MICRO
ADVANCED PROCESS CONTROL, DEFECT REDUCTION, AND
YIELD ENHANCEMENT FOR SEMICONDUCTOR MANUFACTURING

# Selecting proper chamber-cleaning processes for installed-base CVD tools

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***A case study determines that replacing $C_3F_8$ gas with c-$C_4F_8$ gas is an inexpensive and easy way to lower PFC emissions in installed-base CVD chamber-cleaning processes.***

N*umerous studies have been* performed on reducing perfluorocarbon (PFC) emissions from chemical vapor deposition (CVD) chamber-cleaning processes. In new-generation tools, nitrogen trifluoride, a low-emission chamber-cleaning gas, is widely used to reduce PFC emissions. In addition, the development of several new cleaning gases, such as $F_2$ and $COF_2$, has shown promising results.

However, fabs with 150- and 200-mm installed-base tools, which contribute significantly to PFC emissions, require other practical and economical solutions to reduce emissions. The goal of the project discussed in this article was to select a chamber-cleaning gas to replace $C_3F_8$ in Concept-1 tools from Novellus (San Jose). The alternative cleaning gas not only had to be effective at reducing PFC emissions, but it also had to be practical and economical to meet the following requirements:

- No increase in gas use and costs.
- No additional safety, health, and environmental (SHE) management costs.
- Low conversion costs.
- Low conversion effort.

This study presents a c-$C_4F_8$-based chamber-cleaning chemistry that offers both process and SHE benefits while involving minimal cost and process

| Gas Characteristic | $C_3F_8$ | c-$C_4F_8$ | c-$C_4F_8$/$C_3F_8$ |
|---|---|---|---|
| Molecular weight | 188 | 200 | — |
| GWP | 7000 | 8700 | — |
| Estimated gas utilization | 65% | 80% | — |
| Estimated $C_xF_y$ flow (std $cm^3$/min) | 770 | 400 | — |
| Estimated clean time (seconds) | 2250 | 2250 | — |
| Estimated gas use/clean (kg/clean) | 0.242 | 0.134 | 55% |
| Estimated unreacted $C_xF_y$ (kg/clean) | 0.085 | 0.027 | — |
| Estimated kg CE based on $C_xF_y$ | 161.8 | 63.5 | 39% |

**Table I: Estimate of benefits from alternative chamber cleaning process.**

modifications. Based on a balanced approach, this work determined that the benefits of c-$C_4F_8$ compare to those of the $C_3F_8$ cleaning process. Several factors related to gas costs and SHE concerns were evaluated. Other issues investigated included gas delivery. Previously optimized c-$C_4F_8$ recipes were used to minimize c-$C_4F_8$ recipe development work. Fourier transform infrared (FTIR) and optical emission endpoint detectors were used to verify the completion of chamber cleaning and the emissions reductions. The results of the work described here demonstrated that the c-$C_4F_8$ cleaning process reduced PFC emissions by 57% over the $C_3F_8$ cleaning process. Also, reduced gas consumption from the use of c-$C_4F_8$ resulted in a 20% cost savings. This work demonstrates that a low-cost, low-effort approach can reduce PFC emissions in installed-base tools.

## Comparing c-$C_4F_8$ and $C_3F_8$ gases

In chamber cleaning, a fluorine-containing cleaning gas is converted into atomic fluorine for removing deposition process by-products from CVD chambers. A high fluorine conversion rate enables high gas utilization. Cleaning gases that offer high gas utilization reduce the unreacted cleaning gas in tool exhaust, leading to lower PFC emissions.

Various studies indicate that of all $C_xF_y$ chamber-cleaning gases, c-$C_4F_8$ has the highest gas utilization. Based on data from gas suppliers, c-$C_4F_8$ has been shown to attain higher gas utilization than $CF_4$, $C_2F_6$, $C_3F_8$, or $C_4F_8O$.[1] It has also been demonstrated that c-$C_4F_8$ requires a much lower gas concen-

