MINIMIZING PFC EMISSIONS FROM EXISTING PECVD TOOLS: OPTIMIZATION OF THE CHAMBER CLEAN PROCESS OF RECORD

Andrew D. Johnson, William R. Entley, Raymond N. Vrtis, John G. Langan,[#] and Peter J. Maroulis
Air Products and Chemicals, Inc.7201 Hamilton Blvd., Allentown, PA 18195, USA

Masaru Nagata, Inoue, and Omori
Daido Air Products Electronics, Inc., 6-40, 2-cho chikko-shinmachi, Sakai-shi, Osaka 592-8331 Japan

BIOGRAPHY

Andrew D. Johnson, Ph.D., is Senior Principal Research Chemist in the Electronics Division at Air Products. He conducts in situ and process effluent analysis, aiming to minimize emissions associated with semiconductor manufacturing. Dr. Johnson received his Ph.D. from the Massachusetts Institute of Technology. His research programs also include establishing gas purity requirements for semiconductor manufacturing and developing new technologies for the contamination-free delivery of these gases.

INTRODUCTION

Due to strong infrared absorbances and long atmospheric lifetimes, perfluorocompounds (PFCs) are suspected of contributing to global warming. PFCs are used extensively in semiconductor manufacturing, mostly to clean CVD chambers following thin film deposition. Since 1995, semiconductor manufacturers, OEMs, and material suppliers have proposed and evaluated new technologies for reducing the environmental impact associated with CVD chamber cleaning. Indeed, by using NF_3, manufacturers of semiconductor process equipment have developed cleans that essentially eliminate PFC emissions.[1,2,3]

For existing production tools however, it is less feasible to change the chemistry of the clean process. These legacy tools typically use a C_2F_6-based process to clean the CVD chamber. A cost effective approach to reduce PFC emissions for these processes is to adjust the process parameters while maintaining an adequate clean time. This strategy recognizes that older clean recipes were not developed to be efficient with respect to PFC usage.

This paper describes how substantial PFC emission reductions are possible in commercial CVD reactors by optimizing the C_2F_6 chamber clean process. Our strategy is to measure response surfaces for both PFC emissions and clean time. These response surfaces show how the C_2F_6 flow rate, $O_2:C_2F_6$ ratio, and pressure can be adjusted to lower PFC emissions while maintaining a comparable clean time. Examples are described for some of the installed tool base: Applied Materials' DxL, Applied Materials' DxZ, Novellus Concept 1.

FUNDAMENTALS OF PFC PLASMAS

Production CVD tools that are already installed in semiconductor fabs typically use an *in situ* C_2F_6/O_2 RF-plasma for chamber cleaning. The utilization of C_2F_6 in these chamber cleans is usually quite low (20-30 %), meaning that much of the influent C_2F_6 gas is not consumed during the chamber clean but emitted from the process. Laboratory studies have shown how etch rates depend upon process parameters.[4] Figure 1 shows the SiO_2 etch rate as a function of gas composition for C_2F_6 and C_3F_8 plasmas. Both PFCs exhibit similar behavior: the etch rate goes through a maximum as O_2 is added to the feed gas. The conditions resulting in the highest etch rates are different for each PFC (e.g., C_2F_6 or C_3F_8), thin film material (e.g., SiO_2 or SiN_x), and PECVD process equipment (e.g., Applied

---

[#] Present address Novellus Systems, San Jose, CA 95134

Materials or Novellus). The goal of process optimization if to identify those conditions yielding the highest intrinsic etch rate (i.e., fastest clean time) using the lowest flow rate of process gas.

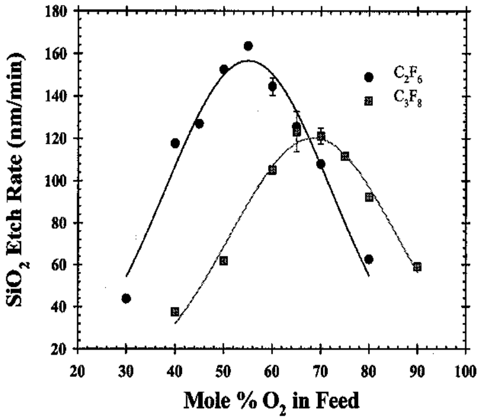

Figure 1.

OPTIMIZATION OF TEOS PECVD CHAMBER CLEAN PROCESSES

Clean processes following TEOS PECVD were optimized using a central composite design of experiments (DOE) methodology which sets alpha to 1. Typical DOE parameters are C_2F_6 flow rate, pressure, and O_2:C_2F_6 ratio. There are two DOE responses: clean time and PFC emissions.

