.

Appendix B - Development of EPA Published Emission Factors for the Tier 2c and Tier 2d Methods

To develop the default emission factors (EFs) for semiconductor manufacturing presented in Tables A-3 and A-4, EPA used industry data provided in cooperation with the Semiconductor Equipment and Materials International (SEMI), which redacted identifying company information prior to sharing the data with EPA.[48] An example of the form in which EPA received data is presented in Figure B-1. All of the data EPA received was compiled in an EF development database. The complete database is presented in Table 5 of the report Draft Emission Factors for Refined Semiconductor Manufacturing Process Categories (EPA-HQ-OAR-2009-0927-0073) ("NODA database").[49] The EF data in the NODA database, which is identified by process sub-types and wafer technology, includes single- and multi-gas process chemistries. EF information is provided for single and multi-gas emission factors for utilization rates and by-product formation rates. The table denotes the dominant gas, the mass fraction emitted and the by-product formation rates expressed as a mass fraction of the dominant gas. The table also denotes the mass-emitted fractions of the other gases used when multiple gases are employed in either chamber cleaning or film etching emission processes.

Some providers of data identified a broad process type (i.e., chamber cleaning, etching and wafer cleaning) as well as a process sub-type. For example, information pertaining to the chamber cleaning process type was identified by a chamber cleaning process sub-type (in-situ plasma, remote plasma, or in-situ thermal) as well. The NODA database identifies all information by the process sub-types of the Refined Method (see section 3.1.6), as the data collected by EPA was originally intended to be used to develop default emission factors for the Refined Method. Although the Refined Method was not included in the final rule, the emission factor data could be used to developed the default factors for the Tier 2c and Tier 2d methods because the information in the database is on a more granular level than is required for these two methods. EFs were developed by wafer technology for the broad etch process type and the broad wafer cleaning process types using all relevant information in the NODA database (e.g., all etch information, regardless of the identified sub-type was used to develop the etch EFs). EFs were also developed for the three chamber cleaning process sub-types (in-situ plasma, remote plasma, and in-situ thermal) for each wafer technology. These EFs are presented in Tables A-3 and A-4.

The EFs presented in Tables A-3 and A-4 are simple (unweighted) averages developed employing an approach similar to that used for the 2006 IPCC Guidelines. Each EF represents an average of the appropriate values in the NODA database with each entry given equal weight. The exact methods used to develop the EFs are further discussed in the report Draft Emission Factors for Refined Semiconductor Manufacturing Process Categories (EPA-HQ-OAR-2009-0927-0073).

Measures Taken to Overcome Data Gaps

As evident by the "NA" entries in Tables A-3 and A-4 (NA denotes not applicable based on currently available information) and the information presented in the NODA database, there are still gaps in the EF data that are available to EPA. Using the rationale described below EPA has addressed these gaps.

[48] See TECHNICAL SUPPORT DOCUMENT (UPDATED) FOR PROCESS EMISSIONS FROM ELECTRONICS MANUFACTURE (e.g., SEMICONDUCTORS, LIQUID CRYSTAL DISPLAYS, PHOTOVOLTAICS, AND MICRO-ELECTRO-MECHANICAL SYSTEMS): PROPOSED RULE FOR MANDATORY REPORTING OF GREENHOUSE GASES (March 22, 2010) and the Subpart I Notice of Data Availability (75 FR 26904) for more information on the data collection process and initiation.

[49] EPA initially intended to use the data provided in cooperation with SEMI to develop emission factors for the Refined Method. Therefore the data in the NODA database was originally used to develop draft emission factors for the Refined Method; however, EPA decided not to include the Refined Method in the final rule.

150 mm

EPA received only one value for fluorinated GHG usage during device manufacture on 150 mm wafers. In the absence of additional emission data for 150 mm wafers, EPA assumed that the EFs for 200 mm technologies apply for 150 mm as well. EPA based this assumption on the belief that EFs for 150 mm processing technology are closer to 200 mm processing technologies than to 300 mm processing technologies [see Beu (2005)]. Moreover, EPA understands that a portion of the EFs for 200 mm processing in the NODA database were developed on early 200 mm equipment prior to efforts by device and equipment manufacturers to reduce fluorinated GHG usage, which occurred during the latter half of the 200 mm wafer era. The average draft EFs in Table A-3 reflect emission measurements made in the earlier and later portions of the 200 mm wafer era.[50] To apply EFs for 300 mm wafer processing equipment to 150 mm might result in reported emissions being understated when EFs for 300 mm are smaller than those for 200 mm [see Beu (2005)]. This concern is supported by comparing the chamber cleaning EFs for 200 mm and 300 mm technologies. Reports in the 200 mm wafer era indicated that chamber cleaning accounted for the majority of fluorinated GHG usage.

Wafer Cleaning

300 mm Wafers

EPA received minimal information about emissions resulting from wafer cleaning in the semiconductor industry for 300 mm wafers. In the available patent literature for plasma based bevel cleaning, a process was identified under the wafer cleaning process type that used two gases, CF_4 and SF_6. [e.g., see Kim et al. (2009)] EPA's EF database, the NODA database, does not contain gas utilization information for SF_6 for wafer cleaning, or any chamber cleaning process that may be analogous for wafer cleaning. EPA filled this gap in SF_6 data by using a draft value based on the SF_6 utilization for in situ chamber cleaning provided in the IPCC Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories (Chapter 3, Table 3.15). (see IPCC, 2000)

150/200 mm Wafers

No information for the wafer cleaning process type was available for 150 mm or 200 mm in the NODA database. As EPA understands, wafer cleaning processes were not used in the 150 mm and early 200 mm eras, but these processes began to phase into the industry in the late 200 mm era and the 300 mm era (F. Burkeen, et al, 2007). Therefore, to make it feasible for a facility processing 200 mm wafers to estimate emissions from any wafer cleaning activities EPA drew an analogy between the 300 mm and 150/200 mm wafer cleaning EFs.

SF_6 Emission Factor for 150/200 mm Etch

The NODA database does not contain any information for SF_6 for etching for the 150 mm or 200 mm wafer technologies. However, based on the information presented in the 2006 IPCC Guidelines, it is known that SF_6 is used for etching processes for these technologies. To fill this gap in information, for the 150/200mm SF_6 etch EF, EPA used the etch SF_6 EF presented in the 2006 IPCC Guidelines.

Modifications to the NF_3 Emission Factor

EPA learned, through discussions with a major supplier of equipment, that its experience suggests that the utilization efficiency, U, of NF_3 in contemporary units for cleaning chambers that process 200 mm and 300 mm wafers are similar, despite the latter having higher NF_3 flow rates. RPS units, both 200 mm and 300 mm, carry the same guaranteed utilization efficiency of 95 percent; RPS units emit 5 percent or less of the NF_3 used during chamber cleaning. Achieving similar utilization efficiencies in the two systems is accomplished by increasing the plasma power to the RPS units with higher flow rates. For 200 and 300 mm systems, the manufacturer's measurement experience indicates that the NF_3 utilization is of the order of 99 percent when operated under manufacturer's specifications. The manufacturer also posited that utilization efficiencies should exceed 95 percent for typical, reasonably maintained RPS units.

[50] In using the term "200 mm era" EPA is referring to the period during which the majority of R&D expenditures by device and equipment manufacturers were directed to 200 mm wafers. Toward the end a wafer technology era, R&D attention shifted to the next generation of wafer technology, 300 mm wafers.

EPA's review of the NODA database showed that the mean complement of utilization efficiencies, ⟨(1- U)⟩ or mean EFs, associated with 200 mm and 300 mm wafer processing for NF_3 RPS were 0.0285 ±0.0390 and 0.0174 ±0.0285, respectively. Statistically, it is evident that the population means are equal, and that all the NF_3 emission factor data in EPA's NODA database may be considered as one population. EPA's analysis is consistent with the manufacturer's expectations although the mean utilizations for both wafer sizes fall below the tool manufacture's measurement experience of 99 percent (EF = 0.01) but is also well above the performance expectation of 95 percent utilization (EF = 0.05).

Review of NF_3 RPS emission factors contained in EPA's NODA database shows values that approach 0.20—80 percent utilization efficiencies, substantially below the expected performance utilization efficiency of 95 percent. Providers of NF_3 utilization data to EPA did not describe the robustness or representativeness of the submitted data. EPA viewed in as reasonable to consider the possibility that the higher EFs might be outliers or anomalously high, that they might reflect one or more of four circumstances: (1) poorly measured EFs, (2) poorly maintained systems, (3) older RPS technologies, (4) operation outside manufacturer's specifications. While the manufacturer agreed such high values could be outliers—especially for values above 0.1 or utilization efficiencies below 90 percent—EPA was uncomfortable with removing such values without further consideration.

EPA combined the 200 mm and 300 mm data points for NF_3 RPS and posed the question whether the resulting distribution was better described with or without the larger values. For this analysis EPA assumed the variability in the set of emission factors could be described by a beta distribution, a distribution that (1) accounts for the skewness of the observations and (2) constrains values between zero and one, $0 \leq (1 - U_i) < s$, where $s < 1$.

EPA's analysis showed that a reasonable fit (p-value = 0.0037, chi-squared test) was obtained with s = 0.09 and removal of the top four EF values (0.1933, 0.1900, 0.1720 and 0.1120), which correspond to utilization efficiencies between 89 and 81 percent, considerably below the manufacturer's expected performance of 95 percent. The mean and standard deviation in emission factor of the reduced dataset was 0.0182 ± 0.0191 (1 standard deviation). A somewhat higher mean emission factor (5 percent) and standard deviation of 0.0191± 0.0211 (1 standard deviation) and somewhat poorer fit (p-value = 0.0096, chi-squared) was obtained with s < 0.115 and removal of the top three values.

Consideration of the information gleaned through industry together with EPA's statistical analysis led EPA to choose the slightly lower mean value for the default EF (=0.0182 ± 0.0191 (1 standard deviation)) for RPS chamber cleaning with NF_3 for both 200 and 300 mm wafer processing systems. After removal of the four highest values, the mean EFs for 200 mm and 300 mm RPS units remained statistically indistinguishable: 0.0204 ± 0.0202 and 0.0141 ± 0.0144, respectively.

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Figure B-1. Data Form Submitted by Semiconductor Device Manufacturers and Equipment Manufacturers to SEMI

Information for Developing EPA's Refined FLUORINATED GHG Emission Process Categories and Corresponding Emission Factors

(one form per process of record)

Field			
Source/Contact (TBR)[1]	**(For SEMI use, information redacted)**		
Date of measurement			
Location of study (TBR)	**(For SEMI use, information redacted)**		
Emission process category and subcategory (s) of process category[2]	Emission Process Category	Subcategory of Process Category	Alternative Patterning/Etching Subcategory
Equipment (Manufacturer name/model number) (TBR)[3] Letter denotes each reporting entity.	**(Information redacted, it is sought to facilitate sufficient consideration of equipment manufacturer when estimating U.S. share equipment usage in device manufacture.)**		
Patterning/etching subcategories (Check preference and explain each). Specify both film type and etched feature regardless of preference.	**Film Etch** ☐ **Feature Etch** ☐	Explanation: Specify/describe film type: Specify/describe etched feature:	
Substrate size (Si wafer)			
Measurement method/protocol[4]	**(Either ISMI Guidelines or equivalent alternative measurement protocol with brief explanation regarding why alternative is considered equivalent to ISMI Guidelines.)**		
Achieved ISMI Fluorine target mass balance >90%? Check answer.[5]	**YES** ☐ **NO** ☐ **(Explain)**		

Corresponding Emission Factors for Emission Process Categories

Process Gases (i)	CF_4	C_2F_6	C_3F_8	$c\text{-}C_4F_8$	CHF_3	SF_6	NF_3	C_4F_6	C_5F_8	C_4F_8O	CH_2F_2	F_2	COF_2	N_2O
Measured emissions: $1\text{-}U_i$[6]														
Standard deviation:														

Meas. CF_4 byproduct, B_{ip}[7]														N/A
CF_4 B standard deviation:														N/A
Meas. C_2F_6 byproduct, B_{ip}[7]														N/A
C_2F_6 B standard deviation:														N/A
Meas. C_3F_8 byproduct, B_{ip}[7]														N/A
C_3F_8 B standard deviation:														N/A
Unit of measurement (mass):														
No. of wafers in study	(number of wafers measured)													
Comments														
Information for developing average emission factors														
Estimate of U. S. share of selected process usage category, % (Check answer)	**10%**☐ **20%**☐ **30%**☐ **40%**☐ **50%**☐ **60%**☐ **70%**☐ **80%** ☐ **90%**☐													

Notes:

1. TBR denotes To Be Redacted by SEMI.
2. Distinguish between four emission process categories: 1. **Chamber Cleaning**; 2. **Wafer Cleaning**; 3. **Patterning/etching**; and 4. **Deposition**. Within **Chamber Cleaning** category distinguish between the subcategories remote plasma cleaning and in situ cleaning. Within **Wafer Cleaning** category distinguish between the subcategories ashing and bevel cleaning. Within **Deposition** category (N_2O only) distinguish between the subcategories thermal and PECVD. There are two candidate Patterning/etching categories under consideration: **Film Etch** and **Feature Etch**. The process subcategories under the **Film Etch** alternative are: silicon, oxide, nitride and metal. The process subcategories under the **Feature Etch** alternative are: Contact, SAC, Gate, Capacitor, Deep Trench, Isolation Trench, Regular Via, Through-silicon via and Metal etch. Select one subcategory from each of the Film Etch and Feature Etch categories and enter onto Data Form in the Subcategory and Alternative Subcategory spaces. Distinguishing between Film Etch and Feature Etch on the Data Form is not necessary.
3. SEMI will assign a separate letter for each entity that provides emission factor data.
4. Provide a brief explanation that supports using an alternative to ISMI Guidelines for characterizing process emissions.
5. Provide a brief explanation that supports the reliability of the reported emission factors despite not achieving the F mass balance target of >90% mass closure.
6. U_i denotes gas utilization, i.e., fraction of gas destroyed or transformed during the process step. Many etch recipes use multiple fluorinated GHG. In those instances, include all of those gases and the measured utilization of each. In this instance also note the convention adopted for reporting the by-product formation factor, B_{ip} explained in Note 7 below.
7. B_i denotes fraction of gas i transformed into other fluorinated GHGs such as CF_4 formed from C_2F_6 or CHF_3, C_2F_6 and C_3F_8 formed from other fluorinated GHGs. In cases when a product such as CF_4 is formed in recipes containing multiple fluorinated GHGs (e.g., CHF_3, c-C_4F_8 and C_4F_6) B_i, by convention, is the ratio of measured mass of CF_4 formed to mass of largest quantity of fluorinated GHG comprising the recipe.

Appendix C – Evaluation of Uncertainty Associated with Alternative Emission Estimation Methods

EPA examined estimates of semiconductor facility fluorinated GHG emissions obtained using alternative emissions estimation methods and one distribution of annual fluorinated GHG gas-usages for a hypothetical facility processing 300-mm substrates that employing nine fluorinated GHGs. The five methods compared in this analysis were the:

(1) IPCC Tier 2b,

(2) Tier 2bM - emission factors modified/updated using the NODA Database,

(3) EPA's Tier 2c -five fluorinated GHG-using process types/sub-types consisting of three chamber cleaning sub-types, one wafer cleaning type and one aggregated etching type,

(4) EPA's Refined Method -the same cleaning sub-types as in Tier 2c but the single aggregated etching type is expanded to four film-based sub-types, and

(5) a proxy for EPA's Tier 2d -the same chamber and wafer cleaning types/sub-types as in Tier 2c but assuming as many groups of similar etching recipes as etching sub-types as there are for the Refined Method.

For each alternative methodology, EPA compared the similarity between simulated emissions and the magnitudes of the spread in the 95 percent Confidence Interval (CI) of the relative error (RE) for the simulated emissions. This spread is the range in the probable error in emissions (PEE) and is calculated as the sum of the absolute value of the estimated lower bound of the RE and the corresponding upper bound. Higher PEE estimates mean higher uncertainties. In the absence of measured emissions, similar nominal emissions and PEE estimates are the only available measures of "goodness."

Methodologies and Sources of Information

Plant Distribution of Fluorinated GHG Usage

In this analysis one gas usage distribution comprised of nine fluorinated GHGs was used. This assumed plant distribution was based on one sample gas use distribution from a fabrication plant of indeterminate industry representativeness. The nine fluorinated GHGs in this analysis in decreasing usage rank order were: NF_3, CF_4, SF_6, C_2F_6, C_4F_8, CH_2F_2, C_5F_8, CHF_3 and C_4F_6. NF_3 comprised 63 percent of total [mass basis] used for chamber and wafer cleaning, with 99.99 percent of total NF_3 used for chamber cleaning. All of the NF_3 used for chamber cleaning was assumed to be used in remote plasma cleaning. CF_4 was used for etching and wafer cleaning [99 percent for etching]. The rest of the gases were used to etch oxide, nitride, silicon, and metal films. (Emissions of HTFs or N_2O were ignored in this analysis.)

Emission Factors and Relative Errors

The IPCC Tier 2b emission factors (both utilization and by-product formation rates) that were used were taken directly from the 2006 IPCC Guidelines. The IPCC published 95 percent CI values for the emission factors were multiplied by two and converted to percent values to obtain relative errors for the IPCC Tier 2b emission factors. Emission factors (EFs) (both utilization and by-product formation rates) and REs for all other methods were developed using data in the NODA database. However, data was sparse for etching sub-types specifically, and the implementation of an analysis required EFs and their REs to be estimated by analogy to other gases in some instances. In cases where gas usage data was available, but a related EF was not available either in the IPCC or NODA database, EFs, and hence REs, were assigned by analogy based on the identical gas used in another process sub-type for which information was available. These analogies are presented in Table C-1 below. For the Tier 2d (proxy) method, because it was not feasible to estimate emissions for "similar recipes" specifically used at the hypothetical fab due to limited available data, EPA elected to estimate emissions for the Tier 2d method by modifying the REs for the four etching film-based sub-types used in the Refined Method analysis. The relative error for each the four etching sub-types for the Tier 2d method was assumed to be 20 percent.

Table C-1. Analogies Made for EFs and REs for Various Fluorinated GHGs for the Alternative Methodologies.

Methodology	Gas	Process Sub-Type	Analogous EF	Analogous RE	Other Notes
EFs for Gas Utilization					
Refined Method	CF_4	Metal Etch	Average of Silicon Etch, Nitride Etch, and Oxide etch	Oxide Etch	
	CF_4	Nitride Etch	--	Oxide Etch	
	$c\text{-}C_4F_8$	Nitride Etch	Oxide Etch	Oxide Etch	
	SF_6	Silicon Etch	--	Average of all available REs for EFs in database	
	SF_6	Oxide Etch/ Nitride Etch	Silicon Etch	Average of all available REs for EFs in database	
	C_4F_6	Nitride Etch	Oxide Etch	Oxide Etch	
	CH_2F_2	Silicon Etch	average of Oxide Etch and Nitride Etch	Oxide Etch	
	CH_2F_2	Nitride Etch	--	Oxide Etch	
	CHF_3	Metal Etch/ Silicon Etch	--	Average of Oxide Etch and Nitride Etch	
	NF_3	Ashing	--	In-situ Plasma	
	C_5F_8	Oxide Etch	$c\text{-}C_4F_8$ Oxide Etch	$c\text{-}C_4F_8$ Oxide Etch	See note 2.b
Tier 2bM	SF_6	Etch	Silicon Etch	Average of all available REs for EFs in database	
	C_5F_8	Etch	$c\text{-}C_4F_8$ Etch	$c\text{-}C_4F_8$ Etch	See note 2.b/ The numbers for C_4F_8 Oxide Etch was assumed for the larger etch category
Tier 2c	SF_6	Etch	Silicon Etch	100%	
	C_5F_8	Etch	0	0	See note 5
	NF_3	Ashing	--	100%	
CF_4 By-Product					
Refined Method	C_4F_6	Nitride Etch	Oxide Etch	Oxide Etch	
	CH_2F_2	Silicon Etch	average of oxide and nitride etch	average of oxide and nitride etch	
	C_5F_8	Oxide Etch	C_4F_8 Oxide etch	C_4F_8 Oxide etch	
	CHF_3	Silicon Etch/ Metal Etch	average of oxide and nitride etch	average of oxide and nitride etch	
	NF_3	Ashing	In-situ plasma	In-situ plasma	
Tier 2bM	C_5F_8	Etch	C_4F_8 etch	C_4F_8 etch	
Tier 2c	C_5F_8	Etch	0	0	See note 5
	NF_3	In-situ Thermal	--	200%	
	NF_3	Ashing	0	0	See note 5
C_2F_6 By-Product					

Refined Method	C_4F_8	Nitride Etch	Oxide etch	Oxide etch	See note 2.b
	C_5F_8	Oxide Etch	C_4F_8 Oxide etch	C_4F_8 Oxide etch	
	C_4F_6	Nitride Etch	Oxide Etch	Oxide Etch	
	CHF_3	Metal Etch/ Nitride Etch/ Silicon Etch	Oxide Etch	Oxide Etch	
Tier 2bM	C_5F_8	Etch	C_4F_8 etch	C_4F_8 etch	
Tier 2c	C_5F_8	Etch	0	0	See note 5

Notes:

1) – = Analogy not required
2) Analogies for process categories for each gas were made according to the following overarching steps:
   a. If, for a gas, an EF/RE did not exist for a sub-type under a specific process type, but existed for another process sub-type under the same process type, the EF/RE that existed for that one specific sub-type was assumed to be analogous for the sub-type with no existing EF/RE. (i.e., if an EF/RE for CF_4 existed for nitride etch but not oxide etch, the EF/RE for CF_4 for oxide etch was assumed to be analogous to the CF_4 EF/RE for nitride etch.) If an EF or an RE for that gas category was missing, a proxy gas was used as an analogy for these estimates. Of note, Table 5 does not have any information for gas C_5F_8. Hence C_4F_8 was assumed as a proxy for all associated values.
   b. In the case of SF_6, no such gas analogies could be made, therefore, an average of all REs for the gas distribution was used.
3) Analogies for the overarching process categories of Tier 2c and Tier 2d methods were based on the analogies made for each individual gas and process category for the refined method.
4) Additionally, where no EF information was available but gas utilization took place, the IPCC Tier 2b EF and RE were used in those rare instances.
5) For the Tier 2c method only REs were assumed based on analogies, in situations where no emission actor existed for a given gas within the database, the related EF for calculations was assumed to be 0.

Type of Emissions Probability Distribution

A beta distribution was assumed for emissions of the gases and their by-products for practical and theoretical reasons. The beta probability distribution constrains the random variable (EFs in this work) in each trial to values between 0 and 1. Alternatives to the beta distribution—normal, lognormal or gamma—would permit trial EFs that are physically impossible, i.e., EFs that could be negative or greater than one (depending on which of those three distributions were used in a simulation), which would require truncating negative values or values greater than one. The number of EFs in the NODA database for any gas and process type/sub-type was insufficient to test the appropriateness of the beta distribution. Parameters for the beta distribution were estimated using information from the 2006 IPCC Guidelines and using the mean and REs estimated from the May 2010 NODA information, as appropriate.

Location and shape parameters of the beta distributions were estimated for each emissions estimation method using the corresponding means and variances from either IPCC tables (converting the IPCC reported 95 percent CI value to a percentage and multiplying by two to obtain REs for the fluorinated GHGs) or the NODA database. EFs for all gases utilized were constrained between 0 and 1, but the by-product emissions were constrained between 0 and the highest value for that specific gas and process type available in the NODA database.

Uncertainty Analysis using @RISK

Monte Carlo simulations were performed for each of the five methods using @Risk software and beta distributions to characterize the variability in EFs. Through @Risk, 10,000 iterations were completed for each simulation. The results of these trials provided estimates of the mean of simulated emissions, and the corresponding upper and lower bound confidence intervals (95 percent) in emissions, and, therefore, PEE estimates, for each of the five methods.

Results

Estimating "Goodness" of Calculated Emissions:

This analysis adopted two measures of goodness: (1) the inter-comparability of nominal emissions for the IPCC Tier 2b, Tier 2bM, Tier 2c, Refined, and Tier 2d methods (i.e., the similarity of emissions calculated using, for the single distribution of fluorinated GHG usage, the total emissions [MMTCE]), and (2) variability in the corresponding nominal emissions for each method as measured by the 95 percent CI. The PEE is used for comparing the variability in reported emissions among methods, because the PEE—a single number— is more convenient than using two numbers, the lower and upper bound of the 95 percent CI of the RE.

Results in detail

The outcome of an uncertainty analysis such as this one may presume that the simulation for each method employed (a) robust estimates for emissions factors and reasonable estimates for the variability in those factors for each gas used and each fluorinated GHG-using process type/sub-type, and (b) a distribution representative of fluorinated GHG usage in semiconductor manufacturing. However, those presumptions don't hold in this analysis as it relies on a paucity of available EF data and only one fluorinated GHG usage distribution whose representativeness is unknown. Therefore, how much weight should be given to the observations below is affected by the concerns about the scarcity of available EF and gas usage information.

Nominal and simulated mean emissions for the IPCC Tier 2b, Tier 2bM, Tier 2c, Refined, and Tier 2d methods are shown in Table C-2 below. This table also illustrates the PEE for each methodology. All the PEE values have been normalized to Tier 2b PEE for ease of comparison.

Table C-2. Comparison of nominal and simulated mean emissions (MMTCE) and normalized estimates of PEE for five alternative emission estimation methods

		Simulated results after 10,000 iterations with @Risk	
Method	**Nominal emissions (MMTCE)**	**Mean Emissions (MMTCE)**	**Normalized spread in 95% CI of RE or PEE**
Tier 2b	0.011	0.011	1
Tier 2bM	0.014	0.014	1.72

Tier 2c	0.014	0.014	1.68
Refined Method	0.014	0.014	1.88
Proxy Tier 2d	0.014	0.014	1.39

As shown in **Table C-2,**the nominal and simulated emissions are equivalent at up to two significant figures for all the alternative methods evaluated. This supports EPA's use of a beta distribution to quantify variability in EFs for this uncertainty analysis.

Inter-comparability of Emission Estimates:

The results (to two significant figures) provided in Table C-2 show that total nominal emissions obtained using the IPCC Tier 2b method are understated. All of the emission estimates from the other four methods are the same (up to two significant figures); with emissions being 27 percent higher than the corresponding emissions estimated using IPCC Tier 2b method (0.014 MMTCE for each of the four updated alternatives vs. 0.011 MMTCE for Tier 2b method). Conversely, Tier 2b emissions are understated by approximately 21 percent relative to the methods based on updated EFs.

Variability of Nominal Emissions/PEE:

The methods vary in their respective probability distribution spreads around the mean as shown by the normalized PEEs presented in Table C-2. Results show that the PEEs for the Tier 2bM, Tier 2c, Refined and proxy Tier 2d methods are greater relative to the PEE for the IPCC Tier 2b method. Of the non-IPCC methods evaluated, the PEE for the proxy Tier 2d method is the lowest, but as noted prior it is higher than the PEE for the IPCC Tier 2b method (*see* Table C-2). Based on this analysis, the IPCC Tier 2b method appears to produce an understated, but the most precise, estimate with the proxy Tier 2d method being a close second in precision.

It is noteworthy that the higher emissions and variability, calculated for the updated methods compared to the IPCC Tier 2b method for the distribution of gas usage used, appears to be attributable to higher CF_4 by-product formation EFs and REs for the updated methods compared to the IPCC Tier 2b method. For instance, the CF_4 by-product formation EF for NF_3 remote plasma clean for the Tier 2bM is twice as large as the corresponding EF for the IPCC Tier 2b. Similarly, the CF_4 by-product formation RE for the Tier 2bM exceeds the corresponding RE for the IPCC Tier 2b by a factor of 7.2 for NF_3 RPS. It seems that the updated EF information contained in the NODA reflects the increased recent manufacturing trend of using carbon-based low-k dielectrics. This increased use of C-films would be expected to lead to higher EFs in both etching and chamber cleaning due to reaction of carbon with F-atoms to form CF_4. Further, the greater REs in EFs developed from the NODA database may be attributable to increase variability in both etching recipes and film C-content that is reflected in the NODA database. Without more information regarding the EF data and gas usages this explanation cannot be explored.

Findings and Conclusions

The results of comparing the PEEs for all methods are both unexpected and expected. On the one hand, these results are unexpected because one anticipates, in principle, that, as the information used to develop EFs improves and as a method's comminution increases, simulated estimates of PEE would decrease. Therefore, in moving from the IPCC Tier 2b to the Proxy Tier 2d method, the normalized estimates of PEEs should decrease, corresponding to a reduction in uncertainty. On the other hand, that outcome presumes that each simulation employed (a) robust estimates for emissions factors and reasonable estimates for the variability in those factors for each gas used and each fluorinated GHG-using technology, and (b) a distribution representative of fluorinated GHG usage in semiconductor manufacturing. Because these presumptions don't hold—the analysis instead relies on a paucity of available EF data and only one fluorinated GHG usage distribution whose representativeness is unknown—the balance tips toward the unexpected. That there is a reduction in the spread of estimates of PEEs from the Refined Method to the proxy Tier 2d method seems noteworthy (see Table C-2). However, how much weight should be given to this observation is affected by the concerns regarding the paucity of available EF and gas usage information mentioned earlier.

Despite the ambiguity in these results, they do point to two reasons for moving away from the IPCC Tier 2b method: (a) emissions estimated with the IPCC Tier 2b methods are understated, and (b) there is a void in facility-level, emissions-relevant information and a need to revise the IPCC Tier 2b EFs. The results of this evaluation also show that moving from the use of a default factor(s) for etch sub-types to the use of recipe-specific measurements appears to increase certainty in emission calculations.

More facility-level, emissions-relevant information would permit an uncertainty analysis to be performed with more meaningful and robust results. However, additional information about facility-level gas usage and EFs is needed before one can have confidence in facility-level reported emissions. While using properly weighted default EFs would yield reliable estimates of total U. S. emissions from semiconductor manufacturing, considerable uncertainty in facility-level emissions would remain.

Given the lack of available facility-level gas usage and emission information, particularly for the etching process type, as made apparent by this analysis, EPA is requiring that larger facilities report EFs for etching technologies and use verified gas apportioning models.

Appendix D - Support for EPA's Definition of Similar Recipe

Accurately tracking fluorinated greenhouse gas (fluorinated GHG) emissions during semiconductor manufacturing is a complex endeavor. Out of as many as seven hundred or so distinctly different manufacturing steps required to simultaneously produce as many as 500 electronic devices or so on a single substrate, which are completed within the course of approximately a month, many of those steps use as many as six fluorinated GHGs, either alone or in various combinations for plasma etching. (Boyd et al., 2009; Linx-consulting, 2010)

Estimating annual facility-level fluorinated GHG emissions can be simplified by grouping manufacturing steps into process types or sub-types and using emission factors within each type or sub-type Accuracy in a facility's annual estimate of emissions would be maintained with this approach provided the variability in the factors that govern emissions across each process type or sub-type is sufficiently small and, ideally, random.

For purposes of estimating and reporting facility-level fluorinated GHG emissions, EPA defines three process types—chamber cleaning, wafer cleaning and etching. The chamber cleaning type is further subdivided into three process sub-types: in situ plasma, remote plasma and in situ thermal. For each sub-type, EPA developed default emission factors—figures for gas utilization and by-product formation, as appropriate—for each gas that all facilities may use.

EPA provides no process sub-types for (plasma) etching. EPA differentiates, for this process type only, the emissions calculating and reporting requirements for large and other semiconductor manufacturing facilities. For other semiconductor facilities, EPA developed a default emission factor for each gas that may be used to estimate and to report emissions for plasma etching. For large facilities, EPA requires that, for each gas used, facilities measure and report emission factors for each plasma etching recipe, that is not included in a set of similar recipes, as well as to report facility-level emissions for each of the recipes. Because there may be scores of plasma etching recipes used during device manufacture EPA expects grouping similar recipes will simplify and reduce the burden of emissions reporting with but a relatively small effect on the overall accuracy of reported facility-level emissions. For recipes and associated gases that meet EPA's definition of similar recipe, a large facility may measure the emission factor(s) for one of those recipes, as well as report, using the measured emission factors, the corresponding emissions associated with gases used in those similar recipes.

This appendix provides technical support for EPA's definition of "similar recipe". The appendix begins with a brief description—a primer—of the physics and chemistry that govern fluorinated GHG-based plasma etching during semiconductor manufacture. This discussion serves two purposes: (1) to identify the experimental parameters that govern current practice of fluorinated GHG plasma etching, and (2) to bring into clear view the influence that variations in those parameters have on etch efficacy. Following this primer is a summary of the parameters that define plasma-etching practices during semiconductor manufacturing and, therefore, that potentially influence the concomitant fluorinated GHG emissions. The appendix then turns to a review of publicly available studies that investigate fluorinated GHG emissions as functions of those plasma-etching parameters. The appendix concludes with a definition for similar recipes, a definition that specifies the parameters as well as allowable ranges in those parameters—an allowable parameter space. EPA expects increases or decreases in these parameters within the specified ranges that define this space would result in acceptably small emission increases or decreases.

Plasma Etching— A Primer

In semiconductor manufacturing, plasma etching practice is predominantly empirical, augmented by rules-of-thumb and heuristics. As Hills and Cook (2000) state, "The complexity encountered in actual processing requires much more information than is available experimentally or that can be derived by even the most complex calculations…A practical plasma etching process involves interacting factors or species production and control in the gas phase, a multitude of chemical pathways inherent to the complexity of the molecules used, many poorly understood interactions with the complex (and 'dirty') wafer surfaces and many device structure specifics…Plasma chemistries are thus chosen by a combination of experience, first principles and to some extent empirical 'lore'."

A phenomenological discussion is sufficient to establish a relationship between etching, emissions and controllable process parameters. In what follows, only as much of the physics and chemistry as needed is presented: the boundary is chosen in order to frame EPA's definition of similar recipes.

Plasma etching—specifically reactive ion etch (RIE), also called dry etch, is most simply defined as "the removal of material from a wafer surface with gaseous reactants to produce gaseous products, which are then pumped away and

appropriately disposed" (Hills and Cook, 2000). The objective of dry etching is to reproducibly produce a pattern into a substrate with certain precision, across a substrate and from one substrate to the next. RIE takes place in specifically designed reactors, of many designs, into which reactants flow, substrates are placed, and power is supplied (to sustain the plasma).[51] The scholarly and patent literature show that developing practical plasma etching recipes involves, for a given reactor design, experimentally identifying the reactor pressure, reactant composition and flow rate, and power that produces suitable etch rates, feature dimension and profile, selectivity, etc. RIE is characterized by two concurring phenomena: physical sputtering and chemical reaction, which result, to varying degrees, material selectivity[52] and etch anisotropy (directionality).

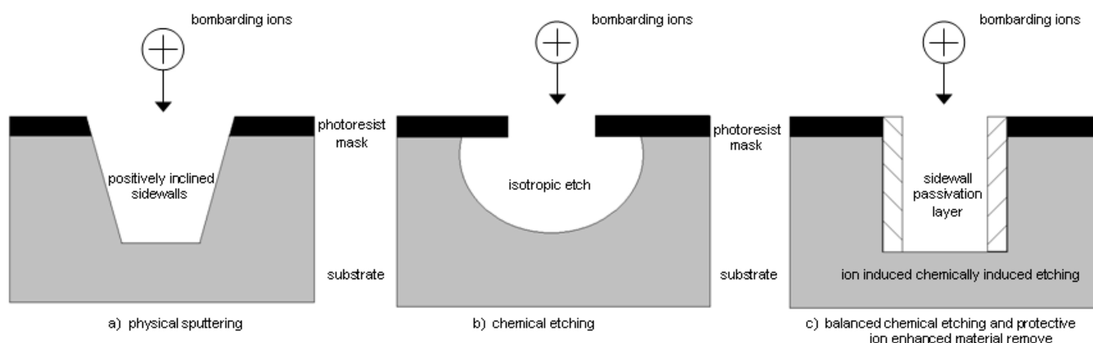

Figure D-1. RIE Etching showing (a) sputtering, (b) chemical etching and (c) sputtering and chemical etching. Top (dark layer) is mask and lower layer is material being removed (etched)

Figure D-1 illustrates these two concurring phenomena; it also shows how the image of a mask is reproducibly transferred into the film (substrate). Physical sputtering describes the dislodging of material, which occurs when sufficiently energetic but chemically inert ions hit a surface and "kick out" atoms or molecular fragments. As the momentum carried by particles transfers energy to surface atoms (which is generally most effective under an angle of $\approx 60^o$ measured from vertical), material removal leads to positively inclined sidewalls. Sputtering also erodes the photoresist mask (See Figure D-1a) (Rossnagel, 2000).

Chemical etching results from reactive species created in the plasma, formed from a mixture of gaseous materials that breakdown into reactive components. These reactants form volatile products upon reacting with the substrate material. Reactants are chosen in part for their selectivity to either not react with the mask material or react at a much slower rate than with the underlying substrate. Chemical etching, however, is isotropic (multidirectional) and, without counterbalancing effects, results in under-etching and rounded profiles (See Figure D-1 b) (Hills and Cook, 2000).

Balanced physical and chemical material removal leads to vertical etch profiles. Additionally, in situ chemistry leads to formation of sidewall passivation layers, which achieves etch directionality. Chemically formed, etch-inhibiting films (e.g., polymer, oxide, etc.) occur on the sidewalls but not on horizontal surfaces where they are continuously removed by ion-bombardment (See Figure D-1 c) (Hills and Cook, 2000).

Etching reagents include fully fluorinated carbon- or non-carbon-containing compounds (e.g., CF_4, C_2F_2, C_2F_4, C_2F_6, C_3F_8, C_4F_6, C_4F_8, C_5F_8, SF_6, NF_3, BF_3) and hydrofluorocarbon compounds (e.g., CHF_3, CH_3F, CH_2F_2, $C_2H_2F_2$).

Characterizing Fluorocompound RIE Processes Using the Film SiN_x Example

Plasma etching of Si, SiO_2, SiN_x films, for example, with fluorocarbon and hydrofluorocabon gases is well studied (Oehrlein,1990; Lehman and Widmer,1978; Booth, 1999; and Standaert, et al., 2004, Lieberman and Lichtenberg, 2005). Argon appears to be a preferred diluent gas. To achieve the proper etch characteristics (e.g., etch rates,

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[51] Because of the numerous loss processes that occur during plasma etching, plasmas are not self-sustaining and therefore, to achieve steady-state, require continuous power input, in the form of high frequency electromagnetic energy. In semiconductor manufacturing, the electromagnetic radiation is in the radio frequency (RF) spectral region. For simplicity of discussion, the term power is used in this report rather than RF power.

[52] Etch selectivity measures the differential etching between photoresist material and silicon-based film. The photoresist forms the pattern to be transferred to the substrate via the etching process (Garza et al., 2000).

verticality, selectivity, uniformity, critical dimension (CD) control, to name an important few[53]) additives such as O_2, H_2 or N_2 are common and patent literature points to the use of H_2O_2, CO, CO_2 and perhaps N_2O (Zhu et al., 2005).

While Kushner and co-workers have successfully modeled the chemical and physical factors that govern etch rates for relatively simple systems such as C_2F_6 (Zhang and Kushner 1999, 2000a, 2000b) that success falters with C_4F_8 (Sankaran, A., A. Vasenkov and M. J. Kushner, 2002). A brief description of the well-studied combination of the SiN_x-PMMA (**p**oly**m**ethyl**m**eth**a**crylate, resist) combination will illustrate this complexity.

In CF_4 or CHF_3 plasma, F atoms and CF_x (x = 1-3) radicals as well as ions, formed by the transfer of the kinetic energy of electrons to reactants, are generated and transported to the substrate surface via diffusive processes or accelerated by the electric field of the DC bias applied to the power electrode of the RF plasma. (The DC bias improves directionality but if too high can result in unwanted increase in substrate temperature, so the DC-bias usually remains fixed; chillers are used to control the substrate temperature.)[54]

Higher reactor pressure may increase or reduce the dissociation (emissions and etch rate) of CF_4 into CF_3, CF_2, CF and F. Higher reactor pressure means higher reactor gas density and therefore increased dissociation (but perhaps lower by-product formation depending on the dominant etching reactant). The etch rate, however may drop because the increased rate of polymer (C_xF_y) formation (vide infra).[55] Decreasing pressure leads to a decrease in ion scattering (ion energy is lost through collisions) leading to higher ion bombardment energies, and, in turn, higher physical etching.

Changes in reactant flow rate affect etching rate and emissions depending on reactor conditions. Under very low flow rates, increasing flow increases etching rate and emissions because reaction rates are limited by the supply of reactants. In this regime, increasing the flow rate would increase etching and emissions. At flows above the reactant-supply-limited regime, reaction rates are limited by the reaction time compared to the reactor residence time. Shortening the residence time (by increasing the flow rate) compared to the reaction time would decrease etching rate and emissions. Increasing the residence time (by decreasing flow rate) would increase etching rate and emissions.

As previously noted, etching rate is the net of competing physical and chemical phenomena. Gas phase oligomerization of CF_x radical results in large C_xF_y molecule formation (Booth, 1999), which forms a fluorocarbon polymer film on all surfaces (Standaert et al., 2004). The main etchant of SiN_x is the F atom (Li et al., 1995). Volatile etch products (SiF_x, CNF, NO, N_2) are generated and pumped away (See Figure D-2). Formed C_xF_y is removed by etching and bombardment leading to reformation of CF_4 (or by-product CF_4 formation when the virgin etchant is only CHF_3).

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53 It will become evident later in this report that fluorinated GHG emissions have not been a major consideration when characterizing the manufacturability of plasma etching processes.

54 A sufficiently high DC voltage assures net transport of positive ions to the surface of the substrate.

55 By-product formation and polymer formation may be reduced because both are second order in reactants resulting in formation rates changing in proportion to the square of reactant gas densities.

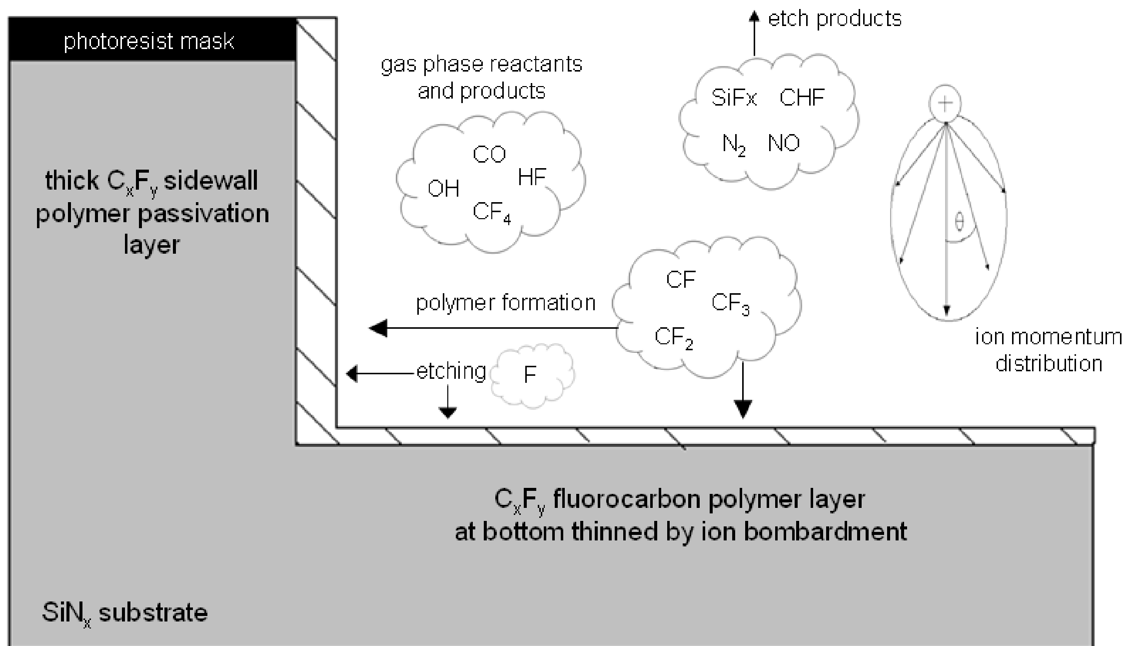

Figure D-2. Illustration of physical and chemical processes and interactions during CF_4 plasma etching of SiN_x film

Much of this complex chemistry can be qualitatively explained by the F-to-C ratio (F/C), where a larger ratio favors etching and a smaller ratio favors C_xF_y formation/deposition (Miyata et al., 1997). The balance between polymer formation and etching also shifts with other process parameters such as pressure and power, although higher power adversely affects etching selectivity via photoresist removal due to increased ion bombardment. In general, it appears that increasing pressure favors C_xF_y formation and more intense ion bombardment (power) favors C_xF_y formation, and concomitantly, SiN_x etching (Dulak et al., 1991), albeit with lower selectivity (vide supra). Recently, Rabilland et al. (2007) provided additional evidence that supports this mechanism for Si, SiCH, SiO_2 and SiOCH films using pulsed plasma.

Adding O_2, H_2 or N_2 gases can achieve some fine control of the chemical aspects of the etching characteristics of fluorocarbon plasmas:

- H_2 extracts fluorine atoms from the plasma via the reaction (H+F→HF),which suppresses SiN_x etching and C_xF_y formation (Oehrlein, 1990)
- O_2 scavenges H and carbon (H+O →OH ad C+xO→CO_x), which suppresses C_xF_y formation and increases F, which, in turn, increases SiN_x etching (Oehrlein, 1990)[56]
- CO scavenges F (CO+xF→COF_x), which enhances polymer formation and suppresses etching (Zhu et al., 2005)
- Argon and N_2 principally cause more intense ion bombardment and a dilution of CF_x radicals, both resulting in thinner C_xF_y layers and therefore enhanced SiNx etching. N_2 is also responsible for promoting the etch rate enhancing the reaction (2N +2 SiN → 2Si +$2N_2$) (Li et al., 1995)

If CHF_3 were used with or instead of CF_4, the affect of hydrogen on etch rate comes with the etchant, which would lower the F/C ratio relative to a pure CF_4 plasma. If required, the etch rate could be adjusted upward by adding a small amount of O_2 to the gas composition, which would lower H via the H+O→OH reaction.

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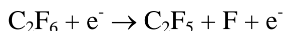
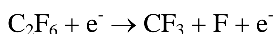
[56] See also Reid and Hughes (2007) who demonstrate a similar effect of increasing O_2 flow on plasma etching of carbon doped ultra-low-*k* dielectric layers.

The description of this relatively simple etching chemistry provides a qualitative model for the chemistry for more complex molecules. A principle difference between CF_4 and, say, C_2F_6 system, is by-product formation: CF_4 is formed when C_2F_6 is the etchant. CF_4 formation is postulated to be the result of the branching reaction



$$C_2F_6 + e^- \rightarrow C_2F_5 + F + e^-$$



$$C_2F_6 + e^- \rightarrow CF_3 + F + e^-$$

where the latter leads to CF_4 formation by recombination of CF_3 and F. It is the exponential increase in these branching reactions that rapidly complicates the chemistry of etchants like C_3F_8, C_4F_8, etc. (Sankaran, Vasanov and Kushner, 2002).

Another essential feature of plasma etching is allowance for flow stabilization. Patent literature (see, for example, Hudson and Tietz, 2005) and EPA experience (EPA, 2008) indicates plasma etching processes allow for periods of <1 second to a few seconds to assure pressure and flows are stable and uniform prior to striking plasma. Because there is no destruction of fluorinated GHG during this period, which can represent a consequential fraction of total process time and, therefore, a substantial part of total emissions for plasma-etching recipes when fluorinated GHG destruction is high (plasma on), this flow stabilization time is also an essential feature of a plasma etch recipe and, in turn, included in EPA's definition of a similar recipe. EPA has demonstrated that because correcting measured emissions for changing recipe time can be made, only stabilization time and not total etching time is relevant when defining similar recipes.

A Precise Definition for Similar Recipes: Defining the Parameter Space for the Purpose of Estimating and Reporting Emissions

As illustrated in the plasma etching primer, the parameters that equipment and electronic device manufacturers manipulate to achieve commercially successful plasma etching recipes are power, reactor pressure, chemical composition, constituent flow rates and flow stabilization time. Anecdotal reports indicate that device manufacturers manipulate these parameters for a variety of reasons and in degrees that are understandably proprietary when developing the manufacturing process steps for a specific electronic device. These, then, are the parameters EPA considered in formulating a definition for similar recipes.

EPA unsuccessfully searched publicly available literature for studies that examined the influence of variations in these process parameters on fluorinated GHG emissions. What emerged were studies on how variations in plasma-etch parameters influence manufacturing benchmarks such as etch rate and etch selectivity as well as dimensional control and uniformity across a surface film of an etch feature. EPA did not identify published studies of fluorinated GHG utilization or fluorinated GHG by-product formation, expressed as functions of plasma etching process variables (vide supra). [57]

Precisely defining "similar recipe" for plasma etching presents challenges because of the absence of published studies of fluorinated GHG emissions as functions of the required process parameters (vide supra). EPA met this challenge by recognizing the parallel between plasma etching, which selectively removes portions of a film in order to transfer a pattern to a substrate, and plasma cleaning, which uniformly removes unwanted film that had been previously and unavoidably deposited on chamber walls. In situ plasma chamber cleaning relies on the same physics and chemistry that produces precise features (which was described in the previous section) to remove (etch-away) undesirable silicon-containing films from chemical reactor surfaces following the chemical deposition of films on substrates.

The practical parallels between plasma patterning and plasma cleaning are many. Both are driven by entangled productivity and performance objectives. Manufacturing productivity—substrate throughput—means film etch rate is an important benchmark in both substrate patterning and chamber cleaning; manufacturers relentlessly pursue increasing substrate processing rates. Performance—device functionality and yield—means feature and defect control are important benchmarks in both substrate patterning and chamber cleaning. Reactor pressures, chemical

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[57] This is not an argument for manufactures' ignoring emissions of fluorinated GHGs with high GWPs when developing plasma etch processes. Considerable work has been expended in searching for alternative gases and chemistries, with some success (Johnson et al., 2004). While celebrating these successes is not the main purpose of this report, the industry's increasing adoption of CH_2F_2, C_4F_6 and C_5F_8, each having lower emissions per unit of input gas (albeit somewhat offset by $C_xH_yF_z$ by-product formation) as well as lower GWPs, has lowered CO_2e emissions compared to alternatives like, for example, CF_4, CHF_3 and C_2F_6 (ISMI, 2005).

composition, flow rate and power affect achieving these objectives. While reactor pressures and flow rates differ in plasma etching and plasma cleaning recipes, the differences can be explained, in large part, by differences in surface area (substrate area being patterned is much smaller, requiring smaller flows, than reactor surface area being cleaned, requiring higher flows) and reactor design (high density, lower pressure reactors for patterning vs. low density, higher pressure for chamber cleaning). While plasma etch patterning seeks anisotropy chamber cleaning seeks isotropy; both can be controlled by the addition of oxygen (higher oxygen decreases polymer formation, which improves the efficacy of chamber cleaning and substrate patterning).[58] Both plasma patterning and chamber cleaning recipes also seek to limit ion bombardment because in plasma patterning ion bombardment reduces selectivity and increases substrate temperature (vide supra) and in chamber cleaning it increases the damage to reactor surfaces.

These parallels between plasma cleaning and plasma patterning together with consideration of the basic physics and chemistry that govern plasma cleaning and plasma patterning, suggest that studies that provide information on fluorinated GHG emissions when parameters of in situ plasma chamber cleaning recipes are varied can inform EPA's considerations about how fluorinated GHG emissions might change were those same parameters varied in plasma etching recipes.

EPA's search of the publicly available in situ plasma chamber cleaning literature identified three studies with sufficient information to estimate the effect that changes in recipe parameters have on emissions. These were optimization studies in which the authors identified the conditions (pressure and flow rate for example) that, for the same cleaning time, resulted in lower emissions and usually lower gas usage. The three studies involved different films and three different recipes: C_2F_6/O_2 (Daniels and Cheng, 1998), NF_3 (Bing et al., 2003) and C_3F_8 with O_2 or N_2O (Kesari et al., 1999). These fluorinated GHGs are also used in plasma etching. Changes in emissions were reported in terms of absolute emissions (e.g., kg carbon equivalent, fluorinated GHG utilization, or both).

C_2F_6/O_2: Daniels and Cheng (1998)

It appears Daniels and Cheng (1998) were the first to report optimizing a popular C_2F_6/O_2 chamber cleaning process for fluorinated GHG emissions. Their study sought identification of the conditions that would give the lowest C_2F_6 emissions for the shortest chamber-cleaning time. Daniels and Cheng reported that Applied Materials (AMAT's) standard process at the time was 600 sscm of C2F6 and O_2, 4 torr reactor pressure and 1000 watts power. By increasing the reactor pressure to 6 torr (a 33 percent increase) and reducing the C_2F_6 flow rate to 550 sccm (an 8.3 percent decrease) while keeping the C_2F_6:O_2 ratio 1, Daniels and Cheng reported a 35 percent reduction in C_2F_6 emissions and a 5 percent reduction in chamber-cleaning time.

Daniels and Cheng provide data that permits estimation of the changes in C_2F_6 emissions from separate changes in reactor pressure and C_2F_6 flow rate. The data given Figure D-3 of this appendix, which is adopted from Daniels and Cheng's Figure 3, shows that a +10 percent change in pressure—from 4 torr to 4.4 torr—results in a 2.3 percent reduction in C_2F_6 emissions. Four torr is chosen because it was the pressure for AMAT's (best known) process (vide supra). Four torr was also the lowest pressure for which Daniel and Cheng reported emissions (Their studies showed that lower pressures would increase emissions and clean times which was counter to their aim.). The authors, however, do provide data for 5 torr. For a 10 percent reduction in pressure (5 torr to 4.5 torr) C_2F_6 emissions increased 5 percent.

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[58] Note also that adding oxygen to in situ plasma chamber cleaning recipes decreases the occurrence of particles that can interfere with waste stream management.

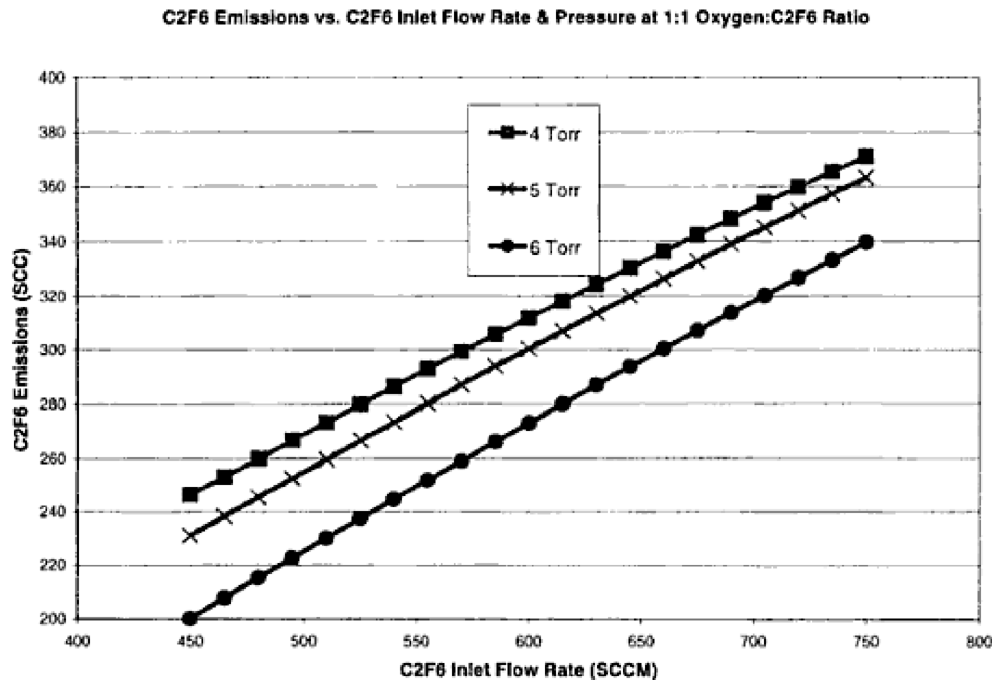

Figure D-3. C_2F_6 Emissions vs C_2F_6 Inlet Flow Rate & Pressure at 1:1 Oxygen:C_2F_6 Ratio (Extracted from Daniels and Cheng, 1998)

A similar analysis for C_2F_6 flow rates follows from the authors' data provided in Figure D-3. For a 10 percent increase in C_2F_6 flow (from the flow of 600 sccm for the best known method [BKM] to 660 sscm) Daniels and Cheng observed a 4.8 percent increase in C_2F_6 emissions while a 10 percent decrease in the BKM flow rate produced a 7.9 decrease in C_2F_6 emissions. The authors did not vary power as the BKM chamber cleaning process called for the highest power setting on the AMAT 5200 DCVD Centura.

Other authors (See Sistern et al., 2004 and references therein) report process optimization studies that result in reducing emissions and chamber-cleaning times for C_2F_6/O_2 process (as well as for C_3F_8 and C_4F_8). However, those studies do not report experimental details. The summary results reported by Sistern et al. (2004) for C_2F_6/O_2 chamber cleaning process are very similar if not identical to those reported by Daniels and Cheng (1998). Sistern et al. (2004) use FTIR and QMS methods for quantifying emissions while Daniels and Cheng (1998) used only QMS.

NF_3: Bing et al. (2003)

Bing et al. (2003) studied optimization of NF_3 in situ PECVD chamber cleaning. Using a design of experiment methodology, Bing et al. observed NF_3 emissions for a range of operating parameters: chamber/reactor pressure (2 – 4 torr), NF_3 flow rate (200 – 350 sccm), and NF_3 fraction in the diluent gas (11.5 – 14.5 mole-percent). Power was fixed at 950 W. Similar to the work of Daniels and Cheng (1998), Bing et al. (2003) showed that, over this range in process parameters, there's a trade-off between cleaning times and NF_3 emissions. Shorter cleaning times are economically beneficial because more equipment time is available for wafer processing, which cannot occur during chamber cleaning.

Bing et al. (2003) provide results for both emissions (kgCE) and gas utilization (U). Table D-1summarizes their results. The percentage changes in NF_3 emission are given for a range percent change in each process variable that EPA incorporates in its definition of similar recipe. Examination of the information presented in Table D-1 shows that, in general, a change of ±10 percent around the process variables that define the BKM results in a corresponding change of 10 percent or less in fluorinated GHG emissions.

Table D-1. Changes in NF_3 emissions (kgCE) and utilization for various indicated changes in parameters for in situ chamber-cleaning process

Variable			Emissions, % change in kgCE, except as noted
Name	Nominal value for BKM, except as noted[1]	Change, %, except as noted	
Pressure, torr	3	+10	+3.6[2]
		-10	-4.6[2]
NF_3, mole%	13	+10	-4.6[2]
		-10	+10.1[2]
NF_3 flow, sccm	300 (Balanced)	+22 (Faster clean)	0.91 kgCE[3]
		-17 (Lower emissions)	0.29 kgCE[3]
Utilization, dimensionless	0.86 (Balanced)	Faster clean	0.79 kgCE[4] (-8.1% from balanced)
		Lower emissions	0.94 kgCE[4] (+9.3% from balanced)

Notes:
[1] BKM denotes best-known method.
[2] Values estimated from Fig. 10 of Bing et al. (2003).
[3] Values taken from Table 6 of Bing et al. (2003); 0.91 kgCE represents an increase of 69 percent in kgCE compared to 0.54 kgCE, what Bing et al. call the balanced process vs. 0.29 kgCE, which represents a decrease of 46 percent in kgCE compared to balanced process (0.54 kgCE).
[4] Values taken from Bing et al. (2003) Table 6. These values denote NF_3 utilization, which Bing et al. call NF_3 destruction efficiency.

$C_3F_8/O_2/N_2O$: Kesari et al. (1999)

Kesari et al. (1999) reported results from studies that examined optimization of in situ C_3F_8 chamber cleaning processes for several kinds of films. These are the only reported results found for the affect of changing O_2 and N_2O flow on fluorinated GHG utilization (for two film types, nitride and oxide). Kesari et al. also provide results of CF_4 formation as a function of O_2 flow when cleaning oxide-coated chambers.

The results from Kesari et al. are summarized in Table D-2. It is evident that, for ±10 percent change in nominal process flow, the corresponding changes in emissions parameters range from 3.3 to 12.8 percent. Kesari et al. did not offer explanations for why C_3F_8 utilization and CF_4 formation rates decreased when either N_2O or O_2 flows were increased or why CF_4 product formation decreased, in the case of oxide film removal, when the O_2 flow was increased. The average change in the nominal emission parameter reported by Kesari et al., disregarding the sign, is 8.3 percent for a ±10 percent changes in O_2 or N_2O flow rates.

Table D-2. Affect of ±10 percent changes in O_2 and N_2O flow rates on C_3F_8 utilization and CF_4 by-product formation during nitride and oxide in situ plasma chamber cleaning.

Process	Process parameter			Emission parameter	
	Name	Nominal value	Change, %	Name	Change, %
Nitride film	N_2O flow rate	400 sscm	+10	Gas utilization[1]	+6.3

			-10		-12.8
Oxide film	O_2 flow rate	450 sscm	+10	Gas utilization[2]	-3.3
			-10		+3.3
			+10	CF_4 formation[3]	-12
			-10		+12

Note 1. Nominal C_3F_8 utilization for nitride film chamber clean = 0.47
2. Nominal C_3F_8 utilization for oxide film chamber clean = 0.60
3. Nominal CF_4 formation per clean = 0.25 grams

Each of these studies indicates that changes in pressure, flow rate and relative chemical composition of ±10 percent produces changes in emissions of the order of 10 percent. The results of Bing et al. (2003) and of Daniels and Cheng (1998) also shed light on the magnitude of emissions changes from changes in process parameters greater than 10 percent. Their results point to nonlinear relationship between fluorinated GHG emissions and variations in process parameters. The results of Bing et al. (2003), for example, show that substantial reductions in emissions can result from optimizing chamber-cleaning processes. This suggests EPA's definition of similar recipes should not permit changes in process parameters beyond 10 percent.

Summary and Conclusions

EPA's review of plasma etching practices during semiconductor manufacturing revealed both the complexity of dry etching processes and the parameter space that govern today's commercial success and fluorinated GHG emissions. EPA's review also revealed an absence of publicly available information about the influence of plasma etching process parameters on fluorinated GHG emissions for commercially efficacious plasma etching recipes. This absence, while restricting the scope of EPA's review, did not restrict its ability to develop a practical definition for similar recipes. To overcome this information gap and to identify the parameters for a practical definition of similar recipes, EPA used an analogy between (in situ) plasma etching and in situ plasma chamber cleaning.

EPA's review confirmed that what influences commercial performance of RIE plasma etching processes is power, DC bias, reactor pressure, chemical composition and flow rate(s). All of these parameters except DC bias influence fluorinated GHG emissions.[59]

EPA's review of three experimental studies of optimizing in situ plasma chamber cleaning showed that changes of the order of 10 percent in reactor pressure, reactant flow rates and relative chemical composition resulted in observed changes in emissions (including emissions of by-products) and gas utilization of the order of 10 percent or less. All of the studies reviewed suggested that changing power would influence emissions but none explicitly presented results. The one study (Liu et al. 2000) that reported measuring the influence on power noted, while not reporting specific measurements, that the optimized recipe conditions "were observed using similar power…as the original manufacturing recipe." This result suggests that changing power is of lesser importance than changes in other parameters in improving recipe performance.[60]

EPA interprets the results of its review as supporting a definition of similar recipe provided that definition does not allow for changes in either the chemical composition and allows changes in power, reactor pressure, gaseous flow

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[59] The DC bias contributes to the removal of material via sputtering, which appears to comprise solid particles rather than gaseous particles. In this manner fluorinated GHG emissions are not affected by changing DC bias. In certain instances if those particles contain carbon, CF_4 might be formed. However, even if this mode for forming CF_4 were occurring in some instances, CF_4 emissions would not change except in response to a change in DC bias, which appears not be a prevalent practice.

[60] Note also that the largest change in power incorporated into the experimental design of Liu et al. (2008) was 10 percent (from 2500 to 2750 watts), which did not evidently, improve chamber cleaning compared to changes in reactor pressure and C_3F_8 and O_2 flow rates.

rates and relative composition of 10 percent or less. Moreover, that definition would not permit change in time for stabilizing gas flows.

It is also worth noting that this definition also applies to in situ chamber cleaning recipes by virtue of the three studies on in situ chamber cleaning presented here. These three studies showed that changes of the order of 10 percent in reactor pressure, reactant flow rates and relative chemical composition resulted in observed changes in emissions (including emissions of by-products) and gas utilization of the order of 10 percent or less.

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