Effective Method to Evaluate CVD Cleaning Gases for PFC Emission Reduction and Total Cost Saving

By J M Hsu*, Max Chen, Y C Kuo T/F module of Fab 8D in United Microelectronics Corp.
Terry T. Lee and Gary Loh, DuPont Zyron® Electronic Gases

Abstract

For Perfluorcarbon (PFC) emission reduction, it is essential to identify an alternative cleaning gas that is both compatible with existing hardware and requires only minimal cost and process modifications. In this paper, we will illustrate the successful replacement of C3F8 with c-C4F8 in the PECVD chamber-cleaning process, which results in substantially reduced PFC emissions, manufacturing costs and cleaning time by an effective and complete evaluation method in Novellus Concept-2 tools. In addition, the critical emission factors of these gases (C3F8 and c-C4F8) are proven to agree with the Intergovernmental Panel on Climate Change (IPCC) 2006 publication in this study.

Introduction

PFC emission reduction has been a heated topic of discussion for the global warming issue over the past decade. In the semiconductor industry, many solutions have been introduced to the market including additional abatement systems, chamber cleaning gas recipe optimization, tool modifications, and alternative cleaning gases for older PECVD tools. While chamber cleaning efficiency continues to improve with the new generation of chemical vapor deposition (CVD) tools, achieving an effective cleaning that is economical and practical for reducing PFC emissions in older PECVD tools remains a challenge. "Older PECVD tools" can be defined as 200mm wafer size and smaller, using CxFy in-situ chamber cleaning gases rather than NF3 (clean gas for new equipment). To balance the factors of cost of ownership and environmental protection the proper gas source selection has been found to be the most efficient solution. [1,2]

The predominant semiconductor PFC emission for older PECVD tools is Hexafluoroethane (C2F6), which is used at 30% efficiency in typical chamber cleaning, processes. This results in 70% of the input gas being emitted. The utilization efficiency of alternate cleaning gases such as Octafluoropropane (C3F8) is approximately 30-60% while cyclic-Octafluorobutane (c-C4F8) is in the range of 70-90% [1]. In this study, we demonstrated a process for converting C3F8 cleaning to c-C4F8 by using an effective analysis method from multiple perspectives.

Experiment

The experiment was conducted in a Novellus C-2 PECVD tool using the C3F8 cleaning recipe as a baseline reference. The same deposition recipe was used to keep film composition and thickness constant while varying chamber pressure, cleaning gas flow and O2 flow in the c-C4F8 cleaning recipe. The various c-C4F8 conditions were developed by Design of Experiment (DOE) for the high-pressure regime of the clean recipe using a three level Box-Benhken matrix, Table.1.

Table.1 DOE matrix of c-C4F8 designed by MINITAB

RunOrder	C4F8 flow	O2%	Pressure
1	500	82.5	3.0
2	400	88.0	2.8
3	600	83.0	2.8
4	400	75.0	3.0
5	500	82.5	3.0
6	600	82.5	3.2
7	400	82.5	3.2
8	600	75.0	3.0
9	500	75.0	3.2
10	600	82.5	3.0
11	450	87.0	3.0
12	400	82.5	2.8
13	500	82.5	3.0
14	450	85.0	3.2
15	500	75.0	2.8

The chamber cleaning endpoint was monitored and verified using the Optical Emission Spectrum (OES) embedded on the chamber. The DOE process data was calculated by using MINITAB. During the production test, film properties (thickness, uniformity index, particle count and stress), product electrical and yield performance, as well as tool and parts appearance were evaluated.

The exhaust gases emitted during the cleaning processes were monitored using Fourier Transform Infrared Spectrometry (FTIR). The exhaust gas was extracted via a sampling pump from a sample port downstream of the process pump, and directed through a MIDAC FTIR analyzer to quantify the species of interest (CxFy, SiF_4, COF_2 and CF_4). The sample was returned to the exhaust line downstream of the sample port.

Result & Discussion

■ **<u>The model analysis of PFC, cost and cleantime</u>**

In this study, we selected c-C_4F_8 as the candidate to be evaluated for comparison with C_3F_8 for cleaning deposition films in a Novellus Concept-2 PECVD tool. Process trends can easily be determined through MINITAB from the results of the DOE matrix by recording OES measurement data, Figure 1. The results show the most efficient O_2 concentration with c-C_4F_8 cleaning gas is approximately 75-78%. The clean time was found to be reduced as a function of reduced chamber cleaning pressure..