Clean times are determined using the optical end-point monitor at the CVD chamber. Fluorine atom emission at 704 nm is monitored and the clean time obtained from the end-point profile. While the chamber is being cleaned, there is little light emission since F-atoms are consumed by etching. As the CVD residue clears, however, the F-atom density increases resulting in an intense emission line.

The concentration of PFCs during CVD chamber cleaning are measured using quadrupole mass spectrometry (QMS) and fourier transform infrared (FTIR) spectroscopy techniques. Process byproducts are sampled in the pump exhaust at ambient pressure and are diluted by the N_2 pump purge. Both the QMS and FTIR instruments are calibrated on-site for the byproducts being measured (e.g. C_2F_6, CF_4). There is good (5 %) agreement between the QMS and FTIR measurements (Fig. 2).

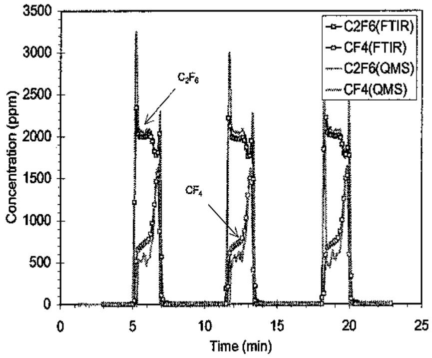

Figure 2.

Integrating under the concentration profile, and multiplying by the N_2 pump purge, allows volumetric emissions (i.e. scc) to be calculated. The metric used to evaluate environmental impact is million metric tons carbon equivalent (MMTCE):

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

Volumetric emissions calculated from the concentration profile are converted to a mass emission Q(kg) and multiplied by the global warming potential (GWP_{100}) for that PFC.[5] All byproducts having a non-zero global warming potential are included in the MMTCE calculation. As shown in Fig. 2, CF_4 is generated during the C_2F_6 clean and its contribution to the total MMTCE value must be included in the summation.

Applied Materials' DxZ

The baseline clean for this Applied Materials' DxZ chamber is a one step C_2F_6-based process. The MMTCE response surface[6] is shown in Fig. 3 as a function of C_2F_6 flow rate and O_2:C_2F_6 ratio (the pressure and RF power have been fixed). Lower PFC emissions are obtained by decreasing the C_2F_6 flow rate and O_2:C_2F_6 ratio. These reduced emissions result from higher PFC utilization at lower flow rates (i.e., more of the influent C_2F_6 gas is used to productively etch the CVD residue). For a net PFC emission reduction, however, this higher utilization must not be offset by increased CF_4 production.

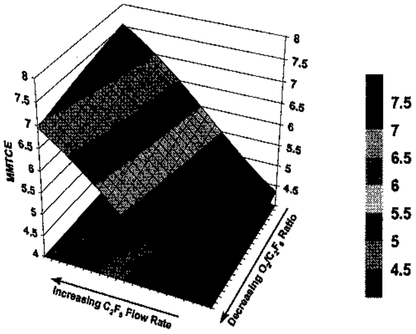

Figure 3.

A successful optimization project must not reduce PFC emissions at the expense of wafer throughput. The clean time for the optimized process must be comparable, or shorter, than that for the original clean process. The corresponding response surface for the clean time is shown in Fig. 4, again as a function of C_2F_6 flow rate and O_2:C_2F_6 ratio (at fixed pressure and RF power). Shorter clean times are favored by higher C_2F_6 flow rates and lower O_2:C_2F_6 ratios. The desired direction of the clean time response to C_2F_6 flow rate is opposite to that for the MMTCE response i.e., a lower C_2F_6 flow rate process has a lower MMTCE value but a longer clean time (at fixed pressure, O_2 concentration, and power). Lower O_2:C_2F_6 ratios, however, result in both reduced PFC emissions and faster cleans. Examination of the response surfaces (Figs. 3 and 4) identifies a clean process having both lower PFC emissions (2.2×10^{-9} MMTCE/µm, approximately 75 % reduction in emissions) and a shorter clean time (9 % reduction in clean time) than the original clean process.

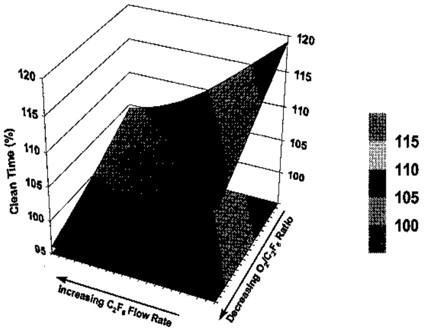

Figure 4.