| Gas Characteristic | c-$C_4F_8$ | $NF_3$ | $COF_2$ | $F_2$ (30%) |
|---|---|---|---|---|
| Health hazard TLV(ACGIH TWA) or AEL* | 1000 ppm* | 2 ppm* | 2 ppm | 2 ppm |
| Acute toxicity (LC50, 1 hour, rat) | 800,000 ppm | 6700 ppm | 360 ppm | 180 ppm |
| Reactivity | Not reactive | Not reactive | Reactive | Very reactive |
| Flammability | Nonflammable | Nonflammable | Flammable | Flammable |
| Corrosivity | Noncorrosive | Noncorrosive | Corrosive | Very corrosive |
| GWP (100-year ITH) | 8700 | 10,800 | 1 | 0 |
| Gas utilization | 80–90% | 99% | >99% | >99% |
| PFC emission | Low | Very low | Very low | Very low |
| Gas use and cost | Low | High | Low | Low |
| Additional SHE management costs | Low | High | Very high | Very high |
| Conversion costs for tool modification | Low (drop-in replacement) | High (needs tool modification) | Very high (needs new gas-delivery system) | Very high (needs new gas-delivery system) |
| Time, effort, resource for conversion | Low (already used in mass production for installed-base tools) | High (not used in mass production for installed-base tools) | High (not used in mass production for installed-base tools) | High (not used in mass production for installed-based tools) |

*AEL (acceptable exposure limit) is the inhalation exposure limit assessment established by DuPont.

**Table II: A balanced approach to chamber-cleaning gas selection.**

| | Inputs (Recipe) | | | Measured Outputs (Clean 1 + Clean 2) | | | |
|---|---|---|---|---|---|---|---|
| Experiments | $C_xF_y$ Flow (std cm³/min) | $O_2$ Flow (std cm³/min) | O2 (%) | Cleaning Time | Gas use (kg) | Cleaning Efficiency ($SiF_4$ Emitted) | PFC Emissions (kg CE) |
| $C_3F_8$ Baseline | 770 | 960 | 55.5 | 1.00 | 1.00 | 1.00 | 1.00 |
| c-$C_4F_8$ Recipe 1 | 400 | 2000 | 83.3 | 1.00 | 0.58 | 1.03 | 0.43 |
| c-$C_4F_8$ Recipe 2 | 450 | 2000 | 81.6 | 1.00 | 0.62 | 0.96 | 0.47 |
| c-$C_4F_8$ Recipe 3 | 450 | 2000 | 81.6 | 1.00 | 0.62 | 1.01 | 0.46 |

**Table III: Chamber-cleaning performance ($C_3F_8$ versus c-$C_4F_8$).**

tration than $C_2F_6$ or $C_3F_8$ to accomplish the same etch rate.[2] In addition, it has been shown that c-$C_4F_8$ has lower PFC emissions and gas use rates than $C_2F_6$, $C_3F_8$, and $C_4F_8O$.[2,3] Many studies indicate that the higher gas utilization of c-$C_4F_8$ enables larger reductions in gas use and PFC emissions.

In the study presented in this article, cleaning-gas utilization was used as a theoretical basis for gas selection. Reductions in gas use and PFC emissions were estimated based on comparing the flow and utilization of c-$C_4F_8$ and $C_3F_8$, assuming that the cleaning time for both processes was the same. Based on that estimation, it was determined that c-$C_4F_8$ can reduce gas use by 45% and PFC emissions by 61%. Those estimated benefits met the goal of the project. Table I presents the estimated benefits of replacing $C_3F_8$ with c-$C_4F_8$.

At the developmental stage, some chamber-cleaning gases have had higher gas utilization rates than c-$C_4F_8$.[3] While these gases can potentially reduce PFC emissions further, more developmental work is required for their implementation. In contrast, c-$C_4F_8$ provides a low-cost, low-effort alternative that can be implemented immediately in installed-base CVD tools to achieve PFC emissions reductions, as highlighted in Table II.

Data from fab tests show that c-$C_4F_8$ conversion can be accomplished with little cost and effort. For example, it has been demonstrated that the drop-in replacement of $C_3F_8$ with c-$C_4F_8$ in the Novellus Concept-2 tool significantly reduces PFC emissions and gas costs without having a negative impact on production and quality.[4]

This study evaluated SHE management of c-$C_4F_8$ in terms of health hazard, flammability, reactivity, and corrosivity, as shown in Table II. The gas is nontoxic and nonflammable. It is not reactive and is compatible with most metals, elastomers, and plastics under normal operating conditions. Based on that information, no change in the gas-delivery system was made to address the safety issues raised by shifting to the use of c-$C_4F_8$.

