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Reducing PFC gas emissions from CVD chamber cleaning

OVERVIEW Reduction of perfluorocompound emissions is a committed goal of the semiconductor industry. The majority of PFC usage is for cleaning of CVD chambers. Three strategies for reducing the emissions are presented here: 1) optimization of traditional C_2F_6-based in situ cleans, 2) substitution of NF_3 for C_2F_6 in in situ cleans, and 3) remote NF_3 cleaning. The improvements are demonstrated on equipment from major manufacturers of CVD tools.

Perfluorocompound (PFC) gases such as CF_4, C_2F_6, and NF_3 are used extensively in semiconductor manufacturing processes. The largest volume use (70–90%) is for chamber cleaning following chemical vapor deposition (CVD) [1, 2]. PFCs have long atmospheric lifetimes (Table 1) and absorb strongly in the infrared region of the electromagnetic spectrum, a region where the earth's atmosphere would otherwise be transparent (Fig. 1). Because of their infrared absorbance and persistence, PFCs are suspected of contributing to global climate change, i.e., global warming.

Through the World Semiconductor Council (WSC), the global semiconductor industry has voluntarily committed to reduce its cumulative emissions of PFCs. For the US, Europe, and Japan, PFC emissions will be reduced to 90% of 1995 levels by 2010, and similar reduction targets have been adopted by Korea [2]. Based on industry growth projections, substantial reductions for individual processes will be necessary to achieve this target level. Both process optimization of traditional C_2F_6 based in situ cleans and substitution of NF_3 for C_2F_6 in situ cleans are effective strategies for reducing the environmental impact of installed CVD tools. For new CVD tools, the manufacturers of semiconductor process equipment have developed and introduced a new clean technology that essentially eliminates PFC emissions — remote NF_3 cleaning. The combination of these three strategies, optimization of traditional C_2F_6-based in situ cleans, the substitution of NF_3 for C_2F_6 in in situ cleans, and the implementation of the remote clean technology, has effectively solved the semiconductor industry's PFC issue.

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Measuring environmental impact

Climate models calculate that global atmospheric temperatures are naturally 35°C higher as a result of trace gases (e.g., CO_2, water vapor, CH_4, N_2O, and O_3) in the atmosphere [3]. These gases absorb infrared radiation that otherwise would be lost to space, giving rise to a "greenhouse effect" that is a generally recognized

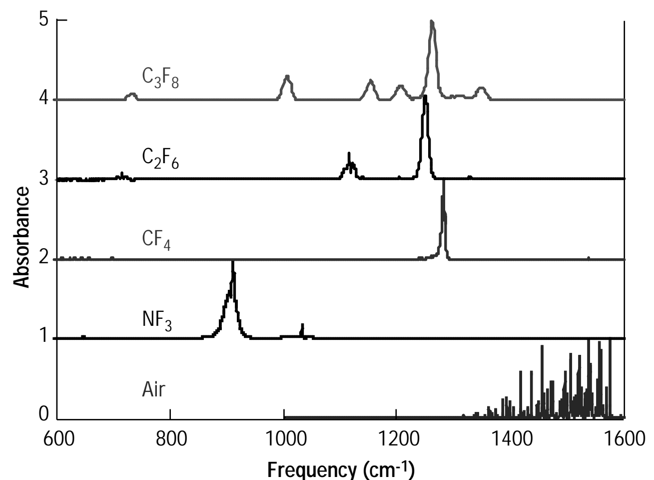

Figure 1. Infrared absorbance spectra for PFC gases used in CVD chamber cleaning.

Table 1. τ* and GWP_{100}** for PFC gases [14]

	τ (years)	GWP_{100}
CF_4	50,000	6500
C_2F_6	10,000	9200
C_3F_8	2600	7000
SF_6	3200	23,900
NF_3	740	8000

*Atmospheric lifetime; **global warming potential with a 100-year integration time

phenomena. Recently, there has been concern about emissions resulting from human activity that could cause an additional temperature increase. While global warming is still a subject of debate, anthropogenic activity (primarily energy-related CO_2 emissions) is increasing the concentration of infrared absorbing molecules in the atmosphere [4]. Since PFCs are strong infrared absorbers (Fig. 1) and have long atmospheric lifetimes (Table 1), they could contribute to global climate change. While the semiconductor industry's contribution to global warming would be small compared to energy-related CO_2 emissions [5], PFC emissions should be minimized because of their persistence. The lifetimes of PFCs are long (Table 1), meaning these molecules will remain in the atmosphere thousands of years after being emitted.