Applied Materials DxL

The standard Applied Materials' DxL chamber clean is a two step C_2F_6/O_2-based process. A high pressure step is first used to clean the wafer chuck and electrode. A low pressure step follows that cleans remote areas of the PECVD chamber. In addition, NF_3 is added to the feed gas during the second step of the clean. Both steps of the clean recipe use the same C_2F_6 and O_2 flow rates and are a timed etch rather than using end-point control.

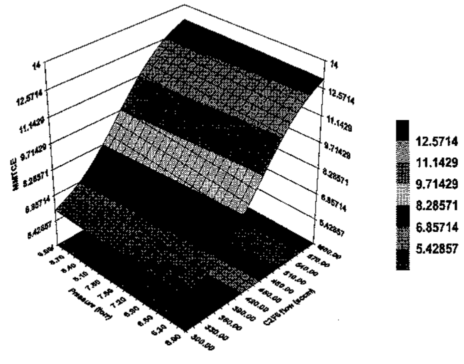

Figure 5.

The response surface for the MMTCE value is shown in Fig 5. Lower MMTCE values are favored by lower C_2F_6 flow rates. Pressure and O2:C_2F_6 ratio have a minor effect on MMTCE value. The corresponding response surface for C_2F_6 utilization is shown in Fig 6. This plot illustrates how lower PFC emissions result from a higher utilization at lower flow rates.

The MMTCE response surfaces suggest an optimized recipe with a C_2F_6 flow rate of 300 sccm and O_2:C_2F_6 ratio of 1.10 should reduce PFC emissions by 70 %. To verify the MMTCE reduction, measurements were made on these actual processes. Volumetric emissions are C_2F_6(335 scc), CF_4 (99 scc), NF_3 (38 scc), and SiF_4 (134 scc). These PFC emissions correspond to 6.2×10^{-9} MMTCE which represents a 70 % reduction from the original clean process.

While lower flows result in lower MMTCE values, there might be concern that lower flows may not completely clean the chamber i.e. the lowest C_2F_6 flows may result in an incomplete clean. Volumetric SiF_4 emissions are a good measure of whether all of the TEOS residue has been removed from the process chamber. If some TEOS residue remains in remote areas then less SiF_4 will be emitted. SiF_4 emissions for the standard and recommended clean processes are 125 scc and 134 scc, respectively. The recommended clean removes an equivalent amount of SiF_4 as the standard clean process indicating that all of the TEOS residue has effectively been removed from the PECVD chamber.

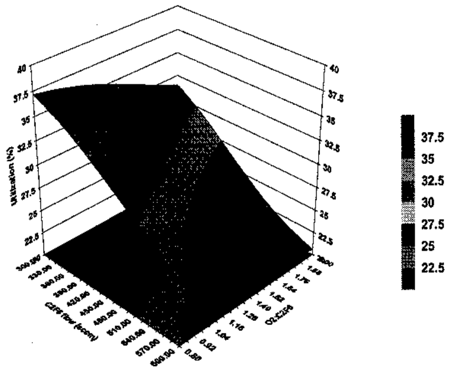

Figure 6.

The optimized 300 sccm C_2F_6 process reduces PFC emissions by 70 % (6.2×10^{-9}). Further MMTCE reductions (up to 85 %) have been demonstrated. Both of these optimized cleans remove all of the TEOS residue from the PECVD chamber as indicated by the volumetric SiF_4 emission (relative to that for the standard clean process). In addition to lower PFC emissions, these clean processes reduce the amount of C_2F_6 required for each clean substantially.

Novellus Concept 1

The clean for the Novellus Concept-1 PECVD chamber is a two-step C_2F_6/O_2-based process: a high pressure (HP) step that cleans the shower head and heater block followed by a low pressure (LP) step that removes residue from the remote areas of the chamber. Typically, the HP step is controlled by end-point detection whereas the LP step is a timed etch. Both the HP and LP steps use the same gas composition and RF power. The pressure of the HP step is a DOE variable, whereas, the LP pressure is fixed at 0.7 torr.

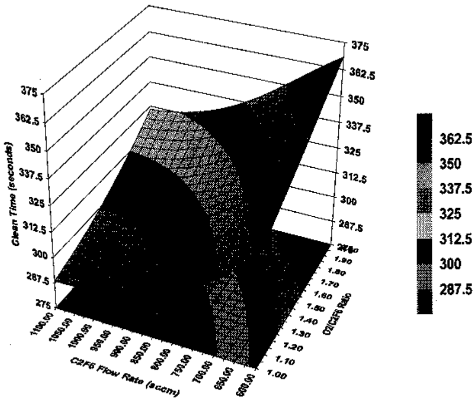

Figure 7.