The cost of converting to the use of c-$C_4F_8$ was evaluated based on the required modification of the gas-delivery system, the tool, and the abatement system. The only change to the delivery system was the installation of a low-pressure regulator for the c-$C_4F_8$ cylinder. Since c-$C_4F_8$ has a lower vapor pressure than $C_3F_8$, the pressure drop across the delivery system was evaluated. The vapor pressure of c-$C_4F_8$ under ambient conditions (21°C) is 25 psig. To ensure at least a 10-psig supply pressure to the mass-flow controller (MFC), the pressure drop at the required c-$C_4F_8$ flow rate should be less than 15 psi. Experimental and modeling studies of c-$C_4F_8$ under various conditions (pipeline length and diameter, the number of bends in the pipe, and c-$C_4F_8$ flow rate) provided the basis for studying the pressure drop.[5] According to those

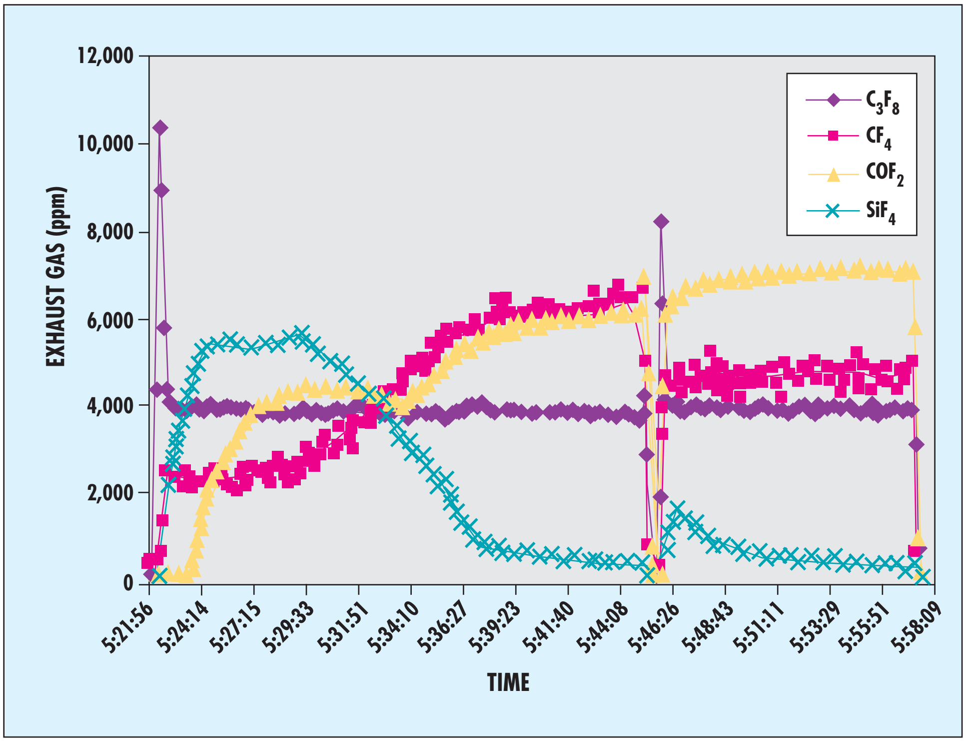

**Figure 1: FTIR exhaust analysis showing chamber-cleaning performance of $C_3F_8$ and other gases. (The $C_3F_8$ flow rate was 770 std cm³/min and the gas mixture contained 55% $O_2$.)**