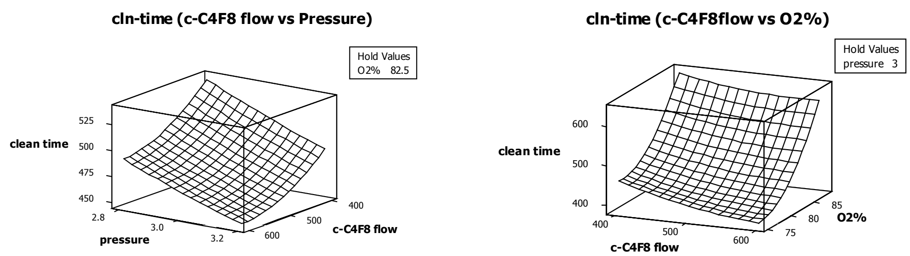


Figure 1. clean time v.s. c-C_4F_8 flow, O_2 ratio and pressure

The chamber cleaning time, gas usage, cleaning efficiency and PFC emissions were calculated from FTIR and OES measurement results for each experimental condition. The gas usage was calculated based on the cleaning time from FTIR and the mass-flow controller (MFC) flow setting. Using the following equation, the researchers were able to integrate the total volumetric output of CxFy and CF_4 during those cleans to calculate PFC emissions in the form of kilogram carbon equivalents (kg CE):

$$\text{Kg C} = \sum Q_i \times (12/44) \times GWP_i$$

In this equation, for every species that contributes to global warming, Q is the amount of gas (kg), and GWP is the global warming potential (100 year integrated time horizon [1TH]). The 100yr 1TH values used for C_3F_8 and c-C_4F_8 are 7000 and 8700 respectively.

We observed significant benefits in PFC emission reduction, with c-C_4F_8 reducing PFC emission by 67% vs. C_3F_8 in the high pressure (HP) step, and 55% emission reduction vs. C_3F_8 in the low pressure (LP) step. In addition, gas usage was greatly reduced vs. C_3F_8. Results indicated that c-C_4F_8 provided a 36% usage reduction vs. C_3F_8 in HP and a 28% gas usage reduction in LP. Furthermore, this optimum recipe shortened overall cleantime with a 10% reduction by moving from C_3F_8 to c-C_4F_8, allowing the Novellus Concept -2 tool to improve wafer throughput, Figure.2

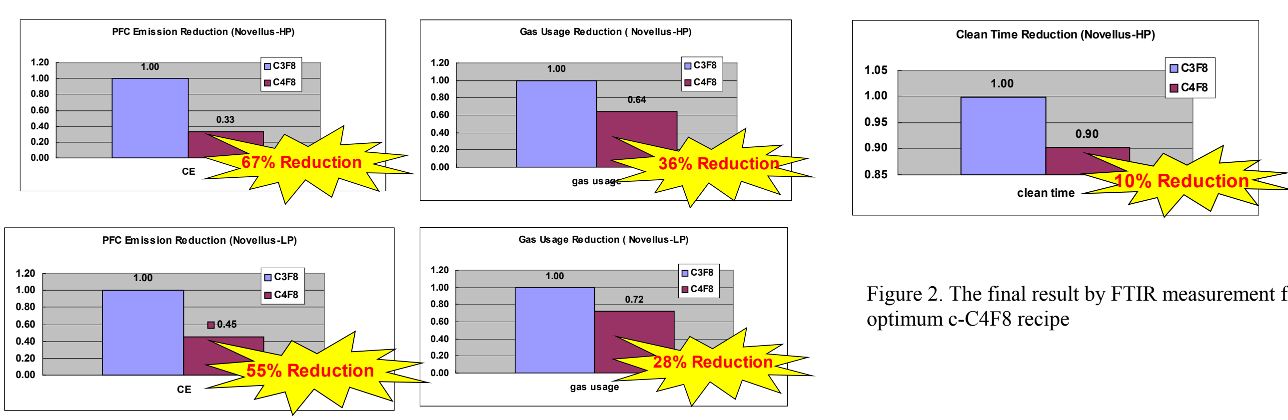


Figure 2. The final result by FTIR measurement from the optimum c-C_4F_8 recipe

■ **<u>The final stability test in production</u>**

Reproducibility of the results was tested using the optimum recipe in mass production for three months. The recipe was found to exhibit stable performance of c-C4F8 comparing with C3F8, as indicated in Figure.3.