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The degree to which a gas causes a temperature rise depends upon how much infrared radiation is absorbed and its concentration in the atmosphere (which is dependent upon the lifetime of the molecule). Many molecules are infrared absorbers, but they must be long-lived to have an appreciable global warming potential. PFCs have both strong infrared absorbance and long lifetimes. The metric for evaluating a PFC molecule's impact on climate change is the global warming potential with a 100-year integration time horizon (GWP_{100}) [5]. GWP_{100} values for PFCs used in CVD chamber clean processes are given in Table 1.

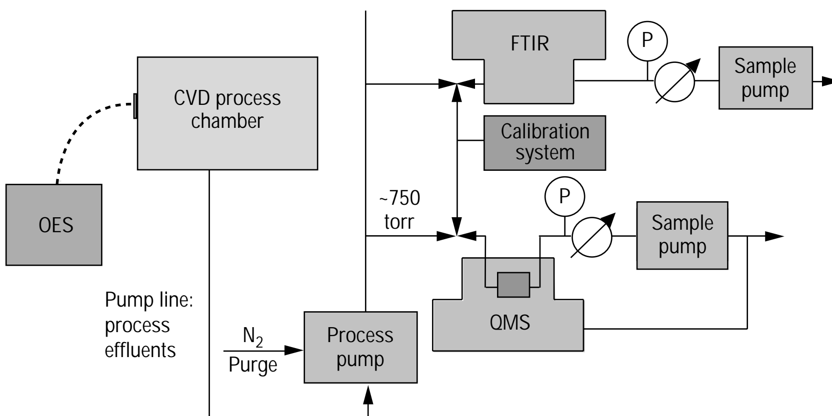

Figure 2. Schematic of analytical methodology used to quantify process effluents (QMS and FTIR) and measure clean times (OES).

The environmental impact of a particular process is described by the GWP_{100} of the PFC emission and the quantity (Q) emitted. CVD chamber cleans are evaluated based upon the million metric tons of carbon equivalent (MMTCE) for that process:

$$MMTCE = \Sigma_{PFC} \frac{Q(kg) \cdot \left(\frac{12}{44}\right) \cdot GWP_{100}}{10^9}$$

It is important that all byproducts having a nonzero GWP_{100} are included in the MMTCE calculation. For example, some CF_4 is generated by C_2F_6 clean processes, and its contribution to the total MMTCE value must be included in the summation [1].

MMTCE values are absolute — a process with lower emissions of weaker global warming potential (GWP_{100}) gases will have a lower MMTCE value. When evaluating CVD clean processes, it is important to compare their MMTCE values rather than a relative PFC reduction from some standard process. Any relative PFC emissions reduction will depend to a large extent upon the baseline process it is being compared to. It is also important to make the comparison for the same thin-film deposition, and it is especially important to standardize the thickness. In this paper, every attempt is made to reference MMTCE values per unit deposition (i.e., per μm).

Quantifying process effluents

The MMTCE calculation requires volumetric PFC emissions for that particular clean process. The concentration of PFCs during CVD chamber cleaning is measured using quadrupole mass spectrometry (QMS) and Fourier transform infrared (FTIR) spectroscopy techniques, as shown schematically in Fig. 2. Both techniques are able to monitor multiple PFCs simultaneously, with the required rapid sample response. It is critical that the QMS and FTIR instruments be calibrated over the appropriate concentration range. Standard concentrations are generated from certified gas standards (e.g., 1% C_2F_6 in balance N_2) using dynamic dilution methods. PFCs are quantified via daily on-site calibration of the QMS and the generation of appropriate reference spectra for the FTIR spectrometer.