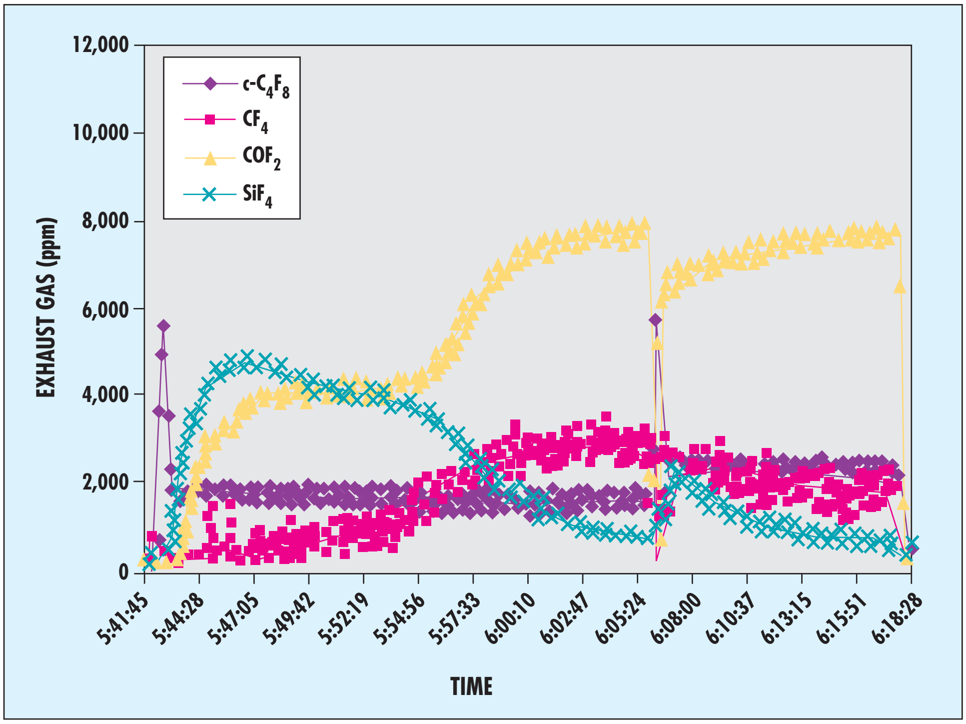

**Figure 2: FTIR exhaust analysis showing chamber-cleaning performance of c-$C_4F_8$ and other gases. (The c-$C_4F_8$ flow rate was 400 std cm³/min and the gas mixture contained 83% $O_2$.)**

studies, the pressure drop for c-$C_4F_8$ at a flow rate of 1 std L/min across a 1000 feet of ¼-in. stainless-steel pipe is less than 1.5 psi. In the Concept-1, which has a c-$C_4F_8$ flow rate of 0.4 std L/min, the pressure drop is negligible.

Using c-$C_4F_8$ vapor-pressure data from DuPont (Wilmington, DE), the effect of temperature on pressure was also evaluated. Based on that evaluation, c-$C_4F_8$ cylinder pressure was adjusted to maintain 15 psi of pressure at the MFC. That pressure level ensured that adequate pressure would be supplied to the MFC and that the pressure of the gas-delivery system would be maintained at well below the c-$C_4F_8$ vapor pressure of 25 psig at 21°C, leaving enough room for unexpected reductions in ambient temperature. A low-pressure regulator on the c-$C_4F_8$ gas cylinder enabled pressure adjustment and control in the low pressure range.

Since c-$C_4F_8$ requires a much lower flow rate than $C_3F_8$, the MFC that was used to control $C_3F_8$ flow with a full flow range of 10 std L/min was replaced. A calibration factor of 0.16 was used for the c-$C_4F_8$ MFC, which was calibrated based on $N_2$.

Because of limited tool availability, c-$C_4F_8$ recipe development work was minimized. Hence, to minimize the number of test runs required, pressure and power were kept unchanged. Instead, the study focused on the c-$C_4F_8$ flow rate and the ratio of c-$C_4F_8$ to $O_2$, which have the greatest impact on PFC emissions, gas use, and cleaning time, according to published data.[6]

## Experimental Procedure

Three $C_3F_8$ chamber cleans were performed to gather baseline data. The cleans were performed according to the following standards:

- Clean 1: 770 std cm³/min of $C_3F_8$, 960 std cm³/min of $O_2$, 3.2 Torr, 2650 W, fixed time of 1500 seconds.
- Clean 2: 770 std cm³/min of $C_3F_8$, 960 std cm³/min of $O_2$, 0.7 Torr, 2500 W, fixed time of 750 seconds.