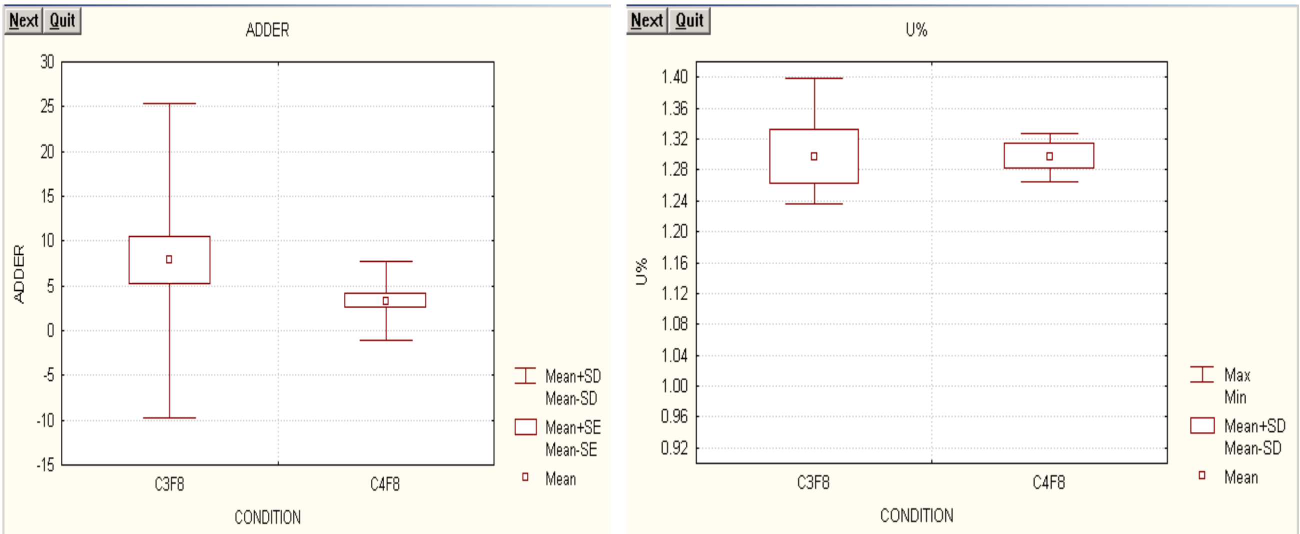


Figure 3. Monitoring particles and uniformity

■ **<u>Verify the key factors of "1-Ui" and "Bi" in PFC emission</u> (C3F8 v.s. c-C4F8)**

IPCC published feature factors for PFC calculation in 2006 is as Table.2 [3]. In this study, we also verified these factors by experiment using the FTIR results, Figure.4. When comparing C3F8 and c-C4F8 results, the effective emission factor, 1-Ui, after cleaning process in the chamber for C3F8 is 0.41-0.56 and c-C4F8 is 0.14-0.22. This means that 41%-56% of C3F8 used in process is emitted as C3F8 and 14%-22% of c-C4F8 used in the processes is emitted as c-C4F8. The byproduct emission factor, B_{CF4}, after the cleaning process in the chamber for C3F8 is 0.10-0.27 and c-C4F8 is 0.10-0.18. Which means 10% to 27% of C3F8 is converted to CF4 and 10% to 27% of c-C4F8 is converted to CF4 in the cleaning process. Un-reacted C3F8, un-reacted c-C4F8, and byproduct CF4 are critical PFC gases which contribute to the global warming issue. The final results from this project are consistent with the IPCC published data in the literature, Table.3.

Table.2 Default emission factors for FC emissions from semiconductor manufacturing [3]

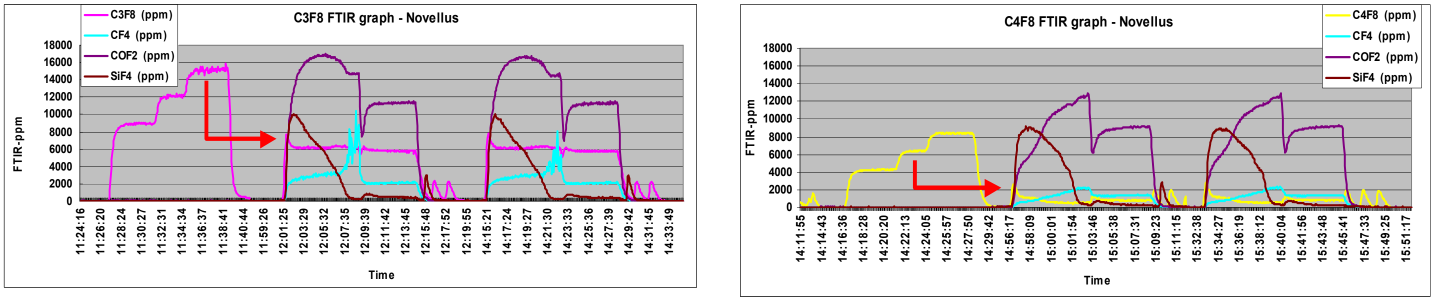
	Greenhouse Gases with TAR GWP									Greenhouse Gases without TAR GWP			Non-GHGs Producing FC By-products‡	
Process Gas (i)	CF_4	C_2F_6	CHF_3	CH_2F_2	C_3F_8	c-C_4F_8	NF_3 Remote	NF_3	SF_6	C_4F_6	C_5F_8	C_4F_8O	F_2	COF_2
Tier 2a														
1-Ui	0.9	0.6	0.4	0.1	0.4	0.1	0.02	0.2	0.2	0.1	0.1	0.1	NA	NA
B_{CF4}	NA	0.2	0.07	0.08	0.1	0.1	0.02†	0.09	NA	0.3	0.1	0.1	0.02†	0.02†
B_{C2F6}	NA	NA	NA	NA	NA	0.1	NA	NA	NA	0.2	0.04	NA	NA	NA
B_{C3F8}	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.04	NA	NA
Tier 2b														
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 B_{CF4}	NA	0.4*	0.07*	0.08*	NA	0.2	NA	NA	NA	0.3*	0.2	NA	NA	NA
Etch B_{C2F6}	NA	NA	NA	NA	NA	0.2	NA	NA	NA	0.2*	0.2	NA	NA	NA
CVD B_{CF4}	NA	0.1	NA	NA	0.1	0.1	0.02†	0.1†	NA	NA	0.1	0.1	0.02†	0.02†
CVD B_{C2F6}	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
CVD B_{C3F8}	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.04	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

