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# Environmental-Friendly Fluorine Mixture for Cvd Cleaning Processes to Replace $C_2f_6$ and $Nf_3$ under Industrial Conditions

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## Introduction

During the climate conference in Paris a binding and universal climate target was established. It was agreed to limit the temperature increase to a maximum of 2 C° until 2100 [1]. The most relevant climate gas is $CO_2$, considered as a primary greenhouse gas with a significant impact on global warming. Although the semiconductor industry is only a small contributor to the global warming, several fluorinated gases having a high global warming potential (GWP), are intensively used [2]. NF3 is the most frequently used gas, having a GWP of 17200, followed by $C_2F_6$ and $CF_4$ with GWPs of 1200 and 7390 respectively [3]. The main application of these gases is to remove residual films remaining inside deposition chambers after a PECVD process (plasma-enhanced chemical vapor deposition). process The most important materials to remove are dielectric layers like silicon dioxides ($SiO_2$), carbon-containing silicon oxides, silicon nitrides (Si3N4) and, to a certain extent, conducting films like doped poly-silicon and silicide layers. According to the World Semiconductor Council, the semiconductor industry used in 2018 12696 t $NF_3$, 2024 t $CF_4$ and 736 t C2F6 on a global basis [4]. Approximately 72% of all semiconductor industry gaseous emissions are caused from these three gases. This article discusses the replacement of $C_2F_6$ and $NF_3$ as cleaning gases thru an environmental-friendly gas mixture named Solvaclean®NO (30% $F_2$, 60%$N_2$ and 10% Ar).

It could be shown that the clean with Solvaclean®NO achieves similar cleaning time with significant lower gas consumption, appr. 60-70% less gas compared to $C_2F_6$. The RF-power during cleaning was reduced by 20% and the amount of fluorinated waste water was as well significantly reduced.

## Experimental

The described studies were done on PECVD production tools from Novellus, Concept 2 Sequel, located at TDK-Micronas, with the goal to replace several different cleaning processes. The objective was to clean with a similar speed and to reduce the gas consumption compared to $C_2F_6$.

The trials started to clean previously deposited, SiH4-based $SiO_2$ films out of the PECVD deposition chamber. Therefore, SiO2 layers of 13 µm were deposited on blank Si-wafers. After the deposition, wafers were removed out of the chamber and the remaining $SiO_2$ was plasma-etched with the $C_2F_6$ / $O_2$ cleaning plasma (POR-process of record) and for comparison, after a second $SiO_2$ deposition sequence, with the BKM (best known method) Solvaclean®NO / $O_2$ cleaning plasma.

In order to monitor the process behavior and the endpoint times of the cleaning process, a RGA (remote gas analyser) and an external optical endpoint system were used simultaneously for recording.

The mass spectrometer, measuring at atmospheric pressure, was located ~3m behind the vacuum main pump; therefore, the pump's N2-purge was reduced to its minimum in order to receive sufficient signal strength for the mass detection during cleaning. A high-resolution optical spectrometer was used to record the fluorine line at 704 nm by looking directly into the plasma at an optical viewport window. Both signals were tracked in parallel for every process run. Figure 1a shows the schematical overview, figure 1b shows the fiber optic mounted to the viewport window of the plasma chamber.

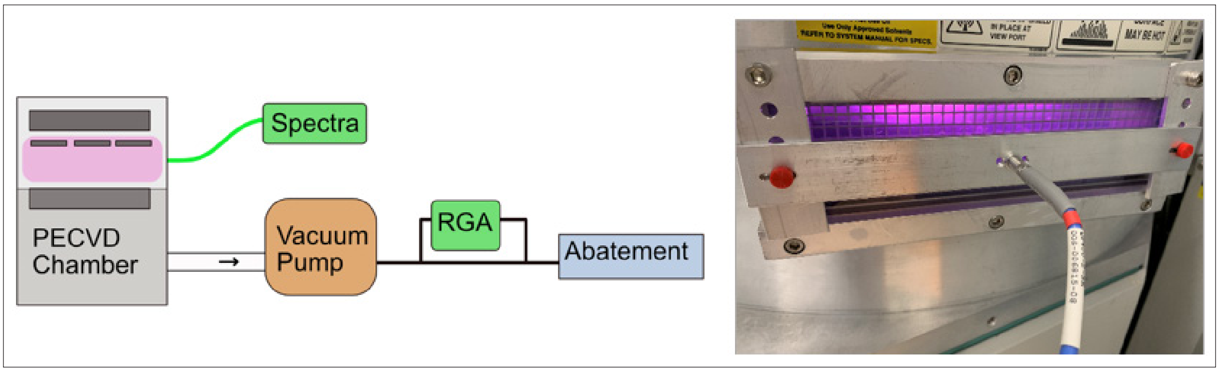

**Figure 1 a/b:** Schematic of optical spectrometer and RGA location (left); Fiber optic cable at plasma chamber's viewport (right)

When interpretation of mass spectrometer curves is required, it should be taken in account that the pump line between process chamber outlet and the vacuum pump inlet was previously contaminated due to standard deposition runs, which leave unreacted TEOS-based $SiO_2$ residuals inside the vacuum line. $F_2$-gas mixtures like the Solvaclean®NO mixture are more reacting with the pump line residuals than, for example $C_2F_6$. Thus, the absolute recorded mass values for $SiF_4$ or $F_2$ molecules can slightly vary from run to run, depending on the actual cleanliness of the vacuum pump line including the small bypass-line (heated) to the RGA.