The recipes for three c-$C_4F_8$ cleans were chosen based on DuPont's previous c-$C_4F_8$ process optimization work on Concept-1 tools. The direct application of the optimized recipes reduced the efforts required to qualify the new gas. For c-$C_4F_8$ cleans, the following test ranges were used:

- Clean 1: 400–450 std cm³/min of c-$C_4F_8$, 1800–2000 std cm³/min $O_2$, 3.2 Torr, 2650 W, fixed time of 1500 seconds.

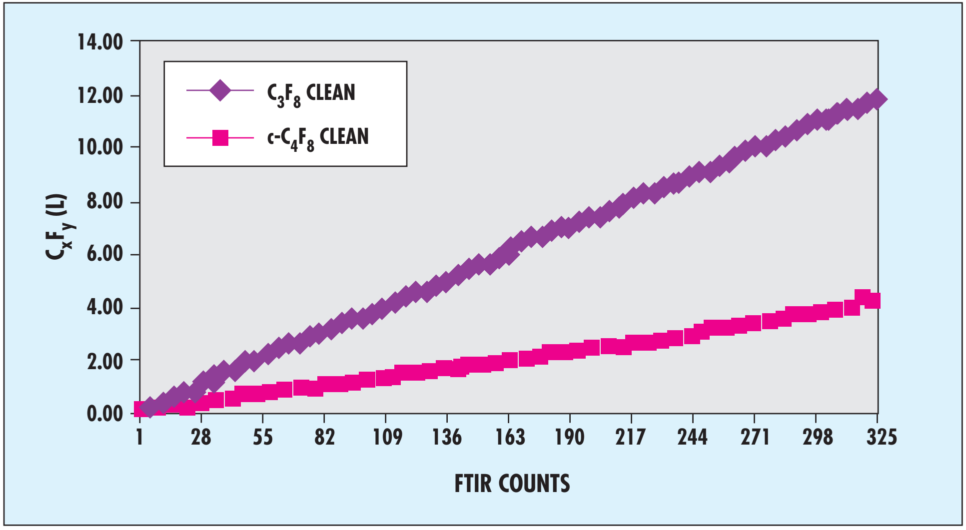

**Figure 3: Comparison of cumulative unreacted $C_xF_y$ from $C_3F_8$ and c-$C_4F_8$ cleans.**

- Clean 2: 450 std cm³/min of $c\text{-}C_4F_8$, 1800 std cm³/min of $O_2$, 0.7 Torr, 2500 W, fixed time of 750 seconds.

Before each experimental cleaning, 25 wafers were processed using the standard nitride recipe. Deposition (including undercoating and precoating) took 90 minutes to control the film thickness at 10 KÅ. Since film thickness was kept constant, comparisons between $c\text{-}C_4F_8$ and $C_3F_8$ cleaning performance were based on films of the same material and thickness.

The $c\text{-}C_4F_8$ chamber-cleaning endpoint was based on the equivalent $C_3F_8$ chamber-cleaning endpoint. The volumetric $SiF_4$ emitted during a standard $C_3F_8$ clean was used as the baseline for an acceptably clean chamber. When the amount of $SiF_4$ emitted from the chamber after $c\text{-}C_4F_8$ cleaning matched the amount emitted after $C_3F_8$ cleaning, it was assumed that both gases had achieved the same level of chamber cleanliness. The endpoint was also verified visually by observing the appearance of a standing-wave plasma pattern in the chamber during the cleaning process. When there was no longer any $SiO_2$ film in the chamber for the fluorine-containing plasma to consume, horizontal stripes in the plasma appeared under the showerhead, indicating that chamber cleaning was completed.