The PFC concentration profile of a C_2F_6/O_2-based CVD chamber clean following tetraethylorthosilicate (TEOS) oxide deposition in a 200mm Applied Materials DxZ CVD chamber is shown in Fig. 3. Concentration measurements were made by both QMS and FTIR, and there is good agreement between these two independent analytical methodologies. There is a sharp increase in the C_2F_6 concentration when the process gases are turned on. Once the RF power is applied, the C_2F_6 concentration drops to 2100ppm, reflecting utilization of the C_2F_6 gas. The PFC by-products are unreacted C_2F_6, as well as CF_4 produced during the plasma clean. The concentration profile shows that more CF_4 is produced when the chamber is clean (i.e., during the overetch), and that the C_2F_6 utilization improves during the overetch. Volumetric emissions for a given PFC are obtained from integrating under the appropriate concentration profile. Note that in addition to volumetric process emissions, the concentration profiles can also provide valuable information on the clean time and the percent overetch for a given process. For example, the concentration profile of SiF_4 could be used to determine both the endpoint and the percent overetch for this process. Minimizing

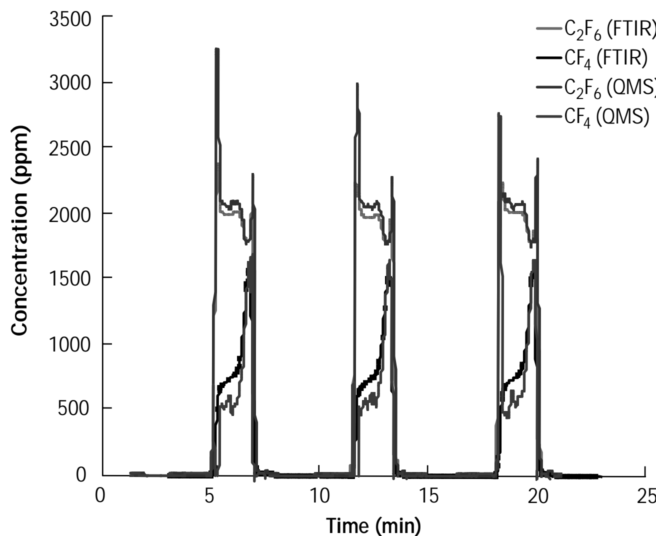

Figure 3. PFC emissions during Applied Materials DxZ chamber clean. Concentrations were measured by both FTIR and QMS.

the overetch can be a very effective strategy for reducing the gas cost and the MMTCE value of a CVD chamber clean.

Optimizing traditional C_2F_6-based in situ cleans

Installed tools already being used in production typically use an in situ C_2F_6/O_2 process chemistry for CVD chamber cleaning. In this traditional in situ clean, a PFC-based plasma is generated within the chamber by the application of radio-frequency (RF) power. The reactive F atoms and ions produced in the chamber result in an ion-assisted etching process that removes the deposition residue from the internal reactor surfaces. Traditional C_2F_6-based in situ CVD chamber cleans (Fig. 3) typically exhibit low (20–30%) utilization efficiencies (the percentage of the influent PFC that is consumed during the clean process), emitting large quantities of unreacted C_2F_6 in addition to other PFC by-products (e.g., CF_4, as shown in Fig. 3). Fundamental laboratory studies have shown that process optimization — adjusting the operating parameters to use the smallest quantity of PFC to remove the maximum quantity of deposition residue in the shortest possible time — can dramatically reduce the PFC emissions of traditional C_2F_6-based clean recipes and maintain high sample etch rates [6].