The two clean chemistries to be discussed differ in three major properties. Firstly, $C_2F_6$ gas is by a factor of 4.3 heavier as the Solvaclean®NO gas mixture, which leads to a different process kit surface impact during cleaning. Secondly, the Solvaclean®NO gas mixture is much easier to dissociate, which in term requires less plasma RF-power for the same or higher F-concentration as is required with $C_2F_6$. Thirdly, a PFC-gas like $C_2F_6$ carries appr. 9 times more F2-molecules into a process chamber than the Solvaclean NO gas mixture.

In figure 2, the plasma-based reactions of $C_2F_6$ and $F_2$ can be compared via the mass spectrometer lines of $SiF_4$ (red line) and $F_2$ (dark green line). As in theory, stable gases like $C_2F_6$ are following a decomposition of second order while $F_2$ as a reactive gas is following a first order of decomposition. A first-order reaction can be defined as a chemical reaction in which the reaction rate is linearly dependent on the concentration of only one reactant. In other words, a first-order reaction is a chemical reaction in which the rate varies based on the changes in the concentration of only one of the reactants. In such reactions, if the concentration of the first-order reactant is doubled, then the reaction rate is also doubled.

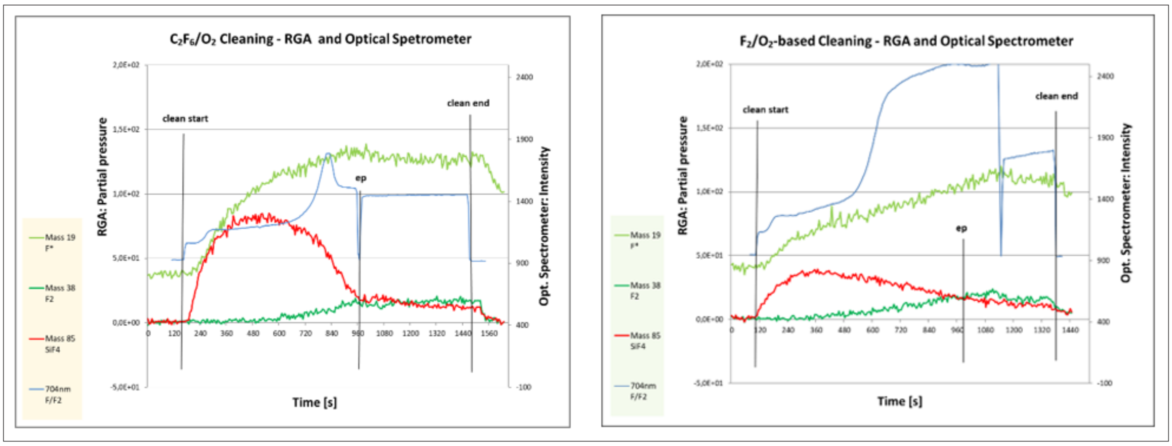

**Figure 2 a/b:** Mass spectrometer (RGAs red and green lines) and optical spectrometer data (blue line) of $SiO_2$ cleans, left with $C_2F_6$ and right with Solvaclean®NO.

In case of the cleaning with Solvaclean®NO, the $F_2$ is immediately and sufficiently available and the related $SiF_4$ concentration is increasing. It can be seen, that the cleaning process is taking place in a linear way, because $SiF_4$ is decreasing and $F_2$ is increasing linear.

At the point where both lines are crossing, the clean of the showerheads is finished. Trials with higher $F_2$ concentration were leading to slightly higher $SiF_4$ concentration at the beginning, however due to the $SiO_2$ limitation in the chamber, the advantage towards the end of the showerhead clean is not significantly relevant and leads only to a higher excess of $F_2$. In term, this results in a higher concentration of inorganic fluorides in the waste water. Therefore, it is better to optimize the reaction with Solvaclean®NO on the efficiency and not on cleaning speed.

The clean with $C_2F_6$ is, by minimum, a reaction of second order, which can be seen in the high amount of F radicals (light green graph). The reactions of second and higher orders are less relevant from the starting material ($C_2F_6$) because several interim products are formed, prior before the final $SiF_4$ is produced. Additionally, there is a high percentage of $C_2F_6$ as $CF_3$ radical in the chamber and not actively contributing to the cleaning process, shown in fig. 3. This is one reason why the cleaning with Solvaclean is more efficient.