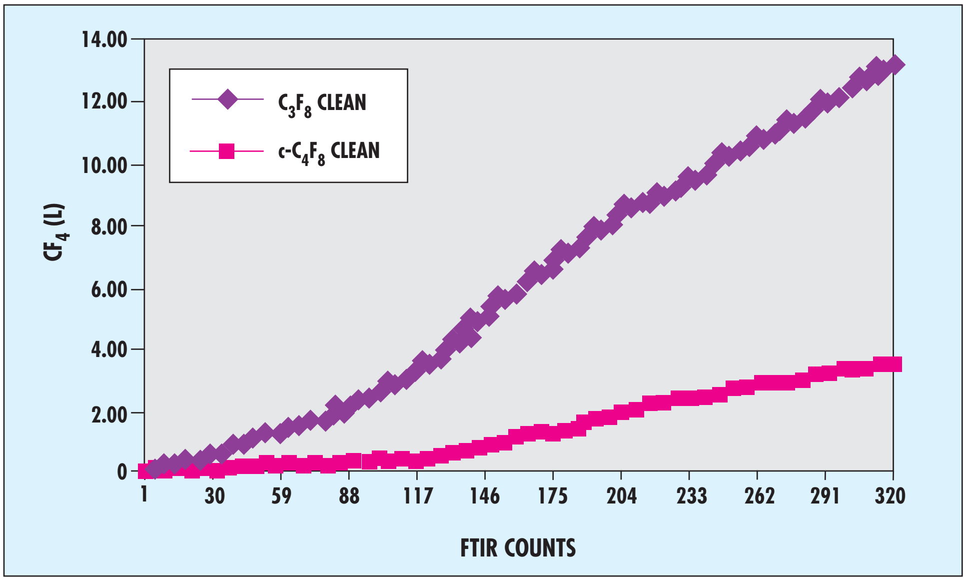

Figure 4: Comparison of cumulative $CF_4$ from $C_3F_8$ and $c\text{-}C_4F_8$ cleans.

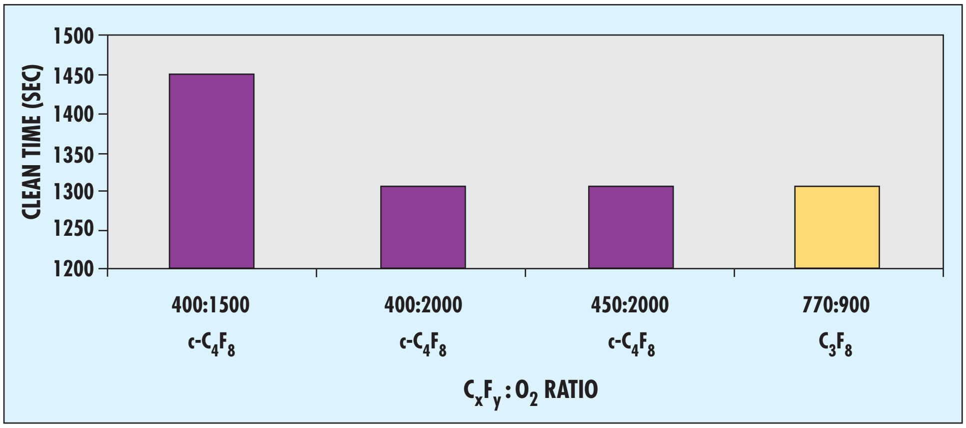

Figure 5: Comparison between cleaning time for $C_3F_8$ and $c\text{-}C_4F_8$ gases and impact of $c\text{-}C_4F_8{:}O_2$ ratio on cleaning time.

The exhaust gas during chamber cleaning was monitored using FTIR. In each experiment, chamber-cleaning time, gas use, cleaning efficiency, and PFC emissions were calculated from the FTIR measurements. Gas use for $C_3F_8$ and $c\text{-}C_4F_8$ was calculated based on the cleaning time and the MFC setting. The amount of $SiF_4$ emitted during cleans 1 and 2 was measured to evaluate cleaning efficiency. Using the following equation, the researchers were able to integrate the total volumetric output of $C_xF_y$ and $CF_4$ during those cleans to calculate PFC emissions in the form of kilogram carbon equivalents (kg CE):

$$\text{kg CE} = \Sigma Q_i \times \left(\frac{12}{44}\right) \times \text{GWP}_i$$

In this equation, for every species that contributes to global warming, Q is the amount of gas in kilograms and GWP is the global warming potential (100-year integrated time horizon [ITH]). The GWP values for $C_3F_8$, $CF_4$, and $c\text{-}C_4F_8$ are 7000, 6500, and 8700, respectively.