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



(a) (b)

Figure 4. FTIR graph of current C3F8 process performance (a) v.s. optimum c-C4F8 process (b)

Table.3 Comparison of emission factors for FC emissions from literature v.s. experiment

	Key Emission Factors				Remark
	C3F8		c-C4F8		Ui: Utilization factor **1-Ui: Emission factor** **Bi: Byproduct emission factor** Ci: Concerntration measured by FTIR $Ui=1-C_{i(RF-ON)} / C_{i(RF-Off)}$ Bi=Mass i / Mass CxFy Mass=Density i x Ci
	1-Ui	$Bi-CF_4$	1-Ui	$Bi-CF_4$	
IPCC Tier 2b	0.4	0.1	0.1	0.1	
Test Value from the particle experiment	0.41-0.56	0.10-0.27	0.14-0.22	0.10-0.18	

■ **<u>Cost of ownership saving and PFC reduction</u>**

A final cost assessment was made and we found that c-C4F8 delivered a dramatic total cost savings of approximately 24% when compared to the existing C3F8 recipe. In addition, PFC emissions vs. C3F8 could be reduced by 61% with the optimum recipe, Table 4. Clean time reduction from the c-C4F8 optimum recipe also allowed us to benefit with a 10% throughput improvement vs. C3F8.

Table.4 Total evaluation table

total (HP+LP)	*CxFy gas usage*	*$*	*PFC*
Reduction of c-C4F8 vs C3F8	32%	24%	61%

The parts lifetime using the optimum recipe with c-C4F8 delivered improved or equal performance than base line in the past.

Conclusion

In this project, we developed an optimum recipe using c-C4F8 successfully in various processes of Novellus Concept-2 CVD tools and then successfully passed process reliability tests over a three month period. We also found the added value of throughput improvement and PM cycle time extension by effectively using this methodology. In addition, we verified the results of feature factors from different CxFy gases, which were in agreement with the data in IPCC literature. In accordance with this complete study, the chamber cleaning gas replacement approach using c-C4F8 is a simple and efficient “drop-in” process to be qualified, without any hardware modification or SHE concerns in operation. In addition to the dramatic environmental benefits, the c-C4F8 optimum recipe was also successful in reducing the production costs in wafer manufacturing at Fab 8D.

Authors :
J.M Hsu, Technical Manager, ThinFilm Module Dept./ FAB8D Division, UMC.
Tel: 886-3-5782258 ext. 8739618, Fax: 886-3-5642150. E-mail: j_m_hsu@umc.com

Terry Lee, Technical Marketing and Service Manager, Zyron, Asia Pacific, DuPont.
Tel: 886-2-25144437, Fax: 886-2-25457098. E-mail: terry.t.lee@twn.dupont.com

Gary Loh, Technical Program Manager, Fluorochemicals Laboratory, DuPont.
Tel: 302-999-4971, Fax: 302-999-2093. E-mail: gary.loh@usa.dupont.com

Reference

1.” Reduction of Perfluorocompound (PFC) Emission : 2005 State-of –the-Technology Report,” Technology Transfer # 05104693A-ENG, International SEMATECH Manufacturing Initiative (2005)

2. Oliver f. Schedlbauer , Hubert F. Winzig,” Cost Reduction in CVD Chamber Cleaning : Strategies to Reduce Gas Costs” FUTURE FAB Internal Issue 13, 164-119 (2004)

3. Scott Barton(USA), Laurie S. Bea(USA), C. Shephered Burton(USA), Charles L. Fraust(USA), Francesca Illuzzi (Italy), Michael T. Mocella(USA) and Sebastien Raoux(France/USA), “Chapter 6: Electronic Industry Emission”, 2006 IPCC Guideline for National Greenhouse Gas Inventories, page 6.17.