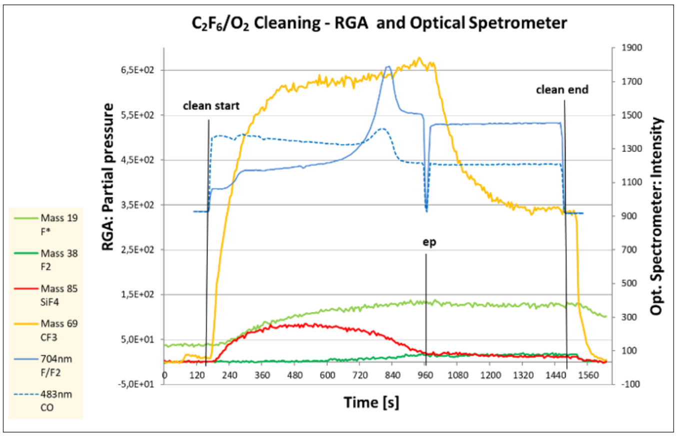

**Figure 3:** RGA and optical spectrometer data during a $C_2F_6/O_2$ cleaning process. High amount of $CF_3$ present

Based on the BKM comparison of $C_2F_6$ and Solvaclean® NO a mass balance and an Ecoprofile was executed based on 30000 wafers to be cleaned.

During the production of 30000 wafer under industrial production conditions, it can be shown that, due to a much lower gas consumption of Solvaclean (102 kg) compared to $C_2F_6$ (356kg), an environmental benefit equivalent to 600 car´s annual emissions could be achieved (assuming 16000 km/a driven). Already the transport of the PFC's from Asia to Europe create more $CO_2$ Equivalent (3288 kg) compared to the production and transport of Solvaclean® within the EU (1093 kg). The production of Solvaclean created 1020 kg $CO_2$ Equivalent and the transport within the Europe create 73 kg $CO_2$ Equivalent(LCA was performed in line with ISO 14040) 2-4].

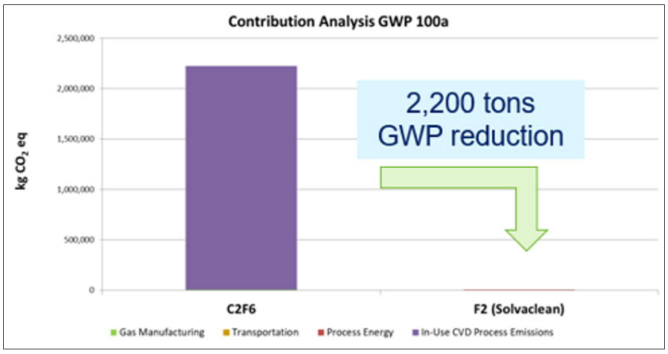

**Figure 4:** Ecoprofile comparison of $C_2F_6$ versus Solvaclean

## Assumptions

- In comparing a set of alternative options, we considered $C_2F_6$ a well-established proxy for competitive materials in this application
- Etching gas dissociation by-products and conversion rates were confirmed by mass spectrometry. Waste gas analysis post in-situ plasma cleaning after $SiO_2$ deposition at 13.56 MHz evidenced nearly complete dissociation of F2 vs. a 70% rate for $C_2F_6$
- Process comparison based on material flow, utilities, and waste generation required to output a functional unit consisting of a pre-determined quantity of $SiF_4$ during cleaning
- The chamber cleaning process including raw material manufacturing and transportation were considered in the LCA boundary
- The fabrication facility produces an average of 30,000 wafers per year based on no in-process abatement

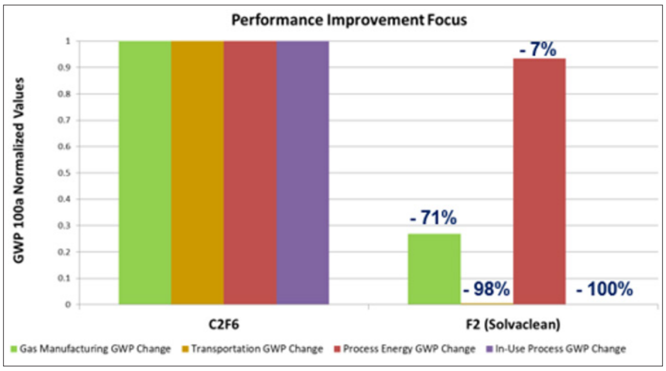

**Figure 5:** Performance improvement of Solvaclean compared to $C_2F_6$

## Key Take-aways (visualized in figure 3)

- Process emissions in-use are the highest contributors to the GWP with $C_2F_6$ leading to undesired GHG emissions (contrary to $F_2$)
- The use of Solvaclean® $F_2$ allows for significant improvement of GWP in the CVD cleaning process with the potential to eliminate ~47000 tons of $CO_2$ eq per year
- Despite a low level of emissions associated with its synthesis, F2 in CVD benefits from: zero GWP in-use; very high conversion rate; less energy in-use; significantly lower transportation impacts
- Potential for wastewater savings up to 50% (based on FAB data)

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