## Results and Discussion

Table III lists the relative values of $C_3F_8$ versus $c\text{-}C_4F_8$ for cleaning time, gas use, cleaning efficiency (amount of $SiF_4$ emitted), and PFC emissions (kg CE). All three $c\text{-}C_4F_8$ recipes consumed less gas and resulted in lower PFC emissions than the $C_3F_8$ gas. With the same cleaning time and cleaning efficiency as the other $c\text{-}C_4F_8$ recipes, $c\text{-}C_4F_8$ recipe 1 (with the lowest flow rate of 400 std cm³/min) consumed the least amount of gas and had the lowest level of PFC emissions. The measured reductions in gas use and PFC emissions were within 5% of the estimated reductions.

Figures 1 and 2 present FTIR concentration profiles from the tool exhaust streams recorded during the $C_3F_8$ and $c\text{-}C_4F_8$ chamber-cleaning processes. The figures demonstrate that

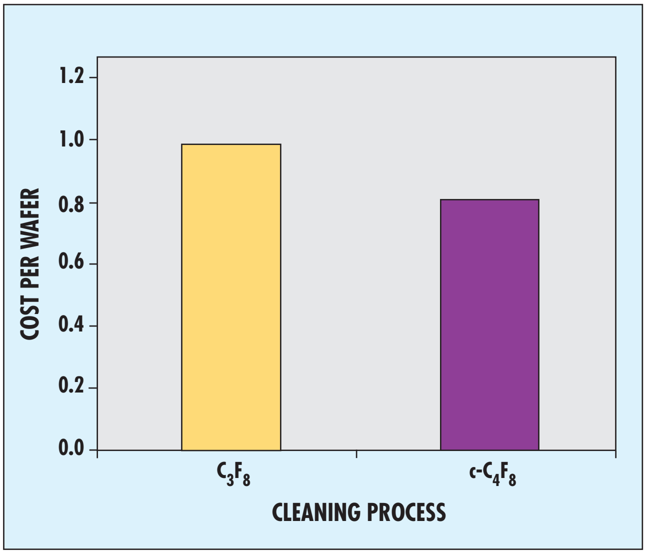

**Figure 6: Chamber-cleaning cost comparison between $C_3F_8$ and c-$C_4F_8$ gases.**

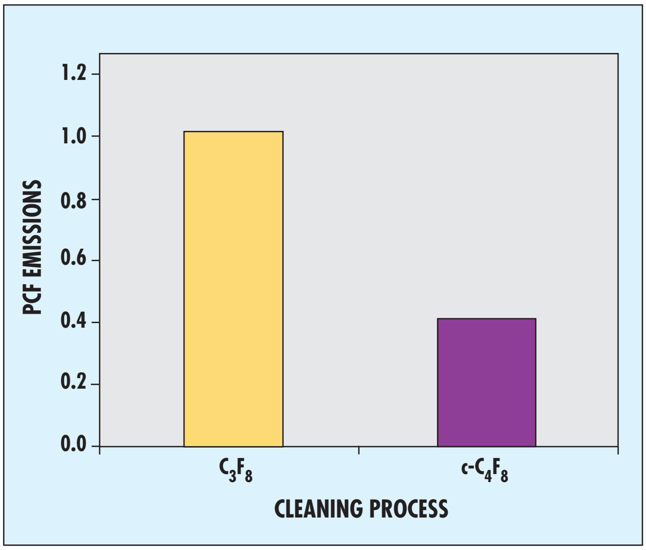

**Figure 7: PFC emissions comparison between $C_3F_8$ and c-$C_4F_8$ gases.**

the c-$C_4F_8$ concentration measured in the exhaust stream was much lower than that of $C_3F_8$, confirming that the high gas utilization of c-$C_4F_8$ leads to lower PFC emissions. Flow control of the c-$C_4F_8$ process was stable, as indicated by the stable c-$C_4F_8$ concentration shown in Figure 2. During cleans 1 and 2, the plasma was also stable. Figure 3 compares the unreacted cleaning gas ($C_xF_y$) that was emitted between cleanings for c-$C_4F_8$ and $C_3F_8$.

The c-$C_4F_8$ cleaning process also generated much less $CF_4$ than the $C_3F_8$ process. The higher percentage of $O_2$ during c-$C_4F_8$ cleaning may convert some $CF_4$ to $COF_2$. Figure 4 compares the cumulative $CF_4$ generated per clean during $C_3F_8$ and c-$C_4F_8$ chamber-cleaning processes.

