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Amorphous- and nanocrystalline-silicon thin-film photovoltaic modules are made in high-throughput manufacturing lines that necessitate quickly cleaning the reactor. Using NF_3, a potent greenhouse gas, as the cleaning agent triggered concerns as recent reports reveal that the atmospheric concentrations of this gas have increased significantly. We quantified the life-cycle emissions of NF_3 in photovoltaic (PV) manufacturing, on the basis of actual measurements at the facilities of a major producer of NF_3 and of a manufacturer of PV end-use equipment. From these, we defined the best practices and technologies that are the most likely to keep worldwide atmospheric concentrations of NF_3 at very low radiative forcing levels. For the average U.S. insolation and electricity-grid conditions, the greenhouse gas (GHG) emissions from manufacturing and using NF_3 in current PV a-Si and tandem a-Si/nc-Si facilities add 2 and 7 g CO_{2eq}/kWh, which can be displaced within the first 1−4 months of the PV system life.

1. Introduction

Chemical vapor deposition (CVD) operations or plasma deposition operations require cleaning the reactor between operations to maintain the purity of the deposited layers. Until the mid- to late-1990s, cleaning was accomplished either by off-line manual scrubbing or by dry-etching using a perfluorocarbon gas (PFC), mainly CF_4 or C_2F_6. Excitation of the gas into plasma creates fluorine radicals that bond with the Si-based residue, converting it to SiF_4 that can be vented. However, increased demands on the size and throughput of semiconductor fabrication facilities (fabs), coupled with the low dissociation of the PFCs drove the move to using nitrogen trifluoride, NF_3. This gas has a higher dissociation rate than PFCs, supporting faster throughputs and lower emissions in manufacturing integrated circuits and thin film transistor-based displays (*1, 2*). Emissions were reduced further by employing remote plasma sources (RPS) that dissociate NF_3 into fluorine radicals before they enter the chamber (*3−8*). This combination of lower emissions, better process per-

formance, faster clean times, and reduced equipment maintenance led the semiconductor industry to adopt NF_3 as their principal cleaning chemical in the last 15 years, as lately did the emerging a-Si/crystalline-Si thin-film photo-voltaics industry.

The indirect carbon emissions in the life-cycle of photovoltaics (PVs), due to using fossil fuels, are extremely small compared to those from fossil-fuel cycles (*9*). However, concerns arose about the PV industry's direct use of potent greenhouse gases (*10*). A few researchers attempted to quantify the carbon footprint from employing fluorinated gases to clean the reactor during PV manufacturing (*11−14*). Thus, Wild-Scholten et al. (*11*) determined that the majority of NF_3 emissions originate during manufacturing. In contrast, Schottler et al. (*12, 13*) concluded that the use phase, not production, may dominate the impact and highlighted the potential value of abatement downtime in significantly lowering the overall environmental impact of a fab (*14*).

Ours is the first study of NF_3 emissions in the PV life-cycle in which actual measurements of NF_3 concentrations were collected from the effluent streams in major manufacturing and end-use facilities. Production and end use are the main two stages where emissions occur. We deemed that transportation was unlikely to contribute; thus, there are no reports of transportation accidents involving NF_3 emissions, and a risk analysis of transportation using International Organization for Standardization (ISO) module packages for the PV end use showed a very small probability of leakage (Supporting Information, Appendix S1).

2. NF_3 Concentrations in the Atmosphere

Nitrogen trifluoride is a potent greenhouse gas, with a projected atmospheric lifetime of 550 years and an estimated global warming potential (GWP_{100}) of 16 800 (*15*). Weiss et al. (*16*) demonstrated an increase in the atmospheric concentrations of NF_3 from 0.02 ppt in 1978 to 0.454 ppt in 2008. Their latest measurements reveal a rate of increase of 0.053 ppt year^{-1} or about 11% per year, corresponding to about 620 t of global NF_3 emissions annually. Estimating a production of 4000 tons per year, these authors forecast an emission rate of about 16%. However, they also noted a recent slow-down of the rise in concentration.

To assess the relative impact of cumulative NF_3 emissions and gauge the potential impact of future ones, we use radiative forcing (RF), attributable to the current atmospheric NF_3 burden. Radiative forcing is defined as an externally imposed perturbation in the Earth's energy balance, induced by changes in concentrations of greenhouse gases and aerosols, the Earth's albedo, and solar energy (*17*).

For long-lived greenhouse gases, such as NF_3, we estimate the globally averaged change in RF from the following equation:

$$\Delta F_{new} = \alpha(X - X_0)$$

Here, α is a gas-specific constant for radiative efficiency (W/m^2-ppb$_v$), X is the atmospheric concentration in parts per billion by volume (ppb$_v$), and X_0 is the unperturbed concentration. For NF_3, α is 0.21 W/m^2-ppb$_v$ (*17*), yielding a net radiative forcing of 0.9×10^{-4} W/m^2 based on the current global atmospheric concentration of 0.454 ppt and zero background concentrations (*16*). The total radiative forcing for all anthropogenic greenhouse-gas emissions from 1750 to 2005 reportedly is 2.63 ± 0.26 W/m^2 (*18*), of which nitrogen trifluoride represents 0.003%. Compared to CO_2 alone, the current NF_3 radiative forcing from the atmospheric burden
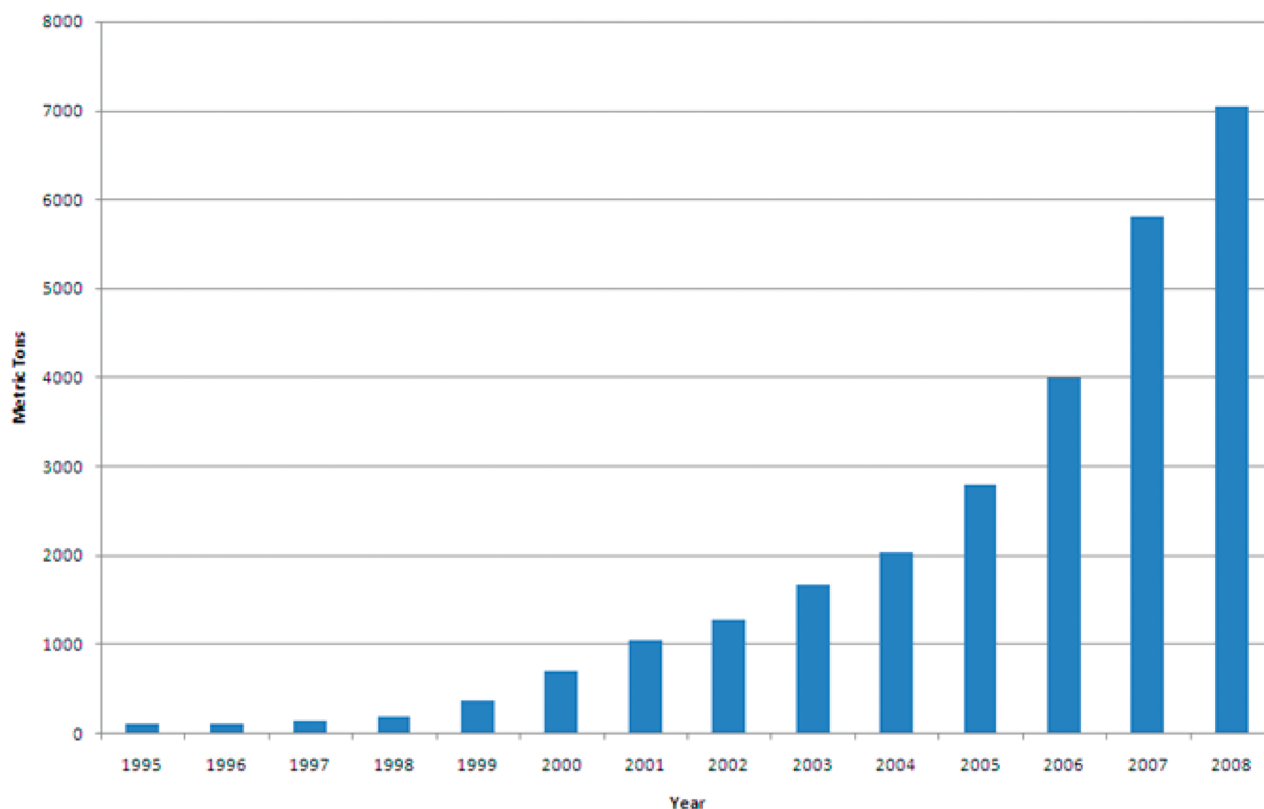
Estimated WW NF3 Manufacturing

FIGURE 1. Annual worldwide NF$_3$ production, 1995–2008.

of 0.454 ppt is 0.005% of the total anthropogenic CO_2 RF of 1.66 ± 0.17 W/m^2.

3. NF$_3$ Emissions in Production and Distribution

A few manufacturers worldwide generate NF$_3$ via the fluorination of ammonia or the electrolysis of ammonia and HF. The estimated annual production capacity of the largest producer, Air Products, is over 3000 tons. Other major producers are Sodiff, Kanto Denka, Formosa Plastics, and Mitsui Chemicals. We estimated that the global production of NF$_3$ in 2008 was about 7200 tons, that grew by an average of 41% per year since 1995 (Figure 1).

Both the rate of NF$_3$ production and its atmospheric concentrations rose over the past decade; however, the former increased annually by an average of 41% and the latter by 11%. Therefore, expressing atmospheric NF$_3$ concentrations as a function of the global annual NF$_3$ production shows a reduction in the NF$_3$ emission factor (Figure 2). On the basis of the estimated global production and the atmospheric concentrations measured by Weiss et al., the emission factor in 2008 was 9%, i.e., below their estimate of 16 ± 4%. In the following, we highlight past and current practices in the various stages of the NF$_3$ lifecycle to identify the underlying reasons for this fall in emission factors.

3.1. Past and Current Practices in NF$_3$ Production. NF$_3$ emissions occur during manufacturing from known or fugitive sources. The former are those from returned product containers and various vent streams operating during manufacturing (e.g., vents for the product-fill manifold, reactor start-up or shut-down, analyzers, and product purification). Fugitive emissions come from leaks occurring during manufacturing of the gas from pressurized manifolds, compressors, and during product fills. Depending upon the size of the customer's fabrication facility, NF$_3$ is distributed in cylinders or ISO containers. Air Products manufactures

NF$_3$ at four facilities worldwide where it is filled into appropriate ISO containers for transportation to end users and to transfills (distribution centers). At their global transfill facility, the gas is transferred into smaller cylinders for shipment to customers. However, with the increase in customer consumption driven by larger fabrication facilities, the substantial majority of NF$_3$ now is shipped to customers directly in ISO containers; cylinders are required only for a very small percentage of the product. Thus, the majority of product fill occurs at the manufacturing sites.

Ambient NF$_3$ monitoring is conducted at the plant using continuous gas monitors, such as those based on nondispersive infrared (NDIR) sensors, able to detect concentrations as low as a few ppm$_v$. Residual product returned by customers is a potential source for fugitive emissions. Estimates suggest that most fabs leave about 5–10% of the total gas volume in the container to avoid contamination. Over the last 8 years, Air Products phased out their venting of product residuals. When containers are returned, their residuals are analyzed, and if purity specifications are met, the containers are top-filled with new product; otherwise, the residuals are recycled into the manufacturing process.

3.2. NF$_3$ Emissions Monitoring Program. Air Products Inc. reported a continuing decline in NF$_3$ emission factor at their production facilities in Hometown, PA, over the last 12 years. The estimated total emission factors were about 7% in 1997, 5% in 2004, and 2% in 2006–2009; they are targeted to decline to 0.5% (19). The Japanese manufacturer, Kanto Denka, also reported a fall from 3.8% in 2006 (when they started a major emissions-reduction program) to 3.1% in 2007, 2.5% in 2008, and 2% in 2009. This company aims for further reductions, likely toward Air Product's 0.5% target (20).