Through field trials at various customer sites, we have demonstrated that substantial PFC emission reductions are possible in commercial tools without any increase in clean time (relative to the traditional C_2F_6-based clean recipes). Indeed, both shorter clean times and lower PFC emissions are possible. Our strategy uses a central composite design of experiments (DOE) methodology to determine the most important factors affecting the clean time and process emissions (i.e., the MMTCE value). Clean times can be determined from the QMS and FTIR concentration profiles (as described above), or via optical emission spectroscopy (OES). Optical endpoint detection provides an additional check on the clean time and is fast, reliable, and nonintrusive. From the results of the DOE screening experiments, clean time and MMTCE response surfaces as a function of C_2F_6 flow rate, O_2:C_2F_6 ratio, and pressure can be generated. These can then be used to identify appropriate cleaning recipes for individual customer requirements. In general, lower PFC emissions are a result of a lower C_2F_6 gas flow with a higher fraction of the C_2F_6 influent being used for productive etching (i.e., SiF_4 formation). The lower C_2F_6 gas flow rates also lead to a substantial gas cost savings/clean. The advantage of this in situ optimization approach is that it is both cost-effective and does not require qualification of a new gas.

The MMTCE response surface for an Applied Materials DxZ chamber clean is shown in Fig. 4a. This response surface shows PFC emissions as a function of C_2F_6 flow rate and O_2:C_2F_6 ratio, at a fixed reactor pressure and power. Clearly, lower PFC emissions are possible using lower C_2F_6 flow rates and lower O_2:C_2F_6 ratios. Lower C_2F_6 flow rates were also found to result in higher C_2F_6 utilization efficiencies. The combination of a higher C_2F_6 utilization efficiency and a lower C_2F_6 flow rate leads to dramatically lower MMTCE values. A successful optimization project generally depends on finding an appropriate set of operating parameters that decreases the C_2F_6 flow rate and maintains, or even decreases, the original clean time. The corresponding response surface for the clean time is shown in Fig. 4b as a function of C_2F_6 flow and O_2:C_2F_6 ratio. Shorter clean times are favored by higher C_2F_6 flow rates and lower O_2:C_2F_6 ratios. Analysis of the response surfaces identified clean processes that result in lower MMTCE values, shorter clean times, and substantial gas cost savings.

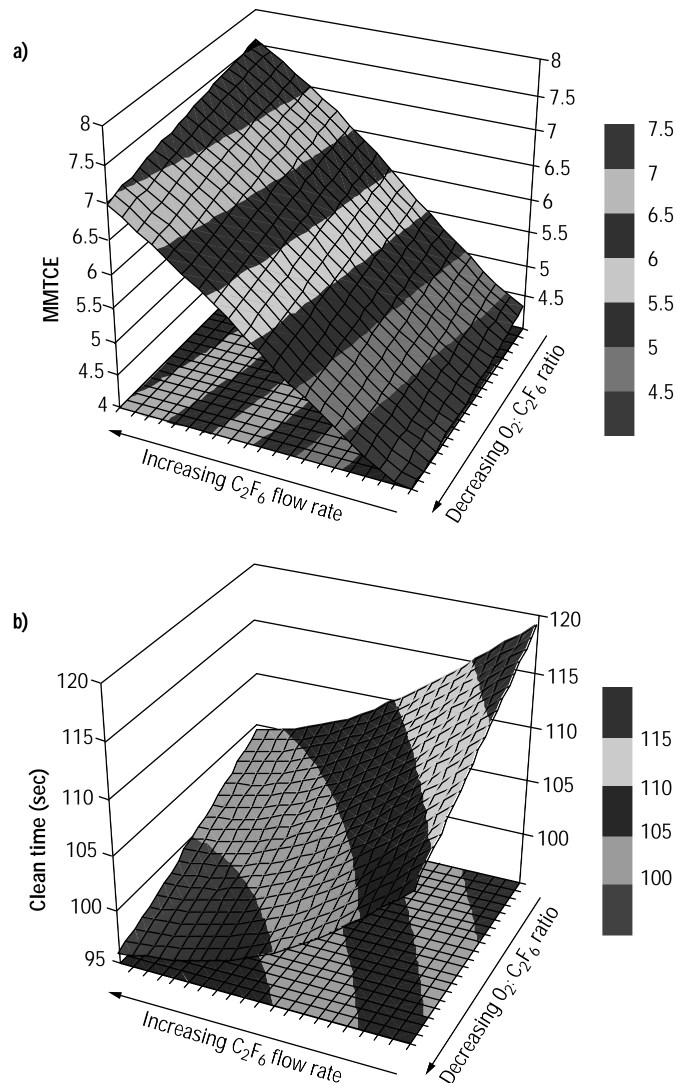

Figure 4. a) MMTCE and **b)** clean-time response surfaces, both as a function of C_2F_6 flow rate and O_2:C_2F_6 ratio, with fixed pressure.