At this point, a dual-wavelength endpoint detector was installed to confirm the completion of chamber cleaning. The optical emissions of fluorine (704 nm) and CO (483 nm) were used to determine the endpoint. The endpoint-detection software scripts used for the $C_3F_8$ cleaning process were also used for c-$C_4F_8$ process, and the same threshold value of 0.85 was used for both gases. The traces observed during the $C_3F_8$ and c-$C_4F_8$ cleaning processes were almost identical, and the times required to reach the threshold ratio were the same. The endpoints for both $C_3F_8$ and c-$C_4F_8$ were equivalent, confirming chamber-cleaning efficiency as determined by the FTIR-based detection of $SiF_4$ emissions from the chamber.

Figure 5 compares the clean 1 performance of $C_3F_8$ and c-$C_4F_8$ after the endpoint detector was installed. The figure also demonstrates that cleaning time as determined by the endpoint detector is affected by the ratio of c-$C_4F_8$ to $O_2$. Reducing the $O_2$ concentration by 4.4% through lowering the $O_2$ flow from 2000 to 1500 std $cm^3$/min at a c-$C_4F_8$ flow rate of 400 std $cm^3$/min increased cleaning time by nearly 12%. However, a 13% increase in the c-$C_4F_8$ flow rate (from 400 to 450 std $cm^3$/min) did not affect cleaning time. To achieve the optimum c-$C_4F_8$:$O_2$ flow ratio, fine-tuning may be necessary to compensate for small MFC errors.

Figure 6 compares the cost per wafer of performing $C_3F_8$ versus c-$C_4F_8$ chamber cleaning. The 42% reduction in gas consumption achieved by shifting to the use of c-$C_4F_8$ resulted in a 20% reduction in cleaning-gas costs.

Figure 7 compares the PFC emissions between $C_3F_8$ and c-$C_4F_8$ chamber cleaning. As the figure shows, c-$C_4F_8$ reduced PFC emissions by 57%.

## Conclusion

The selection of a chamber-cleaning gas requires a balanced approach. For fabs with installed-base CVD tools that must reduce PFC emissions immediately at minimal cost and with little effort, c-$C_4F_8$ offers a practical and economical solution. The goal of the project presented in this article was to reduce PFC emissions inexpensively and easily. The data reported in this article demonstrate that the c-$C_4F_8$ chamber-cleaning process has accomplished that goal. As a result, c-$C_4F_8$ is being implemented in production.

## Acknowledgment

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## References

1. OF Schedlbauer, “Cost Reduction Challenges in CVD Chamber Cleaning: Strategies to Reduce Gas Costs,” *Future Fab International* 13 (2002): 164–169.
2. CC Allgood and MT Mocella, “CVD Chamber Cleaning: A Critical Comparison of Processes and Gases,” DuPont technical paper [online] [cited 1 September 2005]; available from Internet: www.dupont.com/zyron/techinfo/recent/semiconw2000.html.
3. T Beppu, “Emission Reduction from Semiconductor Industry Chamber Cleaning” (paper presented at the ISESH Confer-

ence, Noordwijk, The Netherlands, June 29–July 3, 2003).

4. A Evans, "Advances in Reducing PFC Emissions and Gas Costs: Qualification and Implementation of c-$C_4F_8$ Chamber Clean Gas in a Novellus Concept-2 Chemical Vapor Deposition Tool" (paper presented at the Semicon Southwest Partnership for PFC Emission Reduction Workshop, Austin, TX, October 15–16, 2002).
5. "Pressure Drop Considerations in Gas Delivery Lines for Zyron 8020 (c-$C_4F_8$) CVD Chamber Clean Gas," DuPont technical paper [online] [cited 1 September 2005]; available from Internet: www.dupont.com/zyron/techinfo/briefs/index.html.
6. U Schilling and P Heger, "Evaluation of c-$C_4F_8$ as Cleaning Gas in an Applied Materials Lamp Heated Universal Chamber on 200mm Wafers," International Sematech Technology Transfer 01084152A-TR, 2001.

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