A response surface for the HP clean time is shown in Fig. 7 showing that the clean time is a strong function of C_2F_6 flow rate and O_2/C_2F_6 ratio. The clean time also has a pressure dependence. These response surfaces show that shorter clean times are favored by higher C_2F_6 flow rates, lower O_2/C_2F_6 ratios, and higher pressures.

The most important factor controlling MMTCE is the C_2F_6 flow rate: higher C_2F_6 flow rates result in higher MMTCE's. Lower MMTCE's are also favored by lower O_2/C_2F_6 ratios and higher pressures, although the affect of these factors on the total MMTCE are significantly less than that of C_2F_6 flow rate.

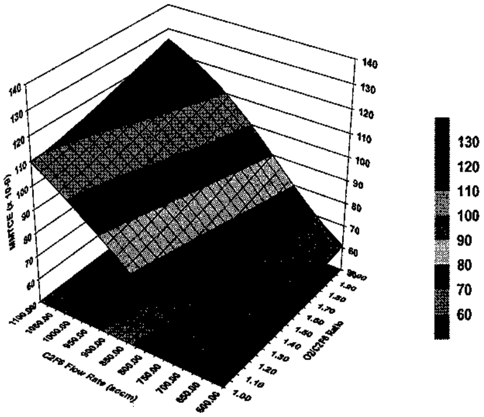

Figure 8.

Through an examination of the MMTCE and clean time response surfaces a process was recommended having a 52 % PFC emissions reduction: 96×10^{-9} MMTCE for the sum of the HP and LP steps. In addition, the HP clean time and volumetric SiF_4 emissions are identical to the original process i.e., equivalent wafer throughput and the chamber has been effectively cleaned.

SUMMARY

Substantial reductions in PFC emissions have been achieved by optimizing traditional C_2F_6 based *in situ* cleans. Examples of this approach for some of the CVD tool base has been presented and typical PFC emissions are summarized in Table 1. 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 uses less C_2F_6 for each clean.

	Standard C_2F_6	**Optimized C_2F_6**
Applied Materials DxL (TEOS): 200 mm	34×10^{-9}	10×10^{-9}
Applied Materials DxZ (TEOS): 200 mm	8×10^{-9}	2×10^{-9}
Novellus Systems Concept-2 (TEOS): 200 mm	8×10^{-9}	n/a
Novellus Systems Concept-1(TEOS): 150 mm	33×10^{-9}	16×10^{-9}

Table 1. Typical MMTCE (per μm deposition) values for CVD chamber cleans. All cleans follow TEOS deposition (n/a: clean process or emissions data not available for this equipment).

REFERENCES

---

[1] "Remote Microwave Plasma Source for Cleaning CVD Chambers: Technology for Reducing Global Warming Gas Emissions," S. Raoux, T. Tanaka, M. Bahn, H. Ponnekanti, M. Seamons, T. Deacon, L.-Q. Xia, A. Johnson, R. Pearce, and J. Langan, *J.Vac.Sci.Technol* **B17**, 477 (1999)

[2] "Remote Plasma Clean Technology for Dielectric CVD Chamber Cleaning to Reduce PFC Emissions," L. Mendicino, P. Thomas Brown, S. Filipiak, D. Loop, R. Basnett, W. Holber, R. Pearce, and A. Johnson, *ECS Proceedings* **99-8**, 40 (1999).

[3] "Reduced PFC Emission Chamber Clean Processes on Novellus CVD Tools," K. Aitchenson, *SEMICON West PFC Technical Update* (1999).

[4] "C_2F_6/O2 and C_3F_8/O2 Plasmas: SiO_2 Etch Rate, Impedance Analysis, and Discharge Emissions," W. R. Entley, W. J. Hennessy, and J. G. Langan, *Electrochemical and Solid State Letters,* **3**, 99 (2000)

[5] "The Science of Climate Change 1995," J. J. Houghton *et. al.*, Editors, Intergovernmental Panel on Climate Change, Cambridge University Press (1995).

[6] “"Optimization of a C_2F_6 Clean for an Applied Materials' TEOS PECVD Process: Lower MMTCE and Faster Clean Time", A. D. Johnson, W. R. Entley, R. N. Vrtis, J. G. Langan, P. J. Maroulis, *197th Meeting of The Electrochemical Society: Symposium on Environmental Issues with Materials and Processes for the Electronics Semiconductor Industries"*