Substituting NF_3 for C_2F_6

An alternative emissions reduction strategy is the substitution of NF_3 for C_2F_6 in in situ CVD chamber cleans. For example, Novellus Systems Inc. has recently developed dilute NF_3/He-based cleans for its 200mm Altus (W LPCVD) and 200mm Sequel (PECVD) platforms [7, 8]. These cleans reduce the MMTCE values (e.g., 0.3×10^{-9}/µm of oxide deposition) more than 90% compared to the standard in situ C_2F_6-based cleans (e.g. 7.5×10^{-9}/µm of oxide deposition), while maintaining a comparable clean time and gas cost of ownership.

IBM has also developed a dilute NF_3/He clean for its 200mm

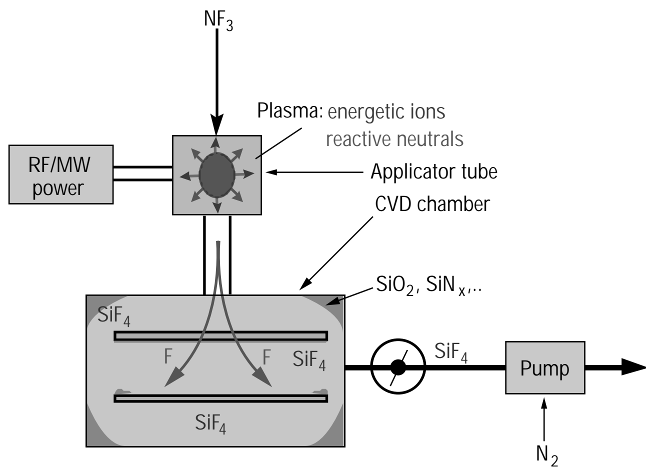

Figure 5. Schematic of the remote NF_3 clean process.

Applied Materials Precision 5000 lamp heated (DxL) PECVD chambers [9, 10]. The new dilute NF_3/He clean results in 95% lower PFC emissions than the in situ C_2F_6-based clean. IBM originally found the in situ NF_3 cleans difficult to qualify due to process drift in a manufacturing environment [10]. By using lower RF powers, lower pressures, and more He dilution, the in situ NF_3 clean process has been successfully implemented in production. (The process drift associated with the in situ NF_3 clean is equivalent to that for the original C_2F_6-based clean processes.) However, the impact of these process changes on clean times and PFC emissions must be evaluated by individual customers.

The extremely low PFC emissions of these NF_3-based in situ cleans are largely the result of the significantly higher utilization efficiency of NF_3 (up to 91%) compared to C_2F_6, and the lack of PFC by-products produced during the clean. While the substitution of NF_3 for C_2F_6 may require the qualification of new gas, it has the advantage of virtually eliminating PFC emissions from CVD chamber cleans.

Remote NF_3 chamber cleaning

More dramatic reductions of PFC emissions are possible with the remote NF_3 clean process, a new technology that has been developed for cleaning CVD equipment [11]. An NF_3 plasma is generated upstream of the CVD chamber using radio-frequency (RF) or microwave (MW) excitation (Fig. 5). The reactive fluorine neutrals drift into the process chamber where they react with the CVD residue (e.g., SiO_2) and form a volatile etch product (e.g., SiF_4) that is pumped out of the CVD chamber. Because there is no energetic ion bombardment of the CVD chamber surfaces, the result is a soft chemical etch rather than ion-assisted etching. Remote NF_3 chamber cleaning has been shown to effectively eliminate PFC emissions from CVD chamber cleaning. While NF_3 is a PFC and absorbs in the infrared (Fig. 1), remote clean processes make much more efficient use of the influent NF_3. Typically, utilization of NF_3 in remote plasma processes approaches 100%. Complete utilization means no unreacted NF_3 is emitted from the reactor. In addition, no other global warming by-products are produced by the remote NF_3 plasma process. As described earlier, C_xF_y processes produce substantial amounts of CF_4 as a by-product of the clean.

Remote NF_3 clean processes have been developed for Applied Materials PECVD chambers. Process effluents were analyzed using QMS and FTIR spectroscopy. Emission results for TEOS PECVD in a DxL chamber are shown in Fig. 6a [12]. This study verified PFC emissions reduction and shorter clean times relative to the baseline in situ C_2F_6 clean process.

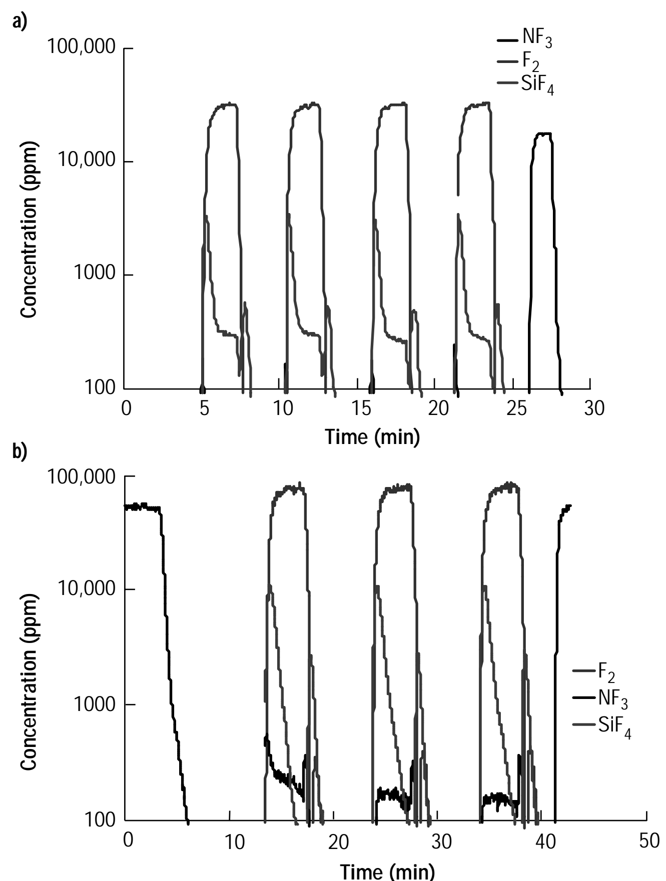

Figure 6. Concentration profile of Applied Materials **a)** DxL PECVD TEOS remote NF_3 clean and **b)** Ultima HDP-CVD Ultima USG remote NF_3 clean.

Table 2. Volumetric emissions during HDP-CVD USG chamber cleaning*

	Before abatement	After abatement
NF_3 (scc)	22	7
SiF_4 (scc)	249	1
F_2 (scc)	7056	13
HF (scc)	100	4

*By-product emissions are before and after Delatech CDO abatement.

By-products of the chamber clean were identified as: NF_3 (3scc), SiF_4 (62scc), F_2 (815scc), and HF (60scc). The MMTCE value for this 5000Å PECVD TEOS clean is 0.02×10^{-9}.

By-product concentration during Applied Materials Ultima HDP-CVD chamber cleaning is shown in Fig. 6b [13]. This remote NF_3 clean follows a 1.5μm deposition of undoped silicate glass (USG). The profile shows that the NF_3 concentration during the clean

process is more than 100 times lower (<200ppm$_v$) than that when the NF_3 gas is turned on but with no plasma power applied (50,000ppm$_v$). That is, the NF_3 utilization is better than 99%. Also, no other PFC by-products are generated during the clean. The volumetric NF_3 emission for this remote clean, calculated by integrating under the concentration profile (Fig. 6b), is only 22scc (Table 2), which results in an MMTCE value of 0.15×10^{-9}.

Table 3. Typical MMTCE (per μm deposition) values for CVD chamber cleans*

	Standard C_2F_6	Optimized C_2F_6	Remote NF_3
Applied Materials DxL (TEOS): 200mm [12,15]	34×10^{-9}	5×10^{-9}	0.04×10^{-9}
Applied Materials DxZ (TEOS): 200mm [16–18]	8×10^{-9}	2×10^{-9}	0.04×10^{-9}
Novellus Systems Concept-2 (TEOS): 200mm [7, 8]	8×10^{-9}	N/A**	N/A
Novellus Systems Concept-1(TEOS): 150mm [15]	33×10^{-9}	16×10^{-9}n/a	N/A
Applied Materials [13] Ultima (USG): 200mm	N/A	N/A	0.10×10^{-9}

*All cleans follow TEOS deposition, except for the Applied Materials Ultima, which is for a USG film.
**N/A = clean process or emissions data is not available for this equipment.

The major by-product from remote NF_3 chamber cleaning is elemental fluorine (Fig. 6b, Table 2). While F_2 has no global warming potential, it is a hazardous material that should not be released into the atmosphere. A number of effective solutions for abating the fluorine effluent are available. For example, the fluorine by-product is efficiently removed by reducing the F_2 by-products in a combustion chamber (Delatech CDO), followed by scrubbing the resulting HF with a neutral water scrubber [13]. The concentration (Fig. 7) and volume (Table 2) of the F_2 effluent are reduced to 20ppm$_v$, and 13scc, respectively. This means that 99.8% of the influent F_2 (7056scc) is abated.

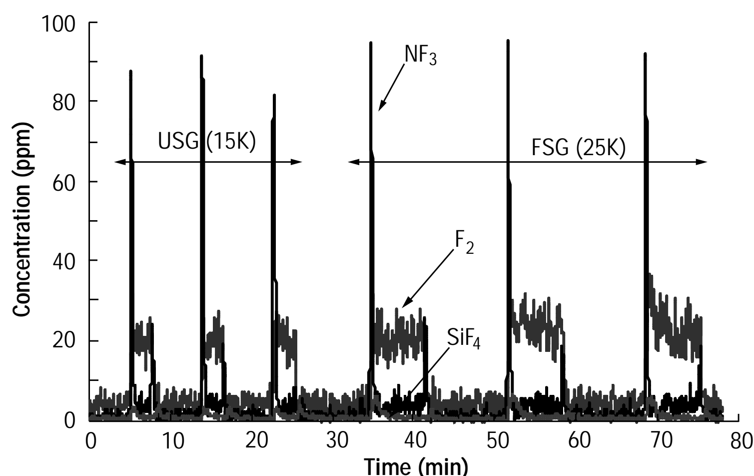

Figure 7. Concentration of chamber clean by-products after Delatech CDO abatement.

Remote NF_3 plasmas clean the process chamber faster than traditional in situ cleans because of high fluorine atom density, minimize plasma damage because of no ion bombardment, and eliminate PFC emissions from CVD processing with complete utilization of NF_3. Because of the complementary environmental and process advantages, there has been rapid acceptance of this cleaning technology for most new CVD equipment (PECVD, LPCVD, HDP-CVD, and SACVD).

Conclusion

Substantial reductions of PFC emissions have been achieved through a combination of optimizing traditional C_2F_6-based in situ cleans, substituting NF_3 for C_2F_6 in in situ cleans, and implementing the remote NF_3 clean technology. The success of this approach for much of the CVD tool base has been described, and typical PFC emissions are summarized in Table 3. For installed CVD tools presently being used for production, it is less feasible to change the chemistry of the clean process. Adjusting the process parameters so as to minimize PFC emissions, while maintaining the same clean time, is an effective strategy.

In addition to reducing PFC emissions, C_2F_6 process optimization can provide a reduction in gas costs, since the low-emissions processes typically use a lower C_2F_6 flow rate. By using NF_3, however, clean processes have been developed that essentially eliminate PFC emissions. It is accepted that most new CVD equipment will be cleaned using NF_3 chemistry. Besides eliminating PFC emissions from CVD chamber clean processes, remote NF_3 cleaning provides additional process benefits. ■

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