To assess the fraction of product emitted to the atmosphere during operations, Air Products conducted two

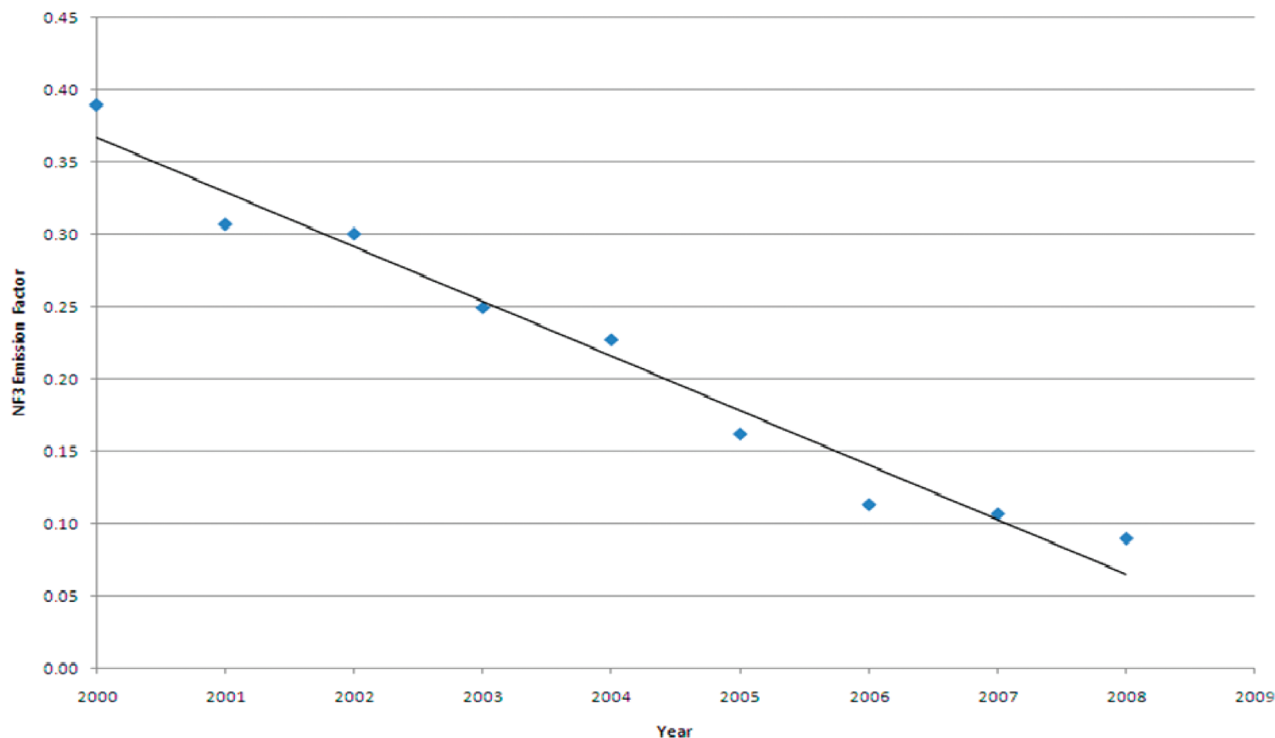## NF3 Emission Factor Relative to Worldwide Production 2000 - 2007

FIGURE 2. Decline in NF$_3$ emission factors over the 8 years, 2000−2008. These data were calculated from the values presented in Figure 1 and the measurements reported by Weiss et al. on NF$_3$ atmospheric concentrations over the same period.

independent calculations based on a combination of engineering data and analytical measurements. The first calculation was based on material balances and included process parameters such as process-flow rates, process efficiencies, process yield, and product produced and transferred into containers. Critical measurements are the mass flow of F_2 to reactors, the efficiency of process conversion, and the quantity of NF$_3$ transferred to containers. Fluorine flow is determined by Coriolis-based mass-flow meters, with the manufacturer's stated precision of ±0.05%. The scales used to weigh NF$_3$ transferred to containers also are very precise (±0.5%). Process-conversion efficiencies are determined using process analytical metrology, such as gas chromatography and Fourier transform infrared (FTIR); their estimated precision is <±2%. Using this approach, total emissions accounted for 2% of production for a 3 month period in late 2008 when the factory was running at capacity. The uncertainty of this calculation is estimated to be ±1% based primarily on uncertainties in determining reactor efficiencies.

The second method employed for calculating emission factors is based on summing known emission sources within the plant. These included dryer vents, reactor vents, liquifier vents, analytical vents, and eight other smaller vent sources. Figure 3 shows the emissions reduction from March 2009, when known emission sources totaled 1.6% of production, to April 2010 where they have been reduced to 0.9%, and includes the targeted reductions to achieve an emission factor of <0.5%. A combination of engineering calculations and analytical measurements were used to quantify these sources (Supporting Information, Appendix S2). The uncertainty of this approach is being determined through analytical measurements of critical processes including the dryer and liquifier vent streams. Potential emissions in the manufacturing area are continuously monitored, as required by OSHA, to ensure that concentrations do not exceed the NF$_3$ threshold limiting value (TLV) of 10 ppm.

Quantification of some known emission sources was conducted using FTIR to measure NF$_3$ concentrations in the captured streams. Figures 4 and S1, Supporting Information, plot the concentration profiles of NF$_3$ from a typical liquifier vent stream. These figures include data on CF_4 which was added as a spiking agent upstream of the sampling point to determine variability of the exhaust volume's flow-rate during transfer of the gas. Combining total exhaust flow with NF$_3$ concentrations gave the NF$_3$ emission volume rates in sl hr^{-1}. The average NF$_3$ concentrations of ca. 1000 ppm in these figures correspond to NF$_3$ flows of 24.3 sl hr^{-1}. Recycling these flows would prevent NF$_3$ emissions of 0.75 tons/year and 0.67 tons/year, correspondingly.

4. NF$_3$ Use and Emissions in a-Si/c-Si Thin-Film PV Manufacturing

The advent of the remote plasma source (RPS) for cleaning chambers may be the leading contributor to the relative decline in NF$_3$ and PFC emissions. RPS technology became the dominant method of cleaning by the late 1990s. In the early part of that decade, the vast majority of new plasma-enhanced chemical vapor deposition (PECVD) processes transitioned to NF$_3$-based RPS clean technology (21, 22). Subsequent improvements in it, coupled with its high adoption rate, increased NF$_3$ consumption and lowered associated NF$_3$ emissions. The rapid growth of its use in the flat-panel display industry and, lately, in the PV industry, caused a recent major spurt in NF$_3$ manufacturing.

The use of NF$_3$ in the PV industry is limited to a-Si/c-Si thin-film PV manufacturing lines that require frequent, fast reactor cleaning. We used data extracted from the reports of six PV manufacturers employing Applied Materials SunFab process-equipment lines, one of the most common in the industry. These lines unify RPS systems for generating plasma with integrated, interlocked emission abatement systems. Figure 5 shows the configuration of the systems where the measurements were made; the sampling and analysis protocols are described below.
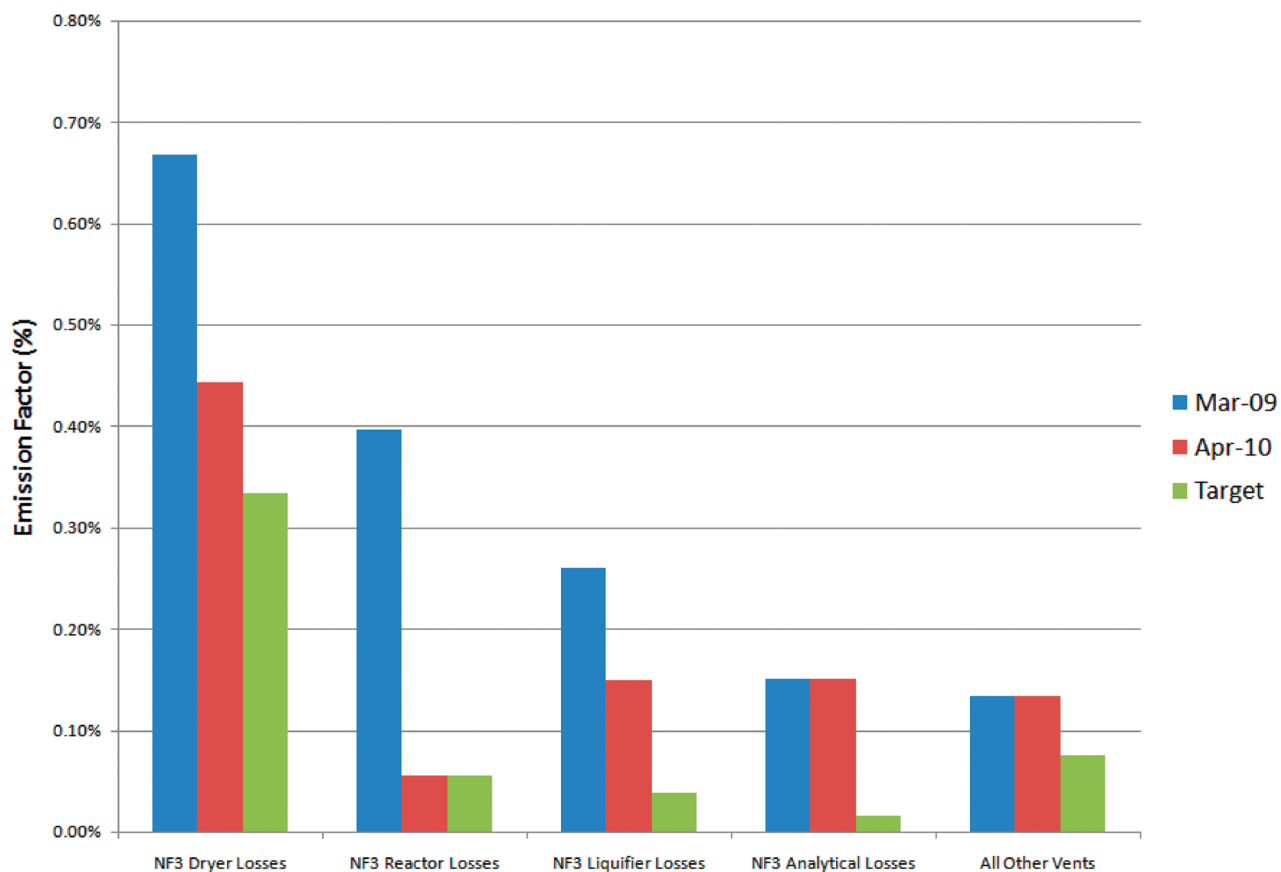
Known NF₃ Emission Sources

FIGURE 3. Known emission sources in NF₃ manufacturing are shown for March 2009, April 2010, and targeted reductions for end of 2010.

FIGURE 4. NF₃ concentrations in a product-purification vent stream that currently is recycled into the process; previously it was vented. CF₄ is introduced as a spiking agent to measure the flow variability (Air Product's manufacturing facility in Hometown, PA).

4.1. Sampling and Detection of NF₃ in SunFab Effluent Streams. *4.1.1. Methods and Apparatus.* We used standard sampling and analytical methods adopted by the semiconductor industry (*23*) for quantifying the greenhouse gas (GHG) emissions. They include time-mapped extractive FTIR spectroscopy and quadrupole mass spectrometry (QMS).

4.1.2. Sampling. The exhaust was sampled downstream of the abatement (Figure 5). A sampling pump continuously

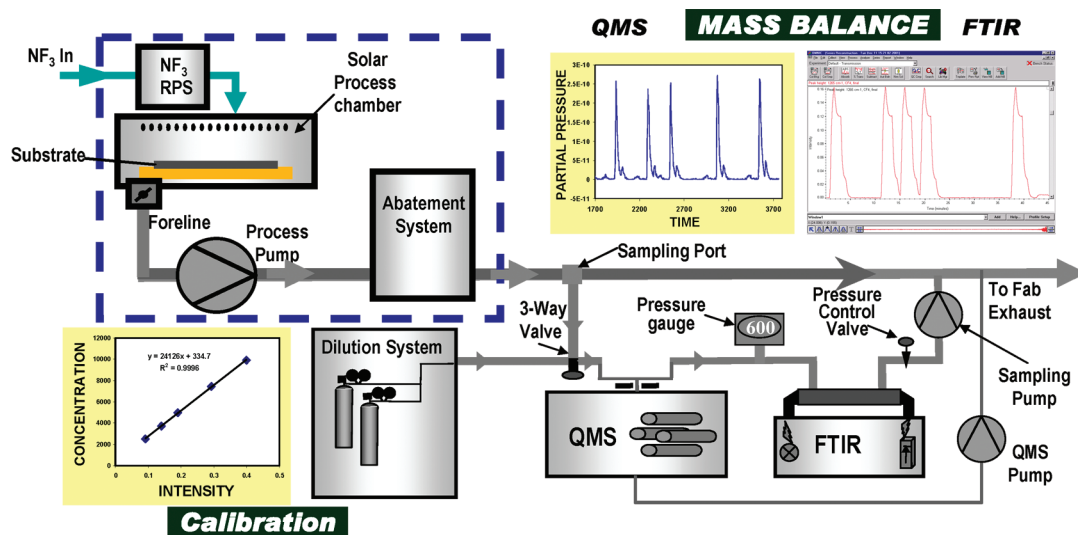**FIGURE 5.** Schematic of process-effluent sampling used to collect NF_3 emissions data at thin-film photovoltaic manufacturing facilities.

drew a slipstream of about 1 slm. A computer-controlled transducer maintained and monitored the sampling pressure through an adjustable valve located just before the sampling point. The exhausts from the FTIR- and QMS-sample pumps were returned to the exhaust line below the sampling point. A three-way valve installed on the sampling line enabled us to easily switch between the abatement system's exhaust system and a dynamic dilution system used to calibrate the FTIR and QMS. Heating to 110 °C prevented condensation in the sampling lines and the FTIR gas cells during testing.

4.1.3. Extractive FTIR. FTIR is chosen as the primary method for quantifying NF_3 due to its strong absorbance in the midinfrared region. We used Thermo Nicolet 6700 FTIR operating at 1 cm^{-1} resolution and equipped with a multipass Gemini 6 m gas cell. The mercury–cadmium–telluride type-A detector (MCTA) produced a full scan of 600 to 4500 cm^{-1} every 0.6 s. Averaging eight scans gave a single data point every 4.8 s. The system's dynamic response time to changes in gas concentration was about 12 s, measured by the rise time from 10% to 90%.

4.1.4. QMS. We employed a Pfiffer Omnistar 300 QMS to determine the total flow of gas through the abatement system. The system was calibrated and tuned for 1 AMU resolution and maximum sensitivity in the range of 2–135 AMU. We spiked a known quantity of Krypton (Kr) into the abatement system, and the QMS determined its concentration at the system's outlet by monitoring m/e 84 for $^{84}Kr^+$. Krypton is inert, absent from the background, not used in process recipes, mixes very uniformly, and has no signal interferences at m/e 84. Total post-abatement effluent flow was determined by dividing the flow rate of injected Kr by the QMS-determined post-abatement concentration.

4.1.5. Detection Limits. The NF_3 detection limit in our FTIR system was 0.08 ppm, on the basis of a 3-fold signal-to-noise ratio for the spectra obtained after calibrating the FTIR's response to NF_3 in nitrogen. During some runs, monitoring interferences raised the noise in the region of NF_3 absorption, thus yielding a higher detection limit. Spectral analysis required deconvolving the interfering species from the intense primary absorption band for NF_3 centered at ca. 903 cm^{-1}. As the quantity of interfering species varied over the six factories where emissions data were collected, the FTIR's detection limit for NF_3 ranged from 0.5 to 30 ppm. When the measurements yielded a nondetect for NF_3, the reported emissions were calculated on the basis of detection limits.

4.1.6. Calibration. All measurements were calibrated, and flows were determined via an onboard calibration system. As shown in Figure 5, the apparatus included a three-way valve for switching from sampling the process exhaust to sampling gas in the dilution-calibration system. We used certified gas mixtures to generate a wide range of known feed concentrations to the analytical tool set with calibrated mass flow controllers (MFCs). For each calibration, test spectral scans of the standard concentrations were taken from a minimum of 6 points, from which we generated a linear regression model, relating concentration to peak intensity or absorbance. We accepted the model only when the correlation coefficient was >95%. The FTIR response was calibrated to NF_3 using this approach; Figure S2, Supporting Information, shows a typical calibration curve. A similar calibration was made of the QMS response to Kr in nitrogen using test atmospheres created by diluting Kr with nitrogen in the calibration system.

4.2. Factory Models and Measurements of NF_3 Consumption. For this study, we modeled the Sunfab single-junction (SJ) and tandem-junction (TJ) silicon thin-film photovoltaics (TFPV) factories to calculate the representative carbon footprint for cleaning NF_3 chambers. The amount of NF_3 used in producing a solar panel was defined by the clean recipe, the amount emitted post-abatement during chamber cleans as measured post-abatement, and the amount of NF_3 lost during chemical production and handling of the clean gas used during the clean. Figure 6 is the factory model for the production of SJ-TFPV panels; the model for manufacturing TJ-TFPV panels appears in Figure S3, Supporting Information.

In both models, large glass substrates, each 5.7 m^2, enter the factory from the left and exit on the right. The AM1.5-rated DC efficiency of the SJ panels is 340 W and that of the TJ panels is 570 W. Integrated robots sequence the glass substrates through the process mainframes. Each mainframe has multiple thin-film CVD deposition chambers, RPS units, and point-of-use (POU) abatement devices around its immediate perimeter. Each factory has multiple mainframes. Every deposition chamber has its own dedicated remote-plasma-source (RPS) and integrated POU devices. The abatement device controls the byproducts of the clean, including F_2, SiF_4, and undissociated NF_3. Factory integration and safety interlocks prevent the initiation of deposition or reactor cleaning should the process chamber, RPS, or occupational space sensors display an unsafe operating
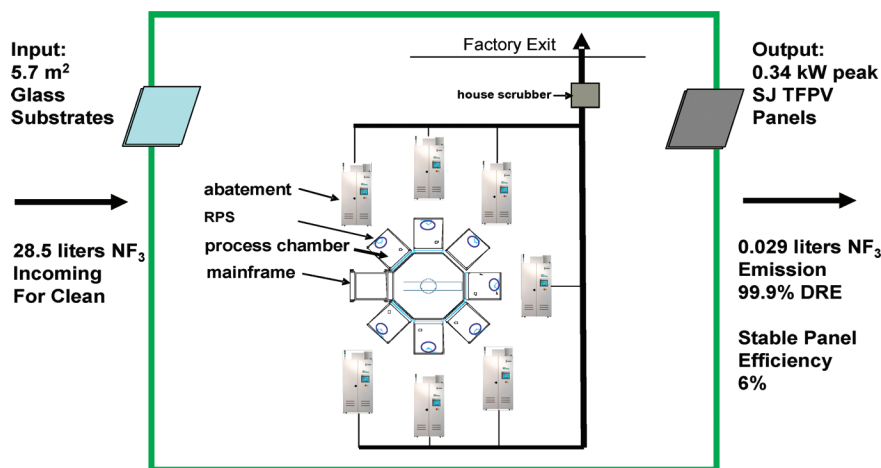
FIGURE 6. Model of a single-junction Sunfab factory, showing NF_3 process requirements and emissions produced per panel fabricated.

Factory Exit

Input:
5.7 m² Glass Substrates

28.5 liters NF_3 Incoming For Clean

house scrubber

abatement
RPS
process chamber
mainframe

Output:
0.34 kW peak SJ TFPV Panels

0.029 liters NF_3 Emission 99.9% DRE

Stable Panel Efficiency 6%

TABLE 1. Typical Sunfab NF_3 Post-Abatement Emissions

factory	source	avg NF_3 conc (ppm)	NF_3 flow (slm)	factory DRE (%)
A	AMAT	2.5	0.00625	99.98
B	AMAT	8.5	0.02550	99.90
C[a]	AMAT	27.5	0.06325	99.75
D	third party	2.0	0.00600	99.98
E	third party	8.6	0.02580	99.90
F[a]	third party	11.0	0.03300	99.87
average				99.89
STD				0.084

[a] Reported values impacted by high detection limits and correspond to them.

condition, including any malfunction of the abatement device, which utilizes independent dual processors and sensors interlocked with the process-tool set. A chamber-clean process step may follow each deposition process, or multiple deposition processes might precede a chamber clean. Deposition occupies the largest overall percentage of the process-cycle time. For factory modeling, the fraction of time the glass substrates spend in transition is included in the deposition-cycle time. For the SJ TFPV process, 7.5% of process time is spent in clean and 9.8% is for the TJ TFPV process.

4.2.1. SJ TFPV Factories. A single glass panel takes 15.1 min of CVD production cycle time, of which 14.0 min are spent in deposition or glass transport, and 1.1 min for chamber cleans. The SJ CVD process includes multiple steps, including deposition of the doped amorphous silicon (p,n) and intrinsic (i) silicon layers. The NF_3 flow rate is 25 slm during chamber cleans. The total integrated NF_3 volume corresponding to a SJ panel is 28.5 sl.

4.2.2. TJ TFPV Factories. A single glass panel takes 75.9 min of the CVD production cycle time, of which 68.5 min are spent in CVD deposition or glass transport and 7.4 min are for chamber cleans. The TJ CVD process contains multiple steps including depositing doped- and intrinsic-amorphous and microcrystalline silicon layers. The NF_3 flow rate during chamber clean is the same as that in the SJ process, viz., 25 slm. The total NF_3 flow per TJ panel is 184.8 sl.

4.2.3. Factory Emission Factors. Table 1 shows six examples of full factory destruction removal efficiency (DRE) for NF_3 cleans, measured by in-house and third-party analytical services, using online FTIR and QMS detection. The factories represented in this table had been operating for about 1 year and are at various locations around the world. In each case, full process emissions for fabricating a solar panel were

measured for three to five deposition-and-clean cycles, and the data from at least three representative multiple-clean cycles were averaged to produce the values shown in this table. The factory-to-factory variation in NF_3 emissions is due to differences in the recipes of the proprietary processes, the protocols employed, the preventative maintenance practices, and the variation in the lower detection limit of analytical tools under sampling conditions.

The data in Table 1 reveal an average factory DRE for NF_3 of 99.89% with a standard deviation of 0.084; this DRE corresponds to a mean emission factor of 0.11%. The 95% confidence level of this mean is ±0.068% (Supporting Information, Appendix S3).

Figure 7a,b shows NF_3-emission profiles measured during chamber cleans at two PV manufacturing sites. Factory A has average NF_3 emissions of 1.5 ppm throughout the duration of the clean, which, when integrated over 1 min, yields an emission rate of 0.0025 slm. In factory C, the baseline noise was relatively high, yielding a high detection limit (i.e., 27.5 ppm); integrating this over 1 min yielded an NF_3 emission rate of 0.063 slm.

These concentrations are typical of operations in current SunFab TFPV module manufacturing plants and represent average annual-emission factors. Schottler et al. 's hypothesis (*14*) that abatement downtime can significantly affect such emissions is invalid since the loss of abatement in these integrated systems automatically shuts down the NF_3 feed and all deposition and clean operations. Fugitive emissions are unlikely as discussed in Appendix S4, Supporting Information.

5. Life-Cycle NF_3 Emissions in PV Manufacturing

5.1. Estimated Carbon Footprint. We calculated the carbon footprint from NF_3 emissions from SJ- and TJ-TFPV panel manufacturing by combining emissions during manufacturing with those upstream at the NF_3 manufacturing plant. Figures 5 and S2, Supporting Information, respectively, depict the input volumes and resulting emissions of NF_3 from producing one SJ or TJ silicon TFPV module.

We applied an emission factor of 0.1% for the end use of NF_3 in the Sunfab system, and an emission factor of 1.6% in the NF_3 production in 2009, declining to 0.5% in the future "target" case. The 2009 number represents the existing facilities listed in Table 1, which have an average life of 1 year.

This assessment, based on actual data from the NF_3 production at Air Products and end use in Applied Materials Sunfab system, accurately represents the production of photovoltaics by the latter, as the former is their main

(a)

Factory A
IN Thin Film Deposition and Clean

Dilution	**2,500 slm**
Peak Concentration	**2.49 ppm**
Average Concentration	**1.5 ppm**
Detection Limit	**0.5 ppm**
NF_3 in	**25 slm**
NF_3 out	**0.0025 slm**
Net DRE (RPS + Abatement)	**99.99%**

(b)

Factory C
IN Thin Film Deposition and Clean

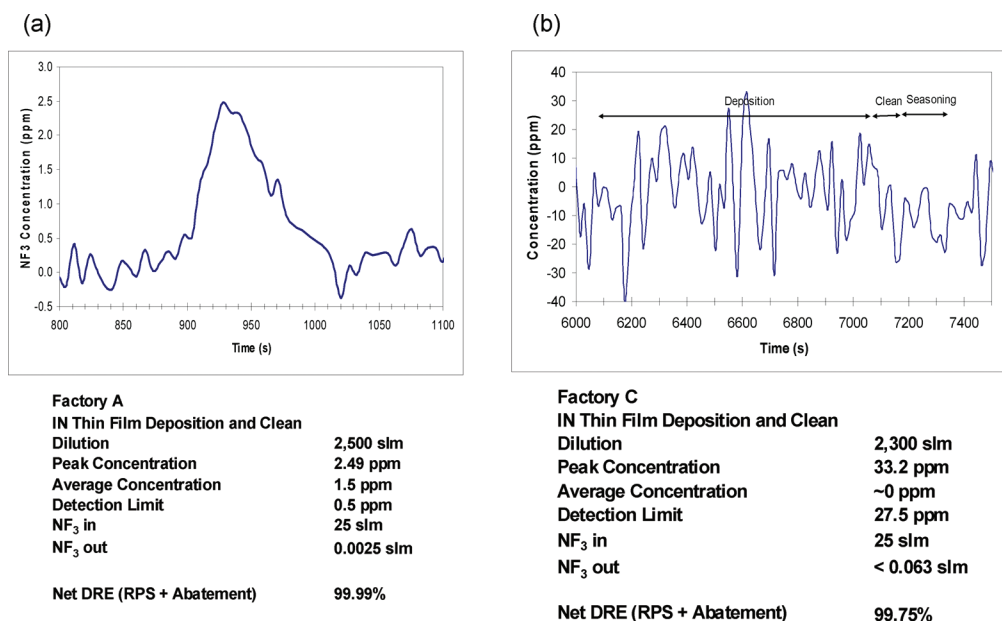|	
Dilution	**2,300 slm**
Peak Concentration	**33.2 ppm**
Average Concentration	**~0 ppm**
Detection Limit	**27.5 ppm**
NF_3 in	**25 slm**
NF_3 out	**< 0.063 slm**
Net DRE (RPS + Abatement)	**99.75%**

FIGURE 7. FTIR spectra collected at PV manufacturing sites. (a) The data from Factory A show a detection limit of 0.5 ppm; (b) those from Factory C show a detection limit of 27.5 ppm due to spectral interferences.

supplier. We also added the carbon dioxide emissions from the electricity and methane required to operate the RPS and the abatement system; they are 0.46 kg CO_2 per SJ panel and 3.02 kg CO_2 per TJ panel. Thus, for average U.S. solar irradiation conditions (i.e., 1800 kWh/m^2/year), the emissions from using NF_3 as a reactor cleaning gas in these facilities added 2 and 7 g/kWh of CO_{2eq}, respectively, in the life cycle of PV; these values are expected to fall to 0.6 and 2 g/kWh by the end of 2010. Such emissions will have a minor effect on the total life-cycle CO_{2eq} emissions in a-Si PV, assessed to be approximately 25 g/kWh. They are insignificant in the context of the avoidance of CO_2 emissions by replacing grid electricity with PV-generated electricity. The modules will "balance" these emissions in the first 11−43 days of their 30 year life (Table 2).

6. Discussion

Using data from the actual production and end uses of NF3 in the PV industry, we determined trends in use and emissions of this potent GHG. Emission factors calculated using global NF_3 production data over the last 10 years and atmospheric measurements of NF_3 over that same period show a declining trend in the fraction of NF_3 generated that is released to the atmosphere. Contributing to this downward trend is a significant reduction of NF_3 emissions during production in the U.S. facilities of the largest NF_3 producer from 7% years ago to 1.6% in 2009. This decline was realized by eliminating losses when refilling returned cylinders and capturing and recycling several small releases in the production- and purification-venting streams. The largest NF_3 producer has a target for lowering the emissions to 0.5% by recycling more process-vent streams during manufacturing. These estimates are based on a large number of data points; the major ones have a variance of about ±1%.

In parallel, drastic reductions of emissions occurred in the end use of NF_3, due to the widespread implementation of the second-generation RPS for chamber cleaning, combined with point-of-use abatement of NF_3 emissions. In 2009, the emissions during reactor cleaning in amorphous silicon-TF PV fabrication was estimated to be 0.11%. The combined NF_3 emission factor in its production and use for reactor cleaning in PV was 1.7%. These numbers are much smaller

TABLE 2. NF_3 Emissions in the Life Cycle of Si Thin-Film PV Modules

module and year	SJ 2009	TJ 2009	SJ Target	TJ Target
module rated power (kWp)	0.34	0.57	0.34	0.57
NF_3 requirement (sl/module)	28.5	184.7	28.5	184.7
total NF_3 emission factor (%)	1.7	1.7	0.6	0.6
total NF_3 emissions (sl/module)	0.5	3.3	0.2	1.1
CO_2-eq emissions (kg/module)[a]	25.7	166.6	8.6	55.9
total CO_2 emissions (kg/module)	26.0	199.2	9.1	58.9
total CO_2 emissions (g/kWh)[b]	1.8	6.9	0.6	2.4
CO_{2-eq} payback time (days)[c]	34	128	11	43
CO_{2-eq} payback time (% of 30 year life)	0.3	1.2	0.1	0.4

[a] Includes CO_2 emissions from energy use in RPS and abatement of NF_3. [b] Assuming US average irradiation of 1800 kWh/m^2/year and 80% performance ratio. [c] Assuming US Grid Mix CO_2 emissions of 606 g/kWh.

than the emission factors estimated in this paper from Air Products global production estimates and Weiss et al.'s atmospheric measurements.

We note that employing NF_3 in the PV industry is a new end use with up-to-date plasma and abatement systems and that the PV industry's usage accounts for only about 3% of global NF_3 production. High emissions may very well reflect other, less-controlled, end uses of the gas and older practices (Supporting Information, Appendix S5). Nevertheless, since the PV industry is likely to be the fastest growing end-user, it is likely that the best practices and control technologies described in this paper soon will become standard practices, thereby drastically lowering global NF_3 emission factors.

Acknowledgments

Supporting Information Available

Additional measurements and the TJ-TFTPV model. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Pruette, L.; Karecki, S.; Reif, R.; Entley, W.; Langan, J.; Hazari, V.; Hines, C. Evaluation of a dilute Nitrogen Trifluoride plasma clean in a dielectric PECVD reactor. *Electrochem. Solid-State Lett.* **1999**, *2*, 592.

(2) Tasaka, A. Electrochemical synthesis and applications of NF3. *J. Fluorine Chem.* **2007**, *128*, 296.

(3) Mendicino, L.; Brown, P. T.; Filipiak, S.; Nauert, C.; Estep, H.; Fletcher, M. PFC emissions reductions and process improvements with remote plasma CVD chamber cleans. *Proc. Electrochem. Soc.* **2002**, *15*, 144.

(4) Mendicino, L.; Nauert, C.; Brown, P. T.; Golovato, S.; Day, B.; Atherton, A.; Nowak, T.; Silvetti, D.; Hartz, C.; Johnson, A.; Maroulis, P. Reduced clean time and PFC emissions reduction through remote plasma clean for lamp heated CVD chambers. *Proc. Electrochem. Soc.* **2001**, *6*, 15.

(5) Reichardt, H.; Frenzel, A.; Schober, K. Environmentally friendly wafer production: NF3 Remote microwave plasma for chamber cleaning. *Microelectron. Eng.* **2001**, *56*, 73.

(6) Kastenmeier, B. E.; Oehrlein, G.; Langan, J.; Entley, W. Gas utilization in remote plasma cleaning and stripping applications. *J. Vac. Sci. Technol.* **2000**, *A18*, 2102.

(7) Goolsby, B.; Vartanian, V. L.; Mendicino, L.; Rivers, J.; Soyemi, A.; Sun, S.; Turner, M.; Esber, C. Characterization of NF3 chamber cleans on multiple CVD platforms. *Proc. Electrochem. Soc.* **2002**, *15*, 127.

(8) Vartanian, V.; Goolsby, B.; Mendicino, L.; Brown, P. T.; Vires, J.; Rose, S.; Babbitt, D. Managing fluorinated byproducts of CVD chamber cleans. *Semicond. Int.* **2003**, *26*, 77.

(9) Fthenakis, V.; Kim, H. C.; Alsema, E. Life-cycle emissions from photovoltaics. *Environ. Sci. Technol.* **2008**, *42* (6), 2168–2174.

(10) Hoag, H. The missing greenhouse gas. News Feature, *Nature Reports Climate Change* **2008**, *2*, 99; www.nature.com/reports/climatechange.

(11) de Wild-Scholten, M.; Alsema, E.; Fthenakis, V.; Agostinelli, G.; Dekkers, H.; Roth, K.; Kinzig, V. *Fluorinated greenhouse gases in photovoltaic module manufacturing: potential emissions and abatement strategies.* Proc. 22nd European Photovoltaic Solar Energy Conference, Milano, Italy, September, 2007.

(12) Schottler, M.; de Wild-Scholten, M. Carbon footprint of PECVD chamber cleaning. *Photovoltaics Int.* **2008**, *2*, 64–69.

(13) Schottler, M.; de Wild-Scholten, M. *The carbon footprint of PECVD chamber cleaning using fluorinated gases.* Proc. 23rd European Photovoltaic Solar Energy Conference, Valencia, Spain, September, 2008.

(14) Schottler, M.; de Wild-Scholten, M. *The life-cycle environmental impacts of etching silicon wafers and (PE)CVD chamber cleaning.* Proc. Electronics Goes Green 2008+, Berlin, Germany, September, 2008.

(15) Prather, M. J.; Hsu, J. NF3, the greenhouse gas missing from Kyoto. *Geophys. Res. Lett.* **2008**, *35*, L12810.

(16) Weiss, R. F.; Mühle, J.; Salameh, P. K.; Harth, C. M. Nitrogen trifluoride in the global atmosphere. *Geophys. Res. Lett.* **2008**, *35*, L20821.

(17) Intergovernmental Panel on Climate Change (IPCC). *Third Assessment Report: Climate Change*, 2001, IPCC: Potsdam, Germany, p 353.

(18) Intergovernmental Panel on Climate Change (IPCC). *Climate Change 2007: The Physical Science Basis*; Cambridge University Press: Cambridge, U.K., 2007; p 141.

(19) *Corporate Responsibility Report*; Air Products & Chemicals, Inc, 2009; Air Products & Chemicals: Hometown, PA, p 20; www.airproducts.com.

(20) Imao S., Kanto Denka, Japan, email communication 10−15−09.

(21) Raoux, S.; Tanaka, T.; Bhan, M.; Ponnekanti, H.; Seamons, M.; Deacon, T.; Xia, L.-Q.; Pham, F.; Silvetti, D.; Cheung, D.; Fairbairn, K.; Johnson, A.; Pearce, R.; Langan, J. Remote microwave plasma source for cleaning chemical vapor deposition chambers. *J. Vac. Sci. Technol., B: Microelectron. Nanometer Struct.* **1999**, *17* (2)), 477–485.

(22) Mendicino, L.; Filipiak, S.; Brown, P. T.; Langan, J.; Ridgeway, R.; Johnson, A.; Pearce, R.; Maroulis, P.; Atherton, A. Evaluation of the Applied Materials uclean Technology for DxZ Chamber Cleans for Perfluorocompound (PFC) Emissions Reductions, International SEMATECH Technology Transfer 98083547B-TR, Sematech: Austin, TX, 1998.

(23) International SEMATECH Manufacturing Initiative, "Guidelines for Environmental Characterizations of Semiconductor Process Equipment" ISMI Technical Transfer Document 06124825A-ENG, Sematech: Austin, TX, 